

Modelization of stable metal clusters containing Group 11 elements

Franck Gam

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Preamble

This thesis manuscript reports a work of applied theoretical chemistry carried out at the Universidad Andrés Bello (Santiago, Chile) and the University of Rennes 1 (Rennes, France) within the framework of a co-tutelle agreement between both institutions. This thesis was rendered possible thanks to a PhD grant co-financed by the Région Bretagne (ARED NANOCLUS n° 9334) and the Universidad Andrés Bello. The work performed in collaboration with Prof. Alvaro Muñoz-Castro was supported by FONDECYT 1180683.

Basically, the reported work is based on the use of density functional theory (DFT) calculations in order to understand, sometimes predict, the stability, structure and some properties of large (nanometric or subnanometric) cluster molecules.

The manuscript is organized in chapters, each of them (except for the introductive Chapter 1) corresponding to a specific investigation devoted to be published. Therefore, any of these chapters is written in the style of an article, already published, accepted or in preparations. Although we have tried to circumvent most of the repetitions inherent to this mode of presentation, some could not be avoided and we must apologize for this fact. The following publications are already published or accepted:

- F. Gam, D. Páez-Hernández, R. Arratia-Pérez, C.W. Liu, S. Kahlal, J.-Y Saillard, A. Muñoz-Castro. Coinage Metal Superatomic Cores: Insights into Their Intrinsic Stability and Optical Properties from Relativistic DFT Calculations. *Chem. Eur. J.* 2017, *23*, 11330.
- F. Gam, R. Arratia-Pérez, S. Kahlal, J.-Y Saillard, A. Muñoz-Castro. [M₁₆Ni₂₄(CO)₄₀]⁴⁻: Coinage Metal Tetrahedral Superatoms as Useful Building Blocks Related to Pyramidal Au₂₀ Clusters (M = Cu, Ag, Au). Electronic and Bonding Properties from Relativistic DFT Calculations. *J. Phys. Chem. C*, 2018, *122*, 4723.
- F. Gam, R. Arratia-Pérez, S. Kahlal, J.-Y Saillard, A. Muñoz-Castro. Symmetry Lowering by Cage Doping in Spherical Superatoms. Evaluation of Electronic and Optical Properties of 18-electron W@Au₁₂Pt_n (n=0-4) Superatomic Clusters from Relativistic DFT Calculations. *Int. J. Quantum Chem.* DOI: 10.1002/qua.25827.

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List of abbreviations

ADF	Amsterdam density functional
AEA	Adiabatic electron affinitiy
AIP	Adiabatic ionization potential
AO	Atomic orbital
BP86	Becke-perdew 86
COSMO	Conductor like screening model
Ср	Cyclopentadienyl
Cp*	Pentamethylcyclopentadienyl
DFT	Density functional theory
DMF	Dimethylformamide
DOS	Density of states
EAN	Effective atomic number
Ec	Cohesion energy
EDA	Energy decomposition analysis
E _{disp}	Dispersion energy
Eelstat	Electrostatic interaction
Ef	Energy of formation
Eorb	Orbital interaction energy
Epauli	Pauli repulsion energy
eV	Electron Volt
fcc	Face-centered cubic
FO	Frontier orbital
GGA	Generalized-gradient approximation
НОМО	Highest occupied molecular orbital
je	Jellium electron
LCAO	Linear combination of atomic orbitals
LUMO	Lowest unoccupied molecular orbital
MLCT	Metal-to-ligand charge-transfer
MO	Molecular orbital

NBO	Natural bond orbital
OAc	Acetoxy group
PAW	Projected augmented wave
PBE	Perdew-burke-ernzerhof
PSEP	Polyhedral skeletal electron pair
SEP	Skeletal electron pair
SR	Scalar relativistic
STO-TZ2P	Slater type orbitals-Triple ζ + two polarization functions
STO-QZ4P	Slater type orbitals-Triple ζ + four polarization functions
TBE	Total bonding energy
TD-DFT	Time-dependent density functional theory
TSH	Tensor surface harmonics
UV-Vis	Ultraviolet-visible
VASP	Vienna ab initio simulation package
ZORA	Zeroth order regular approximation

Résumé

Modélisation de clusters stables contenant des métaux de transition du groupe 11

Les travaux de thèse présentés dans ce mémoire portent sur l'étude théorique de clusters inorganiques de métaux du groupe 11 (Cu, Ag, Au) ou de clusters hétéronucléaires contenant des métaux du groupe 11. Les calculs de chimie quantique effectués en théorie de la fonctionnelle de la densité (DFT) ont été effectués dans le but d'interpréter la stabilité et la structure géométrique des composés étudiés, ainsi que, pour certaines espèces, leurs propriétés optiques ou chimiques.

Le mémoire commence par un chapitre introductif rappelant les conditions que doit respecter la structure électronique d'un composé pour qu'il ait une chance d'être suffisamment stable pour être isolé ou simplement observé. Les règles de décompte électronique qui découlent de ces conditions sont ensuite brièvement rappelées et expliquées.

Nous nous sommes ensuite intéressés à comprendre pourquoi, lorsqu'un complexe du cuivre(I) est traité par NaBH₄ en présence d'un ligand dichalcogénolate (typiquement un dithiocarbonate ou un dithiophosphate), selon les quantités de réactifs, on n'a pu à ce jour isoler uniquement que des polyhydrures de cuivre(I), alors qu'avec un grand excès de borohydrure on forme des nanoparticules métalliques (Cu(0)). Logiquement, des espèces intermédiaires à valences mixtes de degré d'oxydation compris entre +I et 0 devraient être obtenues. C'est en fait ce qu'on observe lorsqu'on utilise des complexes de l'argent(I) dans les mêmes conditions (voir Schéma R.1). Des hydrures sont tout d'abord isolés, puis avec un plus grand excès de borohydrure, des clusters à valences mixtes sont obtenus.

Nous avons cherché à comprendre l'origine de cette différence en évaluant la stabilité intrinsèque de superatomes de cuivre et d'argent débarrassés de leurs ligands (clusters nus), afin de ne pas introduire de variable supplémentaire. Nous y avons ajouté les analogues d'or, non seulement pour compléter la série du groupe 11, mais aussi parce que de nombreux superatomes d'or sont connus et donc cet élément constitue une référence pour Cu et Ag. Les superatomes étudiés sont de taille croissante (de M₄ à M₄₃). Leurs structures, représentées sur la Figure R.1, sont inspirées de celles de clusters réels et leurs charges ont été ajustées de façon à ce qu'ils présentent un nombre « magique » d'électrons tel que prévu par la théorie du jellium sphérique. Nous avons de surcroît calculé leurs propriétés optiques en méthode TD-DFT.

From Copper(I) to Copper(0)



Schéma R.1. Mécanisme général proposé pour la réduction de complexes de Cu(I) et Ag(I) par NaBH₄ en présence de ligands dichalcogénolates, en route vers la formation de nanoparticules métalliques.



Figure R.1. Structures des clusters étudiés.

Comme on peut le voir sur les exemples reportés dans le tableau R.1, le calcul des énergies de cohésion montre que les superatomes de cuivre présentent une stabilité proche de celle de leurs homologues d'or et sont significativement plus stables que les superatomes d'argent. Il devrait donc être possible de stabiliser des clusters superatomiques du cuivre.

Tableau R.1. Données calculées pour $[M_4]^{2+}$, $[M_8]$, $[M_{13}]^{5+}$, $[M_{20}]$, $[M_{32}]^{14+}$ et $[M_{43}]^{9+}$. E_C (kcal/mol) et ΔE_{H-L} (eV) sont respectivement les énergies de cohésion et les écarts HOMO-LUMO. Les distances interatomiques sont en Å et les fréquences vibrationnelles en cm⁻¹.

	$[M_4]^{2+}/1S^2(2-je)$											
	Ec	ΔE_{H-L}	M _{tet} -M _{tet}						Lowest freq.			
$[Cu_4]^{2+}$	-27.8	2.56	2.430						116			
$[Ag_4]^{2+}$	-18.2	3.85		74								
$[Au_4]^{2+}$	-30.0	2.50		66								
	$[M_8] M_4 @ M_4 / 1S^2 1P^6 (8-je)$											
	Ec	ΔE_{H-L}	M _{tet}	-M _{tet}]	Lowest freq.					
[Cu ₈]	-53.8	2.15	2.4	460			52					
[Ag ₈]	-39.4	2.32	2.8	353			2.767					
[Au ₈]	-47.2	2.02	2.8	371			2.740					
	$[M_{13}]^{5+} M@M_{12}/ 1S^2 1P^6 (8-je)$											
	Ec	ΔE_{H-L}	M _{cent} -M _{ico}			Mico-Mico			Lowest freq.			
$[Cu_{13}]^{5+}$	-7.5	1.91	2.514			2.643			70			
$[Ag_{13}]^{5+}$	4.5	2.63	2.8		3.037			39				
$[Au_{13}]^{5+}$	-8.9	2.01	2.8	818		2.963			23			
		[N	M_{20}] M ₄ @M ₁₂	$aM_4/15$	S ² 1P ⁶	$1D^{10} 2S^2$ (.	20-је	2)	Γ			
	Ec	ΔE_{H-L}	M _{tet} -M _{tet}	M _{tet} -M _{tet} M _{tet} -M _{trunc} M _{trunc} -M _{trunc} M _{trunc} -M _{cap}								
[Cu ₂₀]	-62.07	1.34	2.600	00 2.453		2.414-2.489		2.390	67			
[Ag ₂₀]	-45.46	1.64	3.034	2.831		2.755-2.902		2.756	41			
[Au ₂₀]	-56.34	1.81	3.131	2.81	2.674-2.946 2.710		30					
			5 6 - 14	+) ()	r / a	C) 4 D(4 D)	0 / 1	•••				
			[M ₃₂] ¹⁴	$M_{12}(a)$	$A_{20} / 1$	$\frac{S^2 IP^0 ID^1}{M}$	¹⁰ (1	8-je)				
rg 1/4+	E _c	ΔE_{H-L}	M _{ico} -M	ico-Mico		M _{ico} -M _{cap}		M _{cap} -M _{cap}	Lowest freq.			
$[Cu_{32}]^{14+}$	-43.7	0.92	2.541			2.461		2.781	24			
$[Ag_{32}]^{14+}$	-27.9	1.59	2.922			2.821		3.188	-12			
$[Au_{32}]^{14+}$	-44.3	1.11	2.953 2.762 3.143					3.143	-32			
			F) (1 ⁰⁺) ()		1402	106 10 10 0	<u> </u>					
	$[M_{43}]^{2+} M(a)M_{12}(a)M_{30} / 1S^2 1P^6 1D^{10} 2S^2 1F^{14} (34-je)$											
FO - 01	Ec	ΔE_{H-L}	M _{cent} -M _{ico}	M _{ico} -M _{ico}		M_{ico} M_{ico} M_{co}		M _{cap} -M _{cap}	Lowest freq.			
$[Cu_{43}]^{9+}$	-28.4	0.35	2.501	2.63	0	2.475		2.611	47			
$[Ag_{43}]^{9+}$	-14.6	0.63	2.931	3.082		2.843		3.018	23			
$[Au_{43}]^{9+}$	-26.4	0.70	2.894	2.894 3.043		2.797		2.971	20			

Ce résultat étant en contradiction apparente avec les observations expérimentales décrites dans le Schéma R.1, nous nous sommes posés la question de la stabilité relative des hydrures et polyhydrures de cuivre(I) et d'argent(I). Pour répondre à cette question, nous avons calculé un certain nombre de composés modèles, tant de l'état solide (phases de stœchiométrie MH) que moléculaires. Les énergies de cohésion et/ou d'énergies d'interaction entre les hydrures et leurs hôtes métalliques convergent vers la même conclusion, à savoir que les hydrures de cuivre(I) sont plus stables que ceux d'argent(I). Les données calculées pour la phase Wurtzite, qui constitue le modèle limite pour un polyhydrure géant sont données à titre d'exemple dans le Tableau R.2 ci-dessous.

Tableau R.2. Energie de formation (E_F) et énergie de cohésion (E_C) calculées pour les systèmes MH (M = Cu, Ag, Au) dans la structure-type Wurzite. Les valeurs sont en eV et ramenées à une unité MH.

MH	E_{F}	E _C
CuH	0.273	-0.944
AgH	0.414	-0.372
AuH	0.700	-0.409

La conclusion générale que l'on peut tirer de l'ensemble de nos résultats est donc que, même si les superatomes de cuivre sont intrinsèquement plus stables que ceux d'argent, ils sont particulièrement réticents à se former dans les conditions opératoires du Schéma R.1 car la formation de polyhydrures est préférée en raison de leur grande stabilité. Ce n'est pas le cas de l'argent, qui, en présence d'un excès suffisant de borohydrure, pourra former des superatomes à valence mixte. Pour conduire plus facilement à la formation de superatomes de cuivre, nous suggérons de modifier les conditions expérimentales du Schéma 1 en ajoutant des ligands supplémentaires susceptibles d'entrer en compétition avec les hydrures.

Nous nous sommes intéressés ensuite à des clusters dont la structure est apparentée à celle de $[Au_{20}]$. Ce cluster nu, suffisamment stable pour être observé, est de symétrie T_d et peut être vu comme un fragment tiré du métal *cfc*. Il peut aussi se décrire en sphères concentriques Au₄@Au₁₂@Au₄ (Figure R.2). Il possède un nombre « magique » d'électrons (20) et est un rare exemple de superatome du groupe 11 dont le degré d'oxydation « moyen » du métal n'est pas positif (il est égal à 0).



Figure R.2. La structure « *cfc* » de [Au₂₀] (symétrie T_d). Les couleurs correspondent à chacune des trois sphères concentriques (Au₄@Au₁₂@Au^{**}₄).

La première famille de clusters que nous avons étudiée dans ce cadre a pour formule $[M_{16}Ni_{24}(CO)_{40}]^{4-}$ (M = Cu, Ag, Au). L'espèce correspondant à M = Ag a été synthétisée et caractérisée structuralement par Dahl *et al.* Elle contient le noyau interne M₁₆ (M₄@M₁₂) présent dans [Au₂₀] (Figure R.3). Nous avons analysé la structure électronique de cette famille de composés en comparant sa structure électronique à celle des clusters tétraédriques [M₂₀] (M = Cu, Ag, Au). Par ailleurs, des calculs TD-DFT nous ont permis de comparer leurs propriétés d'émission UV-visible.



Figure R.3. Structure moléculaire de [Ag₁₆Ni₂₄(CO)₄₀]⁴⁻.

Nos calculs ont montré que, tant dans $[M_{20}]$ que dans $[M_{16}Ni_{24}(CO)_{40}]^{4-}$ les 20 électrons qui assurent la cohésion du cluster sont délocalisés non seulement sur le noyau interne M_{16} mais aussi sur la sphère externe constituée soit de quatre atomes M coiffant les (petites) faces triangulaires (cas de $[M_{20}]$), soit de quatre entités quasi-planes $Ni_6(CO)_{10}$ coiffant les (grandes) faces hexagonales (cas de $[M_{16}Ni_{24}(CO)_{40}]^{4-}$). Il en résulte que les fragments organométalliques $Ni_6(CO)_{10}$ ne doivent pas être considérés comme des ligands ou entités périphériques « passivantes », mais comme faisant partie intégrante du superatome à 20 électrons.

La question de la stabilité potentielle d'une entité M_{16} à 20 électrons reste donc posée et nous avons cherché à y répondre pour des espèces $[M_{16}]^{4-}$ (M = Cu, Ag, Au). La charge anionique importante de ces modèles et le caractère antiliant de leur HOMO conduisent à des énergies largement positives de celles-ci. Si ces énergies peuvent devenir négatives dans un environnement cationique simulé par des corrections d'effet de solvant (modèle COSMO) (Tableau R.3), les écarts HOMO-LUMO restent dans l'ensemble modestes.

	[Cu	16] ⁴⁻	[Ag ₁	6 ⁴⁻	[Au	6 ⁴⁻	[Cu ₁	6] ²⁻	[Ag ₁	6] ²⁻	[Au	16] ²⁻
Environment	Vacuum	DMF	Vacuum	DMF	Vacuum	DMF	Vacuum	DMF	Vacuum	DMF	Vacuum	DMF
24 x M'-M'' (Å)	2.467	2.444	2.854	2.820	2.836	2.831	2.483	2.482	2.876	2.866	3.071	2.851
12 x M''-M'' (Å)	2.484	2.424	2.868	2.806	2.833	2.737	2.377	2.381	2.753	2.747	2.954	2.733
6 x M''-M'' (Å)	2.447	2.454	2.837	2.828	2.831	2.738	2.336	2.338	2.703	2.696	2.903	2.667
$\rho = (C-M'')/(C-M')^{b}$	1.80	1.75	1.81	1.80	1.76	1.33	1.24	1.25	1.24	1.24	1.26	1.23
$\Delta E_{\text{HOMO-LUMO}}(\text{eV})$	1.32	1.53	1.30	1.41	1.22	0.65	1.02	1.21	1.26	1.45	1.55	1.63
E _{HOMO} (eV)	7.66	-2.98	6.78	-3.03	6.98	-3.14	1.58	-4.05	1.18	-4.08	0.54	-4.97
E _C (kcal/mol)	-39.1	-58.1	-24.6	-41.7	-31.6	-48.0	-58.8	-60.1	-42.8	-43.8	-52.6	-53.0
Lowest vibrational frequencies (cm ⁻¹)	76 (<i>t</i> _{<i>l</i>})	69 (<i>t</i> ₂)	$45(t_l)$	44 (<i>t</i> ₂)	20 (<i>t</i> ₂)	35 (<i>t</i> ₂)	77 (e)	76 (e)	47 (e)	46 (e)	33 (t_1)	33 (t_1)

Tableau R.3. Résultats obtenus pour les espèces hypothétiques $[M_{16}]^{4-}$ et $[M_{16}]^{2-}$ (M = Cu, Ag, Cu) à 20 et 18 électrons (symétrie T_d) dans le vide et dans le DMF.

^a Effet de solvant pris en compte par le modéle COSMO. ^b C = centre du cluster.

Une possibilité pour stabiliser cette architecture tétraédrique M_{16} à 20 électrons serait de ne pas occuper la HOMO en réduisant son compte électronique à 18 électrons, un autre nombre « magique ». Les résultats obtenus pour les espèces homométalliques du groupe 11 $[M_{16}]^{2-}$ apparaissent plus favorables (Tableau R.3), mais les modèles hétérométalliques de la série $[M'_4M''_{12}]^{2+}$ (M' = group 12; M'' = group 11) sont sans doute les plus viables. De plus leur charge cationique autorise une passivation par des ligands anioniques.

Une autre façon de stabiliser le compte de 20 électrons d'une entité M₁₆, c'est de stabiliser sa HOMO de symétrie a_1 par adjonction en son centre d'un élément supplémentaire dont l'OA de valence ne pourra interagir avec cette HOMO en lui conférant un certain caractère liant. Nos calculs indiquent qu'un certain nombre d'espèces de type [X@M₁₆] (X = groupe 14 et M = groupe 11) pourraient satisfaire cette condition, même si leur structure T_d n'est pas toujours le minimum principal. Par ailleurs, des espèces neutres à 18 électrons de type [X@M₁₆] (X = groupe 2 et M = groupe 11) sont aussi susceptibles d'être observées.

Nous nous sommes par ailleurs intéressés à la modulation des propriétés du cluster emblématique [WAu₁₂] icosaédrique à 18 électrons par « dopage » avec des atomes de platine supplémentaires. Comme le platine n'apporte aucun électron jellium ($6s^0$) les espèces calculées [WAu₁₂Pt_x] (x = 1-4) sont aussi à 18 électrons. Nous avons fait une recherche systématique des isomères les plus stables. Ceux-ci sont représentés sur la Figure R.5.



Figure R.5. Structures de plus basse énergie des clusters $[W@Au_{12}Pt_n]$ (n = 1, 4).

Compound	$\mathbf{Pt}_{0}\left(I_{h}\right)$	$\mathbf{Pt}_1(C_s)$	Pt _{2-a} (C_{2v})	$\mathbf{Pt}_{3}(C_{l})$	$\mathbf{Pt}_4(T_d)$
•					
Fragmentation	$W + Au_{12}$	$W + Au_{12}Pt$	$W + Au_{12}Pt_2$	$W + Au_{12}Pt_3$	$W + Au_{12}Pt_4$
Pauli repulsion	68.06	68.37	69.32	67.66	71.82
Electrostatic interaction (eV)	-41.17	-42.04	-42.80	-42.17	-45.43
Orbital interaction (eV)	-40.41	-39.72	-39.71	-39.88	-41.76
Total bonding energy (eV)	-13.52	-13.38	-13.19	-14.39	-15.37
Ec (kcal/mol)	-66.1	-69.3	-72.7	-74.9	-79.1
ΔE _{H-L} (eV)	1.79	1.08	0.99	0.65	1.09
AEA (eV)	1.87	2.55	2.73	3.05	2.93
AIP (eV)	7.28	7.05	6.61	6.88	7.12

Table R.4. Analyse EDA, écarts HOMO-LUMO, (ΔE_{H-L}), énergie de cohésion (E_c), affinités électroniques adiabatiques (AEA) and potentiels d'ionisation adiabatiques (AIP) des isomères de plus basse énergie dans la série **Pt**_n (n = 0-4).

La stabilité de ces clusters a été évaluée à partir du calcul de plusieurs grandeurs (énergie de cohésion, écart HOMO-LUMO, potentiels d'ionisation, affinité électronique). L'analyse de ces données (Tableau R.4) indique que **Pt**₁ et **Pt**₂ sont les plus viables, notamment vis-à-vis d'une oxydation. L'abaissement de symétrie subi par [WAu₁₂] lors du dopage au platine entraine un élargissement du spectre d'absorption UV-vis simulé par TD-DFT. Cette propriété pourrait être intéressante pour la conception de matériaux à large spectre d'absorption utilisables en photocatalyse ou en photovoltaïque. Par ailleurs l'étude du potentiel électrostatique de ces clusters nous a permis d'identifier leurs sites d'activité catalytique potentielle.

La dernière partie de ce mémoire porte sur l'étude théorique d'un nouveau type de clusters organométalliques récemment caractérisés par R. Fischer et collaborateurs. Il s'agit de $[Cu_3Zn_4Cp_5]$ et $[Cu_2Zn_5Cp_5]^+$ ($Cp^* = \eta^5-C_5Me_5$) dont les structures moléculaires expérimentales sont représentées sur la figure R.6. Ces composés présentent un squelette de structure trigonale bipyramidale dont les sommets sont constitués de fragments Zn-ZnCp*. Ils sont uniques en ce sens qu'ils apparaissent très déficitaires en électrons, avec seulement une paire d'électrons de squelette alors que six sont attendues selon les règles de Wade-Mingos.



Figure R.6. Structures moléculaires expérimentales de [Cu₃Zn₄Cp*₅] et [Cu₂Zn₅Cp*₅]⁺.

Nos calculs sur différents modèles ont montré qu'en fait ce déficit en électrons n'est qu'apparent car certains électron 3d du cuivre participent à la cohésion de squelette, apportant les cinq paires d'électron manquantes. Les règles de Wade-Mingos classiques négligent le rôle des électrons du bloc d, du fait de leur caractère essentiellement non-liant. Il apparait que ce n'est pas le cas avec les métaux de transition de la droite du tableau périodique, comme l'illustre le diagramme d'interaction de la Figure R.7 pour le modèle [Cu₃Zn₄Cp₅]. Il s'avère néanmoins que ces cinq paires d'électrons de squelette impliquant des électrons 3d(Cu) ne sont que modérément liantes. Une stabilisation supplémentaire est fournie par les forces de dispersion impliquant les groupements méthyles des ligands Cp*. Nous pensons que la présence d'une enveloppe constituée de Cp* autour de la cage cluster est nécessaire à la viabilité de telles structures non pontées par des ligands car elle apporte un surcroit de stabilité thermodynamique (énergie de dispersion) ainsi qu'une bonne stabilité cinétique grâce à sa protection stérique.



Figure 7. Diagramme d'interaction orbitalaire simplifié de [Cu₃Zn₄Cp₅]. Les fragments considérés sont [Cu₃Cp₃]²⁻ et [(CpZn₂...Zn₂Cp]²⁺. La pseudo-symétrie D_{3h} est assumée.

Resumen

El trabajo descrito en este manuscrito se basa en los cálculos de estructura electrónica de grupos homo y heteronucleares formados por metales del grupo 11, con el fin de comprender su estabilidad, su estructura, y en algunos casos, sus propiedades. Primero, hemos analizado el hecho de que los superátomos de cobre son muy escasos, al contrario de sus contrapartes de oro y plata. Nuestros cálculos indican que los superátomos de cobre son más estables que los superátomos de plata. Sin embargo, el proceso sintético basado en la reducción de complejos de Cu(I) por borohidruro, conduce preferentemente a la formación de polihidruros de Cu(I), los cuales son muy estables. Por otro lado, hemos analizado la estabilidad de clústeres que contienen un nucleo tetraédrico M₁₆, similar al que se encuentra en el clásico cluster [Au₂₀]. Nuestra investigación sobre los clústeres organometálicos de 20 electrones, $[M_{16}Ni_{24}(CO)_{40}]^{4-}$ (M = metales del grupo 11), mostró que las cuatro unidades periféricas de Ni₆(CO)₁₀ son parte de la entidad superatómica, lo que sugiere que la unidad [M₁₆]⁴⁻ no es viable. Los cálculos de diferentes series homo y heteronucleares de especies libres de ligandos, indican que esta inestabilidad se puede evitar reduciendo a 18 el número de electrones, o incorporando un nuevo elemento en el centro del cluster. En otra investigación, también exploramos la posibilidad de dopar el grupo icosaédrico [WAu₁₂] de 18 electrones con átomos de platino donantes de cero electrones, para formar sistemas de tipo [WAu₁₂Pt_x] (x = 1-4). Los cálculos indican que algunos isómeros son estables, y tienen un amplio rango de absorción en el espectro UV-visible, lo que les proporciona potenciales aplicaciones. Finalmente, hemos investigado la estructura electrónica de los grupos organometálicos, $[Cu_3Zn_4Cp_5]$ y $[Cu_2Zn_5Cp_5]^+$, los cuales aparentemente son deficientes de electrones, pero los cálculos demostraron que esta deficiencia no es tan grande como parece.

Chapter 1: General introduction: Relationships between structure and number of valence electrons in clusters

1.1. The meaning of the word "cluster" in molecular and solid-state chemistry

The first definition of the word *cluster* in coordination chemistry was made in the 1960s by F. A. Cotton and expressed as molecules in which "*a finite group of metal atoms are held together entirely, or at least to a significant extent, by bonds directly between the metal atoms, even though some nonmetal atoms may also be intimately associated with the <i>cluster*."¹ The so-called nonmetal atoms associated with the clusters are ligands and constitute the cluster periphery. This original definition has been later extended to main-group and other non-metal clusters as well as metal clusters where no (or weak) metal-metal bonding exists.^{2,3} In the latter case the metal atoms are held together by bridging ligands. It is important to note that there is a cluster core, in which the connectivity is generally (not always) large, and a cluster periphery made of ligands or various substituents, generally bonded to the core atoms in a localized 2-electron/2-center mode. Some examples are given in Figure 1.1.



Figure 1.1. Examples of molecular clusters.

It is also worth mentioning that clusters can exist in solid state compounds. In that case they can be bonded together, covalently linked by bridging ligands or isolated as cations/anions in ionic compounds.³

Chapter 1: General Introduction

1.2. The meaning of the word stability in inorganic chemistry

Generally, a compound is considered as *chemically stable* if it can be isolated and stored in more or less regular laboratory conditions. This means that it is sufficiently both thermodynamically and kinetically stable. Within the framework of quantum chemistry modelization, Hoffmann, von Ragué Schleyer and Schaeffer III have defined this concept in term of *viability* from the various conditions that the computed models should satisfy.⁴

In general, a molecule which is *chemically stable* (or *viable*) satisfies the so-called closed-shell principle which states that the doubly occupied MOs are low-lying and separated by a significant HOMO-LUMO gap from the unoccupied high-lying MOs. Most often, the occupied orbitals are the bonding and non-bonding (if any) ones and the unoccupied MOs are the antibonding ones. This situation is illustrated in Figure 1.2. There are many exceptions to this rule, but the closed-shell principle is by far largely dominating covalent chemistry.





It is possible to provide simple explanations for this situation. From the thermodynamics point of view, it is obvious that occupying bonding orbitals is stabilizing, whereas occupying antibonding orbitals is destabilizing. Roughly, occupying non-bonding orbitals is at first sight thermodynamically more or less neutral. However, first- or second-
order Jahn-Teller stability requires a substantial HOMO-LUMO gap, and Jahn-Teller stability is a form of thermodynamical stability. Generally, a large HOMO-LUMO gap can be achieved when separating the non-bonding from the antibonding orbitals. When a significant value of this gap is not reached, it can indicate that the considered structure is not an energy minimum on the potential energy surface or that it is a shallow minimum existing on a rather flat potential energy surface, *i.e.*, a "fleeting" molecule according to the definition of Hoffmann and coworkers.⁴

From the kinetics point of view, the lowest the HOMO energy, the less electrodonor (or reductive) will be the molecule. Similarly, the highest the LUMO energy, the less nucleophilic (or oxidant) will be the molecule. Thus, a low reactivity will be achieved for a sufficiently large HOMO-LUMO gap.

1.3. Stability and electron counting rules

Starting with a stable molecule which satisfies the closed-shell principle, and formally adding/removing 2 electrons to this molecule (keeping the structure frozen) results in a situation where the closed-shell principle is no more satisfied. Thus, instability arises and the molecular structure (mainly the connectivity) has to change to modify its number of bonding, non-bonding and antibonding orbitals in such a way the closed-shell principle of Figure 1.2 is again satisfied. It follows that, in general, a given valence electron count is associated with a given structure and conversely. The relationships between structure and electron counts are called electron-counting rules.

There are many electron-counting rules which have their own field of application in chemistry. Nevertheless, whatever are these electron-counting rules, it is easy to understand that adding formally 2 electrons to a stable molecule results generally in the occupation of an antibonding orbital. Thus, the new stable structure will be the result of some bond breaking to transform the antibonding character of this occupied MO into a non-bonding one. It results that the more electron-rich the molecule, the more open is its structure.



Figure 1.3. Schematic MO diagram of a 18-electron ML_n complex (M = transition-metal; L = 2-electron ligand, $n \le 9$).

The most popular electron-counting rules are those based on localized 2-electron/2center bonding modes. In other words, they assume that the number of bonds in which an atom is involved should not be larger than its number of AOs and that the number of bonding MOs is equal to the number of antibonding MOs. They are the octet rule for main-group (4 valence AOs) molecules⁵ and the 18-electron rule for transition-metal (9 valence AOs) complexes.⁶ These rules connect the number of valence electrons to the atom connectivity. Both are variations of what is often called the effective atomic number (EAN) rule and as a whole they cover a huge field of chemistry. Figure 1.3 exemplifies the case of the 18-electron rule for a transition-metal complex of general formula ML_n (M = transition metal; L = 2electron ligand). Since M has 9 atomic orbitals, then a localized bonding approach requires that n ≤ 9. The numbers of M-L bonding and antibonding orbitals should be both equal to n. It results that the occupied orbitals will be the n bonding and the 9 – n non-bonding ones, *i.e.*, a total of 9, which will hold a total of 18-electrons. The octet rule can be demonstrated similarly from the general MO diagram of a AH_n (A = main-group element; n ≤ 4), for example.

1.4. The Polyhedral Skeletal Electron Pair (PSEP) theory and its field of validity

When the connectivity between the atoms in a molecule becomes large, such as in clusters, delocalization occurs, so that the validity of the EAN rule fails. This is the case in borane clusters ($[B_nH_n]^{x-}$) for example in which the boron connectivity if most often larger than 4. The PSEP electron counting rules have been firstly set up empirically for borane and carborane clusters^{2,3,7} and later extended to transition-metal clusters^{2,8} with the help of the isolobal analogy.⁹ Within the organometallic community, they are often called the Wade-Mingos rules. The frontier orbitals (FOs) of various fragments isolobal to BH are sketched in Figure 1.4. All these fragments can use in a similar way their 3 FOs (one of σ type and two of π type) to build the bonding within the cluster core. Assuming the closed-shell principle satisfied, their bonding and non-bonding combinations will be occupied in the cluster and the corresponding electrons are named skeletal electrons and usually counted by pairs, the skeletal electron pairs (SEPs). The general MO diagram of a stable cluster made of such fragments is illustrated in Figure 1.5.

One should note that, because the bonding is not localized, the number of bonding skeletal orbitals is generally different from the number of antibonding skeletal orbitals. For example, the octahedral $[B_6H_6]^{2-}$ cluster (see below) has a total of 3 x 6 =18 skeletal orbitals, of which 7 are bonding (and occupied) and 11 are antibonding (and vacant). The 7 bonding SEPs are responsible for the 12 B-B "bonds", leading to a formal B-B bond order of 7/12 = 0.58. In spite of this value significantly lower than 1, $[B_6H_6]^{2-}$ is chemically very stable and exhibits a large HOMO-LUMO gap.

Changing the SEP number will result in a change of the structure. The larger the PES number, the more open (less compact) the structure, but in the case of boranes or organometallic analogs, the clusters can always be described as inscribed in a formal fundamental deltahedron of which the BH (or isolobal) fragments constituting the cluster occupy vertices of the fundamental deltahedron. There is no need for all the deltahedron vertices to be occupied. The basic electron counting rule connects the number of SEP to the number of polyhedron vertices (occupied or not). The SEP number should be equal to the number of vertices plus 1. For example a cluster inscribed in an octahedron is expected to have 6 + 1 = 7 SEPs. This is for example the case of $[B_6H_6]^{2-}$ (Figure 1.1) for which all the octahedron vertices are occupied, each BH fragment providing two electrons and the -2 charge providing two additional ones : $(6 \times 2 + 2)/2 = 7$ SEPs.



Figure 1.4. Illustration of the isolobal analogy between E, EH, and ML₃ fragments (E = maingroup ; M = transition-metal). The three fragments possess a set of similar frontier orbitals (one σ (radial) and two π (tangential)) occupied by the same number of electrons (two). The electron occupation corresponds to C, BH and Fe(CO)₃, respectively.

Adding formally two electrons to $[B_6H_6]^{2-}$ (7 SEPs) leads to $[B_6H_6]^{4-}$ (8 SEPs) which can be isolated in its "protonated" form B_6H_{10} . It adopts a more open pentagonal bipyramidal structure which can be viewed as inscribed in a 7-vertex pentagonal bipyramidal deltahedron with one unoccupied vertex. Thus it follows the PSEP rules, having 7 + 1 = 8 SEPs. Such clusters inscribed in a polyhedron with a vacant vertex are called *nido* species, in contrast with systems in which, as for $[B_6H_6]^{2-}$, all the vertices are occupied and which are named *closo*. Those with 2 unoccupied vertices are called *arachno*. The closo, nido, and arachno borane clusters are shown in Figure 1.6. In this figure, the oblique strokes are connecting the clusters inscribed in the same fundamental deltahedron. Looking at the *closo* column, from top to bottom they correspond to the following deltahedra: trigonal bipyramid, octahedron, pentagonal bipyramid, dodecahedron, tricapped trigonal prism, bicapped square antiprism, octadecahedron and icosahedron.

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Figure 1.5. General MO diagram of a stable cluster made of E, ER or ML_3 fragments as defined in Figure 1.4. This schematic situation can be extended to any type of fragments, providing that the cluster satisfy the regular PSEP theory rules.

Many extension of these simple rules have been established, mostly by Mingos in the 1980s,² and applied to capped clusters, fused clusters, centered clusters, clusters made of fragments having a number of frontier orbitals different from 3.



Figure 1.6. Closo, nido and arachno skeletons of boranes and carboranes. (From ref. 7d).

A theoretical demonstration of the Wade-Mingos rules has been provided by A. J. Stone, also in the 1980s.^{10,11} It is based on the consideration that the fundamental deltahedra are of pseudo-spherical shape and on the assumption that the skeletal electrons are delocalized on the spherical envelope in which the deltahedron is inscribed. Such considerations lead to

the classical problem of an electron gas constrained to move on the surface of a sphere, of which the scalar solutions are the spherical harmonics. These surface harmonics can be identified to the classical skeletal MOs of Figure 1.5. Such a model works for clusters made of fragments having only one FO of σ type. However, these scalar solutions are not sufficient to describe systems made of fragments having in addition π -type FOs, because they are not able to take into account the intrinsic nodes of these FOs. Thus, Stone has developed a theory based on vector surface harmonics which are also solutions of the considered Schrödinger equation. This approach, named tensor surface harmonics (TSH) theory allows to derives theoretically all the qualitative PSEP rules.^{10,11} It is noteworthy that the TSH theory can also take into account δ -type frontier orbitals when the cluster fragments bear such FOs in addition to its σ - and π -type FOs. Considering the qualitative rules arising from the TSH theory, it is possible to predict the electron-count of clusters in which the σ -, π - and δ -type are involved in different amounts, by simply tuning their different interaction strength.²

Because they are based on a model that assumes the electrons to be confined on the surface of the cluster spherical envelope, the PSEP rules work very well with empty (hollow) clusters. They work also relatively well for some clusters containing encapsulated atoms, but fail in the case of compact stuffed clusters of large nuclearity, simply because the interactions between the envelope atoms become less important with respect to the interactions involving the inner atoms. In such a case, another approach based on the spherical jellium model should be used.

1.5. The superatom concept and its field of validity

The spherical jellium model applies to compact (stuffed) clusters. It, is related to the problem of an electron gas constrained inside a sphere. It was first proposed by Knight and coworkers to rationalize mass spectrometry experiments on sodium clusters which showed particularly large peaks for Na_n clusters with n = 8, 20, 40, 58 and 92.¹² In this model, the compact spherical cloud of the individual positive nuclei charges is described in the Schrödinger equation by a kind of averaged potential having a more or less smoothened square-potential shape v(r_i), the "square" width representing the diameter of the spherical cluster.¹³ With such a radial (spherical) potential, the resulting Schrödinger equation looks like that of a polyelectronic atom (see Figure 1.7), except that the radial potential v(r_i) is not in $1/r_i$ like in an atom, but has a more complex and generally parametrized expression. Since

the Hamiltonian derived from the spherical jellium approximation is of the same spherical symmetry as that of an atom, it results that its polyelectronic eigenfunctions can be written, as for the atom case, on the basis of one-electron orbitals of the form $\Psi_{n,l,m}(i) = f_{n,l}(r_i) \times Y_{l,m}(\theta_i, \phi_i)$. The relationship with atomic orbitals is straightforward so that clusters obeying the spherical jellium model are called superatoms. Their radial part $f_{n,l}(r_i)$ depends on the analytical form of the spherical potential. A difference with the atom case is than *n* can be associated with any positive *l* numbers. In the following, the jellium one-electron orbitals corresponding to l = 0, 1, 2, 3... will be written with capital letters as S, P, D, F... in order to avoid confusion with atomic orbitals. In a similar way as there is a level ordering for atomic orbitals (1s < 2s < 2p < 3s < 3p...) which is quasi-independent of the atom nature, the energy levels of the one-electron spherical jellium order in the model of Knight as: 1S < 1P < 1D < 2S < 1F < 2P < 1G < 2D < 1H... This level ordering is also largely independent from the parametrization of the considered potential v(r).



Figure 1.7. Major features of the spherical jellium model.

Going back to the atom/superatom comparison, it is well known that an isolated atom reaches chemical stability when it satisfies the closed-shell principle, *i.e.*, when it is a rare gas or an atomic ion reaching the configuration of a rare gas (Na⁺, Ca²⁺, Cl⁻, O²⁻.., for instance). Such a situation occurs for specific total numbers of electrons (2, 10, 18, 36, 54...). Similarly, in the case of superatoms, the closed-shell requirement principle is satisfied when the 1S, 1P, 1D, 2S, 1F... shells are successively filled up, giving rise to the so-called "magic" numbers of

electrons: 2, 8, 18, 20, 34, 40, 58, 68, 90... Stable clusters satisfying these electron counts are called closed-shell superatoms.¹⁴ This simple model has been extended to non-spherical oblate and prolate cluster shapes (see below).¹⁵ The spherical jellium model is particularly suited for clusters made of atoms which participate to the bonding with only one σ -type orbital. This is the case for alkali clusters for example.¹² This is also the case of Group 11 clusters which participate to the bonding mainly with their (n + 1)s valence orbitals. In this latter case, the (n + 1)p valence AOs also somewhat participate, whereas the nd AOs can be considered as non-interacting at the qualitative level. The participation of np AOs is even more important in the case of aluminum and gallium superatoms.¹⁶

At this stage of the discussion, it is important to realize that the jellium model is not a LCAO model. The superatomic orbitals are not at all expressed on the basis of atomic orbitals since the atom nuclei are not specifically considered in the jellium Hamiltonian of Figure 1.7. Moreover, this model does not take into account the electrons associated with the ligands and other peripheral groups or atoms. As said above, it does not either consider the non-bonding valence nd electrons of the Group 11 metals, for example. Therefore, this model should be considered as a qualitative approach, which provides electron counting rules allowing rationalizing the stability of compact clusters. Nowadays, quantum chemical calculations are most often performed within the LCAO approach and consider all the electrons and nuclei of the computed molecule. Calculations reported in this manuscript were carried out within the standard density functional theory (DFT) formalism. One of the major goals in analyzing the DFT results will be to identify, among all the calculated Kohn-Sham orbitals, those which could be considered as being the jellium orbitals associated with the superatomic core.

The superatom model can be also applied to non-spherical, prolate- or oblate-distorted clusters.¹⁵ They follow specific electron counts associated with Jahn-Teller distortions away from spherical symmetry, associated with degeneracy splitting of their HOMOs. This approach has been first exploited by Mingos *et al.*, and resulted in the prediction of structures which were later experimentally confirmed³³. Mingos has also developed simple electron counting rules for more complex cluster frameworks which can be described as resulting from the condensation of several spherical skeletons.³³

Finally, it is worth mentioning that there is a difference between clusters following the superatom and Wade-Mingos concepts which comes from their total number of electrons, *i.e.*, the electron counts including the peripheral electrons. Focusing on organometallic transition-metal clusters obeying the Wade-Mingos rules, one can say that (Figures 1.4 and 1.5), the total number of electrons and SEP number are linked together, since adding/removing a

ligand (2 electrons) will lead to the creation of an occupied antibonding MO, a stabilityforbidden situation. Thus, the total number of cluster electrons (skeletal + peripheral) should not change if the structure and SEP numbers are kept frozen (Figure 1.8). In the superatom family, the non-bonding accepting orbitals located on the peripheral atoms are usually highlying (combinations of sp-type hybrids pointing outwards) and there is no need to occupy them if not involved in M-L bonding (Figure 1.8, left). Thus, the total number of electrons is, as the total number of ligands, variable whereas the number of jellium electrons remains unchanged. It means that a ligated closed-shell superatom has the same number of jellium electrons as its closed-shell bare metallic core, irrespectively of the number of ligands. In that case, the total number of cluster electrons will substantially depend on the steric hindrance of the "passivating" ligand shell.



Figure 1.8. Simplified MO interaction diagram illustrating the difference between a superatom (left) and a Wade-Mingos type cluster, when interacting with an incoming additional 2-electron ligand.

1.6. General remarks and introduction to the following chapters

The Group 11 superatomic clusters are generally prepared from the reduction of a metal salt (or weakly covalent complex) by borohydride in the presence of ligands. Typical examples are shown in Figure 1.9. The most popular ligands are thiolates. Among the Group 11 clusters, those made of gold are known for several decades, but the gold superatom chemistry has been really booming since the beginning of this century.¹⁷ The first characterized species, such as for example Au₁₁(PPh₃)₇(SCN)₃, [Au₁₃(PR₃)₁₀Cl₂]³⁺, Au₅₅(PR₃)₁₂Cl₆ and $[Au_{39}(PR_3)_{14}Cl_6]^{2+,18}$ have been recently followed by many, such as Au102(SR)44, Au38(SR)24, Au36(SR)24, Au30(S)(SR)18, Au28(SR)20, Au25(SR)18, Au24(SR)16, Au₂₄(SR)₂₀, Au₂₃(SR)₁₆, Au₂₀(SR)₁₆ or Au₁₈(SR)₁₄, all structurally characterized by X-ray diffraction.¹⁹ Most of these compounds are closed-shell superatoms, having a "magic" number of jellium electrons. They can be described as made of a bare mixed-valent $[Au_n]^{x+}$ (n > x) core holding the n - x jellium electrons, "passivated" by a ligand shell made of formally anionic thiolates to which some formally Au⁺ cations are covalently linked, thus forming [Au_m(SR)_n]^{m-n} staples which are mainly bonded to the jellium core by donation of sulfur lone pairs. Whereas the "Au⁺" cations are not part of the mixed-valent core, they contribute to the overall molecular charge (which always tends to reach or approach charge neutrality) and they are susceptible to be involved in the excited states, thus in the optical properties. The understanding of their number and positions is therefore important.



Figure 1.9. Examples of ligated closed-shell Group 11 superatoms.

The chemistry of silver superatoms is quite similar, but it is by far younger and the number of characterized species is substantially smaller. Typical examples are $[Ag_{44}(SR)_{30}]^{4-}$,

 $[Ag_{62}S_{12}(SR)_{32}]^{2+}$ or $[Ag_{21}{S_2P(OR)_2}_{12}]^{+,20}$ which can be described similarly as their golden homologs. On the other hand, the superatom chemistry of homometallic copper clusters is almost inexistent at the time of writing this manuscript, with only four fully characterized examples, all having 2-*je* (1S² closed-shell configuration).²¹ A few heteronuclear superatoms made of copper and another metal are also known.²² In fact, the treatment of copper(I) by borohydride in the presence of ligands does not usually lead to the formation of superatoms (as in the case of silver(I), for example), but to giant copper(I) polyhydrides.²³ The question which arises then is: Why are copper superatoms so scarce as compared to their silver, and more specifically gold analogs ? Is it because they are less stable or because the copper(I) polyhydride clusters (Figure 1.10) are particularly stable as compared to their silver and gold counterpart ? In this work, we evaluate the relative stabilities of various Cu, Ag and Au superatoms. In particular, their size are varied to understand their stability with respect to their number of jellium electrons. We also evaluate the relative stability of molecular and solid state M(I) hydrides within the group 11 series in order to understand why Cu(I) hydrides are so easy to isolate as compared to gold or silver analogues.



Figure 1.10. Examples of copper(I) polyhydrides from ref²³.

Another center of interest of this work is focused on structures related to the tetrahedral fcc M_{20} architecture, exemplified by the bare $[Au_{20}]$ cluster (*20-je*), which is a unique example of a stable non-ligated homometallic group 11 superatom with metal oxidation state equal to zero (Figure 1.11a).³⁴ Such a T_d architecture can be described as made

of M₄@M₁₂@M₄ concentric shells and we will investigate the possibility for a 20-*je* [M₁₆]⁴⁻, *i.e.*, [M₄@M₁₂]⁴⁻, to exist. Indeed, such a cluster core exists in [Ag₁₆Ni₂₄(CO)₄₀]⁴⁻ (Figure 1.11b).^{25b} Thus, we will present first the rationalization of the electronic structure of the [M₁₆Ni₂₄(CO)₄₀]⁴⁻ (M = Cu, Ag, Au) series, showing that the four peripheral Ni₆(CO)₁₀ units should not be considered as ligands, but as full parts of the superatomic entity. In a subsequent step, we will investigate the hypothetical bare group 11 homometallic clusters [M₁₆]⁴⁻ (20-*je*) and [M₁₆]²⁻ (18-*je*). Their neutral heterometallic relatives [M'₄M''₁₂] (M' = Zn, Cd, Hg; M'' = Cu, Ag, Au) (20-*je*) and the corresponding 18-*je* dications are also investigated. Finally, the doping of group 11 M₁₆ units by an heteroelement at the center of the following [X@M₁₆] models where M = Cu, Ag, Au: (X= C, Si, Ge, Sn, Pb and Ti, Zr, Hf; 20-*je*) and X = Zn, Cd, Hg; 18-*je*).



Figure 1.11. Molecular structures of $[Au_{20}]$ (a)³⁴, $[Ag_{16}Ni_{24}(CO)_{40}]^{4-}$ (b)^{25b}, $[WAu_{12}]$ (c)^{36a} and $[Zn_4Cu_3Cp^*_5]$ (d).

The next part of this thesis is devoted to the investigation of hypothetical species isoelectronic to Pyykkö's emblematic icosahedral *18-je* [W@Au₁₂] cluster³⁶ (Figure 1.11c). This series is generated by adding supplementary 0-electron (d^{10}) Pt atoms to the Au₁₂ cage, namely [WAu₁₂Pt_x] (x = 1-4). Calculations indicate that such species should be stable enough for being observed. TD-DFT allows simulating their UV-vis optical spectra which could be valuable signature for their experimental characterization.

The last chapter of this thesis is devoted to the rationalization of the stability and structure of two very newly synthesized organometallic clusters, namely $[Zn_4Cu_3Cp_5]$ (Figure 1.11d) and the isoelectronic and isostructural $[Zn_5Cu_2Cp_5]^+$. Indeed,

these architectures, being of trigonal bipyramidal geometry (5 vertices) are expected from the classical Wade-Mingos rules to possess 5 + 1 = 6 SEPs. A standard PSEP electron counting ends up with a count of only 1 SEP. Our calculations provide an explanation for this huge discrepancy and allow understanding why such hypoelectronic species have enough bonding electrons for keeping such clusters stable enough to be isolated.

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Chapter 2: Insights into the intrinsic stability and optical properties of coinage metal superatomic cores

Introduction

Coinage metal nanostructures have received considerable interest owing to their unique physical and chemical behavior,¹⁻¹⁰ delivering promising building blocks for functional nanomaterials. Particularly, the knowledge of stable gold clusters has been well developed leading to the understanding of both structural and electronic properties,¹¹⁻¹⁸ with promising applications in biomedicine, catalysis and sensing, among others.^{9,10,19-24}

The last decade has witnessed tremendous advances in synthetic strategies for atomically precise aggregates, where ligand-protected architectures rise as an effective method towards obtaining size-controlled structures.^{12,17} In such systems, an inner metallic core composed of a finite number of atoms is embedded into an outer protecting layer made of various stabilizing groups. Usually, chalcogenolate, halogenide and/or phosphine ligands are employed: the former often leads to a protecting layer involving both ligands and M^I atoms,^{6,25-27} which prevents further degradation.^{5,28-31} Owing to the presence of formally anionic ligands on the outer shell, the inner metallic core is generally in a positive oxidation state ($[M_n]^{x+}$).

The stability of the overall core is controlled by the interplay between electronic and structural requirements,³² favoring certain numbers of valence electrons, or *magic* numbers, as depicted by the superatom concept,^{6,11,33-37} as developed above in Chapter 1). Let's recall that these *magic* electron counts (2, 8, 18, 20, 34...), which provide closed-shell configurations to the $[M_n]^{x+}$ cores, have been rationalized within the spherical jellium-type model leading to one-electron cluster orbitals somehow resembling the atomic orbitals⁵⁸ and ordering as $1S < 1P < 1D < 2S < 1F...^{11}$ In the case of coinage metals, the M valence nd electrons are supposed not to be involved significantly in the bonding and cluster jellium electrons (*je*) can be considered as provided by the metal's (n + 1)s valence atomic orbitals (AOs).

Owing to the efforts seeking the formation of novel nanoscale devices displaying exceptional electronic, optical and structural properties, special attention should be paid to the

inherent characteristics of the cluster cores existing in ligand-protected architectures. One of the most prominent and widely studied example is $[Au_{25}(SR)_{18}]^-$ which displays a high stability owing to its geometric and electronic peculiarities. Its X-ray structure exposes an aesthetic icosahedral Au_{13} core surrounded by a layer composed of six dimeric $Au_2(SR)_3$ staple units.⁵ The formally $[Au_{13}]^{5+}$ core exhibits an *8-je* count denoting an $1S^21P^6$ electronic configuration, accounting for its high stability owing to the shell-closing electron count.^{11,14,38-40}

Whereas the chemistry of gold superatoms is nowadays very well documented, with characterized atom-precise species ranging up to more than one hundred of atoms,^{17,39} that of silver is so far developed to a lesser extent.⁴²⁻⁴⁹ In the case of copper, as far as we know, only four closed-shell superatomic species have been structurally characterized at the present time, as mentioned in the introduction. A few mixed-metal superatoms containing copper are also known, such as for example the 8-*je* [(CuCNtBu)₄(ZnCp*)₄],⁴⁹ the *18-je* series [Au_{12+n}Cu₃₂(SR)_{30+n}]^{4-,50} the *20-je* [Ag₂₈Cu₁₂(SR)₂₄]⁴⁻⁵¹ and the very recently published *67-je* (open-shell) neutral cluster [Cu₄₃Al₁₂Cp*₁₂] (Cp* = η^5 -C₅Me₅).⁵⁹

Thus, one of the major questions we will try to answer in this chapter is why is the superatom chemistry of copper so poor and that of gold so rich. Getting rid of the passivating outer shells and of their huge variability in terms of composition and structure, we will focus on the intrinsic electronic structure and energetics of the $[M_n]^{x+}$ superatomic core and on the differences between the three Group 11 metals. The following pseudo-spherical structures of increasing sizes are investigated according to the symmetry: M₄ (tetrahedron), M₄@M₄ (tetracapped tetrahedron, M₈), M₄@M₁₂@M₄ (tetrahedron embedded into a truncated tetrahedron and the resulting structure capped by 4 atoms forming a big tetrahedron, M₂₀) which have T_d symmetry and M@M₁₂ (centered icosahedron, M₁₃), M₁₂@M₂₀ (icosahedron embedded into a dodecahedron, M₃₂) and M@M₁₂@M₃₀ (centered icosahedron embedded into a icosidodecaedron, M₄₃) which have I_h symmetry. They are depicted in Figure 2.1.

The occurrences of the M@M₁₂ and M₁₂@M₂₀ core architectures in superatom chemistry are very well documented.^{5,39,46,55,56} That of M₄@M₁₂@M₄, it adopted by the unique and emblematic ligand-free Au₂₀ cluster.⁵⁷ This structure will be discussed in more details in Chapter 3 and 4 of this thesis. Tetrahedral and tetracapped tetrahedral cores exist also, as exemplified by $[{Au(P'Bu_3)}_4]^{2+58}$ and $[(CuCNtBu)_4(ZnCp^*)_4]$.⁵³ On the other hand, the Au@Au₁₂@Au₃₀ structure has been proposed and found to be stable by DFT calculations.⁵⁸ It constitutes the largest innermost part of icosahedral M₅₅ particles, which have been extensively computed.⁶⁰





M₂₀



Figure 2.1. Structural representation of the studied cluster cores.

Each of these structures has been investigated for one or two different magic electron counts (precisely for I_h symmetry). The differences along the group were studied by using relativistic DFT methods involving isoelectronic and isostructural cores, which will shed light on possible stability and properties prior to carrying out exploratory synthetic efforts. We have also investigated the optical properties of these species in the UV-vis range, as they may constitute fingerprints for such architecture and electron counts when present as superatomic cores in real ligated species.

2.1. Computational details

Relativistic density functional theory (DFT) calculations⁶¹ were carried out by using the ADF code,⁶² incorporating scalar (SR) corrections through the ZORA Hamiltonian.⁶³ We employed the triple- ζ Slater basis set, plus two polarization functions (STO-TZ2P) for valence electrons (except for $\left[M_{32}\right]^{14+}$, see below), within the generalized gradient approximation (GGA) according to the Becke–Perdew (BP86) exchange functionals.^{64,65} The

frozen core approximation was applied to the $[1s^2 - 4f^{14}]$ inner electrons for Au, $[1s^2 - 4p^6]$ for Ag, $[1s^2-3p^6]$ for Cu, $[1s^2-3p^6]$ for S, and $[1s^2]$ for C, leaving the remaining electrons to be treated explicitly. Geometry optimizations were performed without any symmetry restrain, by using the analytical energy gradient method implemented by Versluis and Ziegler.⁶⁶ In the specific cases of the highly charged $[M_{32}]^{14+}$ and $[M_{13}]^{11+}$ models, geometry convergence could only be obtained with the incorporation of solvent effects through a polarizable continuum model, which consists of a conductor-like screening treatment through the COSMO module,⁶⁷ to take into account the effects of counterions for these highly charged ions. The considered solvent was dimethyl formamide (DMF), which is usually employed in the coinage metal nano-cluster synthesis. Moreover, in the case of $[M_{32}]^{14+}$, the larger STO-QZ4P basis set (quadruple- ζ plus four polarization functions) was found to be necessary. Vibrational frequencies were computed to ascertain energy minima. Owing to the flat energy landscapes and possibly to vibrational anharmonicity, small imaginary frequencies were found in a few cases (< 30i cm⁻¹, Table 2.1 and Table 2.2), in particular for the highly charged $[M_{32}]^{14+}$. Owing to their persistency in our minimum search, they were considered negligible. Time-dependent DFT (TD-DFT) calculations were employed at the same level, but by using the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional⁶⁸ because of its improved performance on long-range interactions and relatively low computational cost. Being employed in similar clusters, it allows a direct comparison with other computational studies of superatomic nanoclusters.^{39, 46, 69–71} The use of GGA functionals leads generally to an underestimation of approximately 0.4 eV for excitation energies in comparison to the experiment.^{14,72–74} Spin-orbit calculations were done at the TZ2P/PBE level by using the twocomponent ZORA Hamiltonian.61,63

2.2. Results and discussion

The structures for the studied cores are summarized in Figure 2.1. The Kohn–Sham MO diagrams of the 2-*je* $[M_4]^{2+}$, 8-*je* $[M_8]$, 8-*je* $[M@M_{12}]^{5+}$, 20-*je* $[M_4@M_{12}@M_4]$, 18-*je* $[M_{12}@M_{20}]^{14+}$, 34-*je* $[M@M_{12}@M_{30}]^{9+}$ are shown in Figure 2.2 and Figure 2.3. The corresponding major computed data are given in Table 2.1. The electron counts of the first five architectures have been shown to exist in real ligated clusters.^{6, 39, 43, 46, 52, 57, 75}



Figure 2.2. Relevant Kohn-Sham molecular orbital diagrams for $[M_4]^{2+}$ (left), $[M_8]$ (right) and $[M_{20}]$ (below) with (a) for copper, (b) for silver and (c) for gold. Jellium level denoted in blue.

These electron counts can be ascribed to the $1S^2$, $1S^21P^6$, $1S^21P^61D^{10}$, $1S^21P^61D^{10}2S^2$ and $1S^21P^61D^{10}2S^21F^{14}$ superatomic configurations along the series. They also correspond to the occupation of all the bonding orbitals that one would get by carrying out a simple Hückel calculation, assuming each atom participates with only one (n + 1)s valence orbital. Adding more electrons would result in the occupation of somewhat antibonding Hückel orbitals. In the DFT results, these orbitals can be picked out by their large (n + 1)s character. They can be identified as the jellium-type orbitals of the superatom model (levels in blue in the MO diagrams), denoting different numbers of nodes mimicking atomic orbitals with different angular momentum numbers (l = 0, 1, 2, 3, etc...).^{11,25, 32, 37} The valence nd-type combinations (in black) are roughly nonbonding in character. The superatomic orbitals of the computed models are plotted in Figure 2.4 and Figure 2.5. An interesting feature of the coinage metal cores is that the obtained superatomic shells for gold cores are more stabilized than that found for silver counterparts, as a result of the strong influence of the relativistic effects in gold.^{76–80}



Chapter 2

Figure 2.3. Relevant Kohn-Sham molecular orbital diagrams for $[M_{13}]^{5+}$ (above), $[M_{32}]^{14+}$ (middle) and $[M_{43}]^{9+}$ (below). Jellium level denoted in blue.

Another feature related to this peculiarity of gold is that the calculated HOMO–LUMO gaps of the Ag species are always larger than those of their Cu and Au analogs, illustrating the non-monotonous Cu/Ag/Au variation. In any case, the HOMO–LUMO gaps are significant, in agreement with the assumed favored electron counts. Indeed, for all the cores, the frontier levels are dictated by the superatom shell structure demonstrating that the validity of the superatom approach for gold and silver can be extended to copper structures. A comparison between the relative location of the superatomic shells reveals a similarity between the different cores, where a destabilization of the relevant shells is found for silver, in comparison to gold and copper.



Figure 2.4. Jellium orbitals of $[Au_4]^{2+}$ (left), $[Au_8]$ (right) and $[Au_{20}]$ (below). Color legend: Occupied blue and red, vacant turquoise and orange.

This destabilization can induce a difference in the interaction with a core-protecting shell, in comparison to the other coinage metal relatives. The metal–metal distances (Table 2.1), ranging from approximately 2.4 to 3.1 Å, denote a strong aggregation between the constituting atoms. The calculated data exhibit a shorter M–M separation for copper, followed by the gold structures. Silver clusters denote larger M–M distances in the series.⁸¹ From the 2-*je* $[M_4]^{2+}$ cluster, the *8-je* $[M_8]$ structure can be obtained by addition of four capping atoms to

the M₄ core. In [M₈], the M–M distances in the inner M₄ are slightly elongated owing to the presence of the outer structural shell. Similarly, for the *8-je* [M@M₁₂]⁵⁺ core, the distances are slightly shorter than that found for the ligand-protected structure, namely, $[(M@M_{12})M_{12}(SMe)_{18}]^{-}$, which has been structurally characterized for Ag and Au.^{39,45} In the *18-je* [M₁₂@M₂₀]¹⁴⁺, the inner M₁₂ icosahedron exhibits shorter distances than that found in the [M@M₁₂]⁵⁺ core in the calculated ligand-protected [(M@M₁₂)M₁₂(SMe)₁₈]⁻ structures. To evaluate the intrinsic stability of our [M_n]^{m+} models, the per-atom cohesion energy was computed as follows:

 $E_{C} = [E_{cluster} - (n - m)E(M) - mE(M^{+})] / n (n = number of atoms) (1)$



Figure 2.5. Jellium orbitals of $[Au_{13}]^{5+}$ (left), $[Au_{32}]^{14+}$ (right) and $[Au_{43}]^{9+}$ (below). Color legend: Occupied blue and red, vacant turquoise and orange.

The computed values (Table 2.1) cannot be compared from one cluster structure to another one because of the large variation of the coulombic nuclear repulsions in these highly

(and differently) charged models, which, in the real life, approach neutrality through coordination of anionic ligands.

Table 2.1. Relevant computed data for the $[M_4]^{2+}$, $[M_8]$, $[M_{13}]^{5+}$, $[M_{20}]$, $[M_{32}]^{14+}$ and $[M_{43}]^{9+}$ metal cores. E_C and ΔE_{H-L} are the per-atom cohesion energy and HOMO-LUMO gap, respectively. E_C are in kcal/mol, ΔE_{H-L} are in eV, distances are in Å and lowest frequencies are in cm⁻¹. All calculations with TZ2P basis sets in vacuum, except for $[M_{32}]^{14+}$, in which a QZ4P basis set associated with solvent (DMF) corrections was employed.

	$[M_4]^{2+}/1S^2(2-je)$								
	Ec	ΔE_{H-L}	M _{tet} -M _{tet}					Lowest freq.	
$[Cu_4]^{2+}$	-27.8	2.56	2.430				116		
$[Ag_4]^{2+}$	-18.2	3.85	2.800					74	
$[Au_4]^{2+}$	-30.0	2.50			2.7	27			66
		$[M_8] M_4 @ M_4 / 1S^2 1P^6 (8-je)$							
	Ec	ΔE_{H-L}	M _{tet} -M _{tet}		M _{tet} -M _{cap}		Lowest freq.		
[Cu8]	-53.8	2.15	2.460			2.390			52
[Ag ₈]	-39.4	2.32	2.853			2.767			34
[Au ₈]	-47.2	2.02	2.871			2.740		20	
	$[M_{13}]^{5+} M@M_{12}/ \mathbf{1S^2 1P^6}(8-je)$								
	Ec	ΔE_{H-L}	M _{cent} -M _{ico}			Mico-Mico		Lowest freq.	
$[Cu_{13}]^{5+}$	-7.5	1.91	2.514			2.643		70	
$[Ag_{13}]^{5+}$	4.5	2.63	2.888			3.037		39	
$[Au_{13}]^{5+}$	-8.9	2.01	2.818			2.963		23	
	1								
		[]	M_{20} M ₄ @M ₁₂	$aM_4/15$	S ² 1P ⁶	$1D^{10} 2S^2$ (20-је	2)	
	Ec	ΔE_{H-L}	M _{tet} -M _{tet}	M _{tet} -M	trunc	M _{trunc} -M _t	runc	M _{trunc} -M _{cap}	Lowest freq.
$[Cu_{20}]$	-62.07	1.34	2.600	2.453		2.414-2.4	89	2.390	67
$[Ag_{20}]$	-45.46	1.64	3.034	2.831		2.755-2.9	02	2.756	41
	-56.34	1.81	3.131	2.81	/	2.6/4-2.9	46	2./10	30
			г м 114	+ M @N	π / 1	C? 1D6 1D	10 (1	9 : -)	
	Б	٨E	$[M_{32}]^{1+}M_{12}(a)M_{20} / 1S^2$			<u>S² IP[*] ID^{**} (18-je)</u>			Lowest frog
$[C_{11}, 1]4^+$	E_c	ΔE_{H-L}	2.541			2.461		2 791	Lowest freq.
$[Cu_{32}]$	-43.7	0.92	2.341	+1 22		2.401		2.701	12
$[Ag_{32}]$	-27.9	1.39	2.922	922 052		2.821		3.100	-12
[Au ₃₂]	-44.3	1.11	2.933			2.702		5.145	-32
		$[M_{42}]^{9+}$ M@M ₁₂ @M ₂₀ / 1S ² 1P ⁶ 1D ¹⁰ 2S ² 1F ¹⁴ (34-ie)							
	Ec	ΔEh-l	Mcent-Mico	Mico-Mico		Mico-Mcan		M _{cap} -M _{cap}	Lowest frea.
$[Cu_{43}]^{9+}$	-28.4	0.35	2.501	2.63	0	2.475	"T	2.611	47
[Ag ₄₃] ⁹⁺	-14.6	0.63	2.931	3.082		2.843		3.018	23
$[Au_{43}]^{9+}$	-26.4	0.70	2.894	3.043		2.797		2.971	20
L '~]		1				· · · ·			I

On the other hand, comparisons can be made within one particular $[M_n]^{m+}$ structure. The computed values are found to be negative, indicating a favorable situation, except in the case of $[Ag_{13}]^{5+}$ where a small positive E_C is found, owing to the particularly high cationic charge associated with a relatively small number of bonding electrons (*8-je*). Nevertheless, the existence of $[Ag_{13}]^{5+}$ superatomic cores is experimentally evidenced^{45,47–49} thus pointing out that for the silver counterpart, the role of the ligand shell is more crucial in the stabilization of the $[Ag_{13}]^{5+}$ core, in comparison to gold. In addition, owing to the similar E_C found for $[Cu_{13}]^{5+}$ and $[Au_{13}]^{5+}$, it is suggested that the copper counterpart is likely to be obtained, although its elusive characterization is due to its challenging synthetic strategy. In the case of the 20-*je* $[M_{20}]$ which is known for the gold cluster, E_c suggests that $[Cu_{20}]$ cluster would be even more stable than $[Au_{20}]$.

More generally, the E_C values follow the trend given by $E_C^{Au} < E_C^{Cu} < E_C^{Ag}$ (Table 2.1), indicating that bare copper superatoms are less stable than their gold homologs but more stable than their silver counterparts. It is noteworthy that relativistic effects are not crucial in the above relative order, for nonrelativistic calculations lead to the same trend. Three other electron counts were also investigated, namely the 2-je $[M_{13}]^{11+}$, the 34-je $[M_{32}]^{2-}$, and the 40*je* $[M_{43}]^{3+}$. Indeed, the first one has been shown to exist in $[Cu_{25}H_{22}(PPh_3)_{12}]^{+,50}$ The second one appears accessible by adding 14 electrons into the virtually nonbonding 1F orbitals of $[M_{32}]^{14+}$. Similarly, the 2P level of M_{43} appears also potentially accessible, although somewhat antibonding. The major data are listed in Table 2.2. In the case of $[M_{13}]^{11+}$, they show the same trend in E_C as those in Table 2.1 (the positive values result from the domination of nuclei repulsions). In the case of $[M_{32}]^{2-}$ and $[M_{43}]^{3+}$, they even follow the E_C^{Cu} $< E_C^{Au} < E_C^{Ag}$ order, indicating better stability for the copper species. However, the computed HOMO-LUMO gaps are smaller, suggesting that these electron counts are less favored. The optical properties of atomically precise ligand-protected clusters have been widely explored,^{17,75} giving strong experimental evidence of their electronic structures, allowing us to characterize and distinguish clusters with different nuclearities. In this concern, we aim to evaluate the characteristic fingerprints given by the cluster cores, and the differences between the coinage metals. The low-energy optical absorption spectrum was evaluated theoretically (up to 3 eV). For one of the most prominent ligand-protected gold clusters, namely $[Au_{25}(SR)_{18}]^{-}$ (R = Me) containing the 8-*je* $[Au_{13}]^{5+}$ core, the employed level of TD-DFT theory (ZORA/PBE/TZ2P) exhibits similar results to recent calculations,^{70,71,82} indicating a first peak calculated at 1.41 eV, with a mainly $1P \rightarrow 1D$ transition character. Also, when R =

H, similar results have been obtained⁷⁴ thus supporting the used approach to model the optical spectra.

Table 2.2. Relevant computed data for the $[M_{13}]^{11+}$, $[M_{32}]^{2-}$, and $[M_{43}]^{3+}$ metal cores. E_C and ΔE_{H-L} are the per-atom cohesion energy and HOMO–LUMO gap, respectively. E_C are in kcal/mol, ΔE_{H-L} are in eV, distances are in Å and lowest frequencies are in cm⁻¹. All calculations done with the TZ2P basis sets in vacuum, except for $[M_{13}]^{11+}$, the computations included solvent (DMF) corrections.

	$[M_{13}]^{11+} M@M_{12}/ 1S^2(2-je)$							
	Ec	ΔE_{H-L}	Mcent	-M _{ico}	Ν	M_{ico} - M_{ico}	Lowest freq.	
$[Cu_{13}]^{11+}$	10.5	0.54	2.584			2.721	31	
$[Ag_{13}]^{11+}$	23.6	1.72	2.937			3.090	4	
$[Au_{13}]^{11+}$	-0.2	0.64	2.799			2.942	-9	
	$[M_{32}]^{2-}M_{12}@M_{20} / \mathbf{1S^2} \mathbf{1P^6} \mathbf{1D^{10}} \mathbf{1F^{14}} (34-je)$							
	Ec	ΔE_{H-L}	Mico-Mico	M _{ico} -	Mcap	M_{cap} - M_{cap}	Lowest freq.	
$[Cu_{32}]^{2}$	-64.2	0.26	2.590	2.3	888	2.726	43	
$[Ag_{32}]^{2}$	-45.8	0.26	3.003	2.7	764	3.156	12	
$[Au_{32}]^{2-}$	-55.9	0.34	3.002	2.7	764	3.156	-32	
	$[M_{43}]^{3+}$ M@M ₁₂ @M ₃₀ / 1S² 1P⁶ 1D¹⁰ 2S² 1F¹⁴ 2P⁶ (40-je)							
	Ec	ΔE_{H-L}	M _{cent} -M _{ico}	M_{ico} - M_{ico}	M _{ico} -M _c	ap M _{cap} -M _{cap}	Lowest freq.	
$[Cu_{43}]^{3+}$	-67.7	0.41	2.417	2.541	2.430	2.551	40	
$[Ag_{43}]^{3+}$	-47.3	0.42	2.788	2.932	2.808	2.946	35	
$[Au_{43}]^{3+}$	-54.7	0.13	2.802	2.947	2.799	2.944	19	

The major TD-DFT computed results for the $[M_n]^{m+}$ models are given in Figure 2.6 and Figure 2.7. The calculated spectrum for the smaller 2-*je* $[M_4]^{2+}$ exhibits some differences between Cu, Ag, and Au, showing a first relevant peak at $\approx 3.00 \text{ eV}$ ($\approx 400 \text{ nm}$) for $[Cu_4]^{2+}$, which is blueshifted for $[Au_4]^{2+}$ ($\approx 3.50 \text{ eV}$; $\approx 350 \text{ nm}$). The character of such transition is given by a "d-block" \rightarrow 1P transition, owing to the fact that the 1S orbital is located below the "d-block". Interestingly, for $[Ag_4]^{2+}$, this transition is largely blueshifted, being observed below 3.54 eV ($\approx 350 \text{ nm}$). In the 8-*je* $[M_8]$ case, more bands are allowed in the low-energy range, showing a small peak at around 2.25 eV ($\approx 550 \text{ nm}$) for $[Cu_8]$ and $[Au_8]$, followed by two shoulders (2.48 eV; $\approx 500 \text{ nm}$) in the former counterpart, which appears as a single peak in the latter, which is slightly blueshifted (2.58 eV; $\approx 480 \text{ nm}$). The character of the latter peak is given by a "d-block" \rightarrow 1D transition. For $[Ag_8]$, the first relevant peak appears at

2.98 eV ($\simeq 415$ nm), which is of 1P \rightarrow 1D character. In the *8-je* icosahedral [M₁₃]⁵⁺ structure, the lower energy peak is depicted for the copper counterpart followed by the gold analog, with a three-peak pattern in the low-energy range (Figure 2.2). For copper, such peaks are related to a d-block \rightarrow 1D transition, which differ from the gold counterpart, namely 1P \rightarrow 1D, d-block \rightarrow 1D, and 1P \rightarrow 2S, for each peak, respectively. In contrast, the silver system exhibits a first peak appearing at 3.44 eV (not shown in Figure 2.2) with 1P \rightarrow 1D character. For the case of [Ag₂₀], all the peaks are mainly transitions between jellium orbitals whereas in the case of copper and gold, only the first two peaks correspond to these transitions. More precisely, these are of 1D \rightarrow 1F character for the three metals.



Figure 2.6. Calculated absorption spectra for the different cluster cores. Note that M_4 (M = Cu, Ag, Au) exhibiting peaks outside of the 0-3 eV window, a different scale was employed in this case. Color code: Orange, copper; grey, silver; blue, gold. (Lorentzian broadening of 0.05 eV was applied to account for experimental broadening).

For the *18-je* core, $[M_{32}]^{14+}$, the most redshifted peak is found for the gold and copper counterparts, followed by the silver analog. Interestingly, the silver cores are able to reproduce a common peak at about 490 nm ($\simeq 2.50$ eV), for silver nanoclusters, as observed

for $[Ag_{25}(SR)_{18}]^{-}$, $[Ag_{35}(SR)_{18}]$, and $[Ag_{44}(SR)_{30}]^{.44-46}$ However, for $[Ag_{13}]^{5+}$ such peak appears at 370 nm ($\simeq 3.35$ eV), suggesting that the ligand-protecting shell plays a relevant role in such properties. Such a result tends to suggest that the formation of a plasmonic band in the silver cluster will occur for a smaller size in comparison to copper and gold aggregates. Thus, the optical properties from these silver clusters can be ascribed as a pre-plasmonic character.



Figure 2.7. Calculated absorption spectrum for $[M_{13}]^{5+}$ and $[M_{32}]^{14+}$ cores (top), and $[M_{25}(SR)_{18}]^-$ and $[M_{44}(SR)_{30}]^{4-}$ clusters (bottom) (M = Cu, Ag, Au), with R = methyl (-CH₃). Color code: orange copper; grey silver; blue gold. (Lorentzian broadening of 0.10 eV was applied to account for experimental broadening).

In comparison to the characterized architectures found in real ligated clusters, for the prominent $[{Au_{13}}Au_{12}(SR)_{18}]^{-,39}$ and the $[{M_{12}}@Ag_{20}}Ag_{12}(SR)_{30}]^{4-}$ (M = Ag, Au),⁴⁶ structures, namely $[M_{25}(SR)_{18}]^{-}$ and $[M_{44}(SR)_{30}]^{4-}$ for simplicity, the M = Cu, Ag, and Au clusters reveal that the protecting layers induce a change in the absorption spectrum patterns, leading to a redshift of certain peaks.

However, the character of the transition remains similar, allowing a rationalization of the optical properties of the overall cluster in terms of the inner cluster core. Hence, the

analysis and rationalization of the electronic transitions can be evaluated and expected from the inner bare structural core.

A recent example of an hypothetical cluster with a designed character of optical transitions is given by the hollow 32-je $[Au_{32}@Au_{12}(SR)_{18}]^{6-}$ cluster,⁸³ indicating a unprecedented 1F \rightarrow 1G transition, owing to the frontier orbitals of the Au₃₂ core.⁸⁴ Thus, different models for cluster cores can be employed to envisage novel optical transitions.

Lastly, we explore the role of the spin-orbit coupling in the electronic structure of the studied cluster cores. This has been explored earlier for the O_h -/ I_h -[Au₁₃] .^{85,86} The spin-orbit coupling causes the splitting of the atomic levels with l > 0, owing to coupling of l and s for each electron. In this sense, total angular momenta j ($j = l \pm s$), are employed to designate the atomic or superatomic spinors, instead of the pure orbital angular momentum (l) atomic orbital representation. This effect has been accounted for the 18-je cluster [W@Au₁₂],^{80,87-89} among other superatomic clusters,^{90,91} where the 1P⁶ and 1D¹⁰ superatomic shells split into $1P_{1/2}^2$ $1P_{3/2}^4$ and $1D_{3/2}^4$ $1D_{5/2}^6$, respectively. As the frontier orbitals of the cluster cores are generally dominated by superatomic orbitals (see above), the cases with P, D, and F orbitals are expected to split into $P_{1/2}P_{3/2}$, $D_{3/2}D_{5/2}$, and $F_{5/2}F_{7/2}$.⁶¹

Cluster	1P	1D
$[Cu_4]^{2+}$	253	
$[Ag_4]^{2+}$	360	
$[Au_4]^{2+}$	2635	
[Cu8]	678	114
[Ag ₈]	412	155
[Au ₈]	3322	1327
$[Cu_{13}]^{5+}$	944	290
$[Ag_{13}]^{5+}$	573	402
$[Au_{13}]^{5+}$	3768	2395

Table 2.3. Spin-orbit splitting in representative cores [cm⁻¹].

In $[Cu_4]^{2^+}$, $[Cu_8]$, and $[Cu_{13}]^{5^+}$, the calculated splitting (Table 2.3) of the 1P shell, accounting for the respective spin-orbit constant (ξ_{SO}) obtained as the difference (gap) between $1P_{1/2}$ and $1P_{3/2}$ (ξ^{1P}_{SO}), amounts to 253, 678, and 944 cm⁻¹, respectively, denoting an increase when the core becomes larger. Similarly, for the related 1D shell, in $[Cu_8]$ and $[Cu_{13}]^{5^+}$, an increase of the splitting obtained as the gap between $1D_{3/2}$ and $1D_{5/2}$ (ξ^{1D}_{SO}), is observed from 114 to 290 cm⁻¹. The related silver counterparts show a similar trend with ξ^{1P}_{SO} = 360, 412 and 573 cm⁻¹, where the ξ^{1D}_{SO} varies from 155 to 402 cm⁻¹. As anticipated for the strong relativistic effects in gold chemistry, the spin-orbit coupling is remarkably larger. The values of ξ^{1P}_{SO} increases from 2635 to 3768 cm⁻¹, and ξ^{1D}_{SO} from 1327 to 2395 cm⁻¹, in [Au₈] and [Au₁₃]⁵⁺, which is a few times larger than the splitting found in the lighter counterparts.

A comparison to the widely discussed and characterized thiolated-protected $[Au_{25}(SR)_{18}]^{-}$ cluster, allows us to point to the role of the protecting layer in the splitting of superatomic shells. The calculated 1P splitting in $[Au_{25}(SMe)_{18}]^{-}$ (ξ^{1P} so) amounts to 1452 cm⁻¹ (0.18 eV), similar to the value found by Jiang and co-workers⁷⁰ (1613 cm⁻¹, 0.20 eV), which is related to the experimental value found by low-temperature optical spectra measurements, of 1855 cm⁻¹ (0.23 eV).⁹² Thus, when the protecting layer is incorporated into the structure, the overall spin-orbit splitting is decreased by more than 50%, suggesting a variation from 3768 to 1452 cm⁻¹ between the bare $[Au_{13}]^{5+}$ core and $[Au_{25}(SMe)_{18}]^{-}$. This effect is inherent to gold nanoclusters, and is not found in the copper or silver counterparts.

Conclusion

From the current study involving several cluster core motifs, with several nuclearities and electron numbers, it is observed that silver does not follow a trend along the coinage metal group. Our results indicate that copper clusters are more or less as stable as gold clusters and more stable than silver clusters. Thus, for silver superatomic cores, the role of the stabilizing ligands is more crucial in the stabilization of the overall structure, in comparison to copper and gold. This indicates that the use of different ligands can be a useful synthetic approach to achieve the characterization of multiple silver superatomic clusters. The estimated stability of the bare copper superatomic cores is similar to that found for their gold

counterparts, which does not preclude further characterization of related copper analogs to the rich chemistry of gold nanoparticles. Therefore, the chemistry of copper nanoclusters should grow quickly, with at least characterizations of species related to that found in the related gold and silver series, which requires tackling synthetic challenges.

As the cluster core increases in nuclearity, the absorption bands are redshifted, revealing a fingerprint pattern that is able to differentiate between the studied clusters. Interestingly, the optical properties of silver cores are quite different to those expected for Cu and Au cores, which are prone to exhibit a single absorption band mainly in the range of 2-3 eV.

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Chapter 3: Comparison of the stability of group 11 metal (I) hydrides

Introduction

Hydrogen (Z = 1) is the smallest chemical element and one of the most important in chemical sciences as well as in Nature. Indeed, it is the most abundant element in the Universe and largely present on the surface of Earth, in particular in the form of water but also as a constituent of almost any living matter. Organic chemistry would not be what it is without hydrogen, but it is also a very important element in inorganic chemistry. It can adopt three different oxidation states (-I, 0, +I) and form stable compounds with most of the other elements of the periodic table. When combined with transition metals, it is generally in its –I oxidation state (hydride). As well as other hydrides, metal hydrides, whether as simple complexes or as molecular clusters, are, since several decades, the subject of a constant interest in inorganic chemistry. This is due to their numerous potential applications in many fields such as, for example, catalysis, electrochemistry and of course hydrogen storage.¹⁻⁷ In this chapter, we focus on clusters of the group 11 elements.

Molecular complexes or clusters of copper hydrides or polyhydrides are numerous. This includes giant Cu(I) polyhydride clusters.^{6,8-14} On the other hand, the hydride chemistry of silver and gold is much less rich¹⁵⁻¹⁸. As mentioned in Chapter II, we are interested in understanding why the similar treatment of M(I) complexes by borohydrides in the presence of dichalcogenolate ligands leads to the formation of M(I) polyhydrides in the case of copper, whereas in the case of silver non-hydridic superatoms are formed as far as a sufficient amound of borohydride is used. This work, largely developed by C.-W. Liu and collaborators¹⁹ is summarized in Scheme 3.1 below. For both metals, when a large excess of borohydride is used, metal(0) nanoparticles are obtained. Thus, the intermediate formation of silver superatoms with an average metal oxidation state comprised between +I and 0, makes senses, especially in the presence of dichalcogenolate anionic ligands (L) which can easily stabilize and protect such cationic $[M_n]^{x+}$ (n > x) kernels. So far, this is not the case for copper to which borohydride behaves exclusively as a hydride donor. On the other hand, in

the case of silver, if the smallest isolated species are Ag(I) hydrides (like in the copper case), the largest isolated clusters are mixed-valent superatoms which do not contain any hydrogen atom. Thus, with respect to silver, borohydride behaves mainly as an electron donor (a reductant).

From Copper(I) to Copper(0)

 $[Cu(CH_{3}CN)_{4}]PF_{6} \longrightarrow [Cu_{7}HL_{6}] \longrightarrow [Cu_{8}HL_{6}]^{+} \longrightarrow [Cu_{15}H_{2}L_{12}]^{+} \longrightarrow [Cu_{20}H_{11}L_{9}] \longrightarrow$ $[Cu_{26}H_{14}L_{12}] \longrightarrow [Cu_{28}H_{15}L_{12}]^{+} \longrightarrow [Cu_{32}H_{20}L_{12}] \longrightarrow [Cu_{36}H_{23}L_{12}]^{+} \longrightarrow \longrightarrow$ $\longrightarrow Copper Nanoparticles$

From Silver(I) to Silver(0)

 $[Ag(CH_3CN)_4]PF_6 \longrightarrow [Ag_7HL_6] \longrightarrow [Ag_8HL_6]^+ \longrightarrow [Ag_{11}HL_9]^+ \longrightarrow [Ag_{20}L_{12}] \longrightarrow$

 $[Ag_{21}L_{12}]^+ \longrightarrow \longrightarrow$ Silver Nanoparticles

Scheme 3.1. General mechanisms proposed for the reduction of Cu(I) and Ag(I) complexes by NaBH₄ in the presence of dichalcogenolate ligands (L), en route to copper and silver nanoparticles.

In the preceding chapter, we have shown that copper superatoms are intrinsically more stable than their silver counterparts and almost as stable as gold superatoms of which many examples exist in the literature. Therefore, the question we are asking ourselves now concerns the stability of hydrides: are copper hydrides so stable that their formation will be always favored over that of superatoms when in the presence of borohydrides in the reaction conditions described in Scheme 3.1 ?

In the followings, we investigate the relative stability of copper, silver and gold hydrides, first looking at the simplest MH composition in the solid state, and subsequently on different molecular models. The major computed systems are depicted in Figure 3.1.





Figure 3.1. Structural representation of the studied systems.

3.1. Computational details

All the calculations of the extended (periodical) systems were done in collaboration with Pr. X. Rocquefelte and Dr. W. Lafargue-dit-Hauret of the Rennes Institute of Chemical Sciences. They were performed by using the Vienna *ab initio* simulation package (VASP) based on the density functional theory (DFT).²⁰ The projector augmented wave (PAW) potentials²¹ was applied. The [5d¹⁰-6s¹] electron states were treated as valence for Au, [4d¹⁰-5s¹] for Ag, [3d¹⁰-4s¹] for Cu and 1s¹ for H. The exchange-correlation effects were included by means of the Perdew, Burke and Ernzerhf (PBE) functional.²² The cut-off energy of 500 eV, the atomic relaxation of 10⁻⁵ eV/Å, the relaxation of the electronic degrees of freedom of 10^{-8} eV were used to reach geometry convergence. Moreover, the geometry and a supercell approach were taken into account and the *k*-mesh was centered at the Γ -point.

For the case of molecular systems, all density functional theory calculations were carried out by using the Amsterdam Density Functional (ADF) program²³ and the zeroth-

order regular approximation (ZORA)²⁴ was applied to incorporate scalar relativistic effects in our calculations. The triple- ζ Slater basis set was employed, plus two polarization functions (STO-TZ2P) for valence electrons, within the generalized gradient approximation (GGA) according to the Becke-Perdew (BP86) exchange functionals.^{25,26} The frozen core approximation was applied to the [1s²-4f¹⁴] inner electrons for Au, [1s²-4p⁶] for Ag, [1s²-3p⁶] for Cu, leaving the remaining electrons to be treated explicitly. A gradient convergence criterion of 10⁻⁵ and an energy convergence criterion of 10⁻⁶ were utilized to perform our geometry optimizations. Analyses of the interaction energy between fragments constituting the investigated clusters have been carried out within the Morokuma-Ziegler energy decomposition method.²⁷⁻²⁹

3.2. Results and discussion

3.2.1 The periodic MH(M = Cu, Ag, Au) systems.

In this section we focus on the simplest group 11 hydrides that could exist, that is the binary MH hydrides. In fact, CuH is known since 1844 when it was reported by A. Würtz.³⁰ Its X-ray crystal structure was first solved in 1926³¹ and later confirmed by neutron diffraction.³² It adopts the hexagonal wurtzite-type structure in which each atom it tetrahedrally bonded to four atoms of the other element. In fact, according to some authors³³⁻³⁵ CuH is not perfectly stoichiometric and should be better formulated as CuH_{1-x} ($0 \le x \le 0.26$). Such a characteristic could be related to a surface phenomenon of the powder microcrystals.³⁶ Indeed, CuH is not very stable at room temperature and/or when exposed to air or moisture.

On the other hand, silver and gold do not form hydrides under ambient conditions.³⁷ According to some experimental observations, a high-pressure AuH structure has been suggested to adopt a basic tetragonal body-centered cell that is very similar to the mercury structure Hg-*t*/2. In this proposed structure, the metal coordination number is equal to 10.³⁸ Several theoretical calculations on group 11 binary metal hydrides have also been published.³⁹⁻⁴¹ From the detailed analysis of Ceder and coworkers,³⁹ three low-energy structure-types are likely to compete for the stability of group 11 binary hydrides. In our investigation, we have selected these three structures, depicted in Figure 3.1 and described below.

The first structure-type is of course wurtzite, which is that adopted by CuH at ambient conditions (see above). It has a hexagonal crystal system and the corresponding space group is

 $P6_{3}mc$ in the Hermann-Mauguin notation. The second one is blende. It has a cubic crystal with $F\overline{4}3m$ as space group. As for wurtzite, each atom in blende is tetrahedrally bonded to four atoms of the other element (Figure 3.1). The third structure is the cubic rocksalt structure ($Fm\overline{3}m$ space group) in which each atom is octahedrally coordinated to six atoms of the other type (see Figure 3.1). The calculated lattice parameters optimized for the three structures are reported in Table 3.1, together with the corresponding M-H distances. They are in a satisfying agreement with the known experimental of calculated available data.³⁶⁻³⁸

Table 3.1. Calculated lattice parameters and M-H distances (in Å) for the three MH systems(M = Cu, Ag, Au).

MH	Wurtzite		Blende		Rocksalt	
CuH	a = 2.85 c = 4.55	Cu-H 3 x 1.735 1 x 1.731	a = 4.01	Cu-H 4 x 1.738	a = 3.87	Cu-H 6 x 1.937
AgH	a = 3.21 c = 5.16	Ag-H 3 x 1.967 1 x 1.950	a = 4.53	Ag-H 4 x 1.962	a = 4.36	Ag-H 6 x 2.183
AuH	a = 3.10 c = 6.16	Ag-H 3 x 2.724 1 x 1.823	a = 4.54	Au-H 4 x 1.966	a = 4.42	Au-H 6 x 2.210

Among the three optimized structure-types, wurtzite is the most stable structure for the three metals (see Table 3.2). In the case of Cu and Ag, the blende structure is only slightly less stable. The rocksalt structure is by far energetically disfavored, especially in the case of gold.

Table 3.2. Relative energies (in meV/MH) unit for the studied structures.

MH	Wurtzite	Blende	Rocksalt
CuH	0	17.5	483.4
AgH	0	16.1	740.9
AuH	0	88.1	1084.6

The calculated phonon spectra and density of states (DOS) of the wurtzite structure for the three MH systems are shown in Figure 3.2. Whereas the lack of imaginary frequencies for the case of CuH and AgH confirms the stability of these species when adopting the wurtzite

structure, imaginary frequencies (negative frequency values in Figure 3.2) are found for AuH, indicating that the wurtzite-type structure is not an energy minimum. This is consistent with the fact that the DOS of AuH in Figure 3.2 does not exhibit a band gap, contrarily to that of its Cu and Ag relatives. A look at the optimized M-H distances reported in Table 3.2 allows interpreting the peculiar behavior of gold, as compared to copper and silver. For the two latter metals the four M-H distances are almost equal indicating regular tetrahedral coordination. In the case of gold, the three symmetry-related distances (2.72 Å) are very long, indicating the absence of a bond. Thus, only one of the four M-H contacts (1.82 Å) is bonding. This result suggests that in these binary phases gold prefers coordination numbers lower than 4. This is consistent with the general behavior of gold(I) in coordination chemistry for which dicoordination is frequent.



Figure 3.2. Representation of the phonon spectra (left) and DOS (right) of the wurtzite structure for the MH systems (M = Cu, Ag, Au).

The different band gaps corresponding to these optimized structure-types are provided in Table 3.3. It appears that no band gap can be found for gold, whereas for the three structures, both Cu and Ag exhibit a significant band gap.

MH	Wurtzite	Blende	Rocksalt
CuH	0.53	0.78	0
AgH	0.81	1.01	0
AuH	0	0	0

Table 3.3. Band gap (in eV) for the optimized MH systems (M = Cu, Ag, Au).

Since wurtzite is computed to be the more stable structure at low pressure and temperature, in agreement with the previous work of Ceder and coworkers,³⁹ we focus now on this structure for the energetical analysis. Owing to the fact that AuH is not an energy minimum for this structure-type, we will concentrate our discussion on the comparison between copper and silver.

The formation energies (E_F) were computed assuming the reaction:

$$M_{(solid)} + \frac{1}{2} H_{2(gas)} \rightarrow MH_{(solid)}$$

The energies of the bulk metals were computed assuming the *fcc* structure and that of free H₂ in placing a single molecule in a large cubic unit cell (a = 20 Å). The E_F values corresponding to one MH formula unit are given in Table 3.4. They are positive, indicating an endothermic reaction. This is consistent with the unstability of CuH with respect to heating. Nevertheless, the lowest E_F value corresponds to M = Cu, indicating that the more stable (or less unstable) hydride with respect to decomposition is CuH.

The cohesion energies E_C were calculated assuming the equation:

$$E_{C} = E(MH) - [E(M) + E(H)]$$

E(M) and E(H) were calculated in placing a single atom in a large cubic unit cell (a = 20 Å). The values are negative, indicating substantial bonding. That of CuH has an absolute value which is larger than twice that of Ag and Au. Whereas it is difficult to conclude for AuH because the wurtzite structure-type is not an energy minimum, it is clear that the bonding in CuH is much stronger than in AgH.

As a whole, the results given in Table 3.4 are consistent with the fact that CuH is much stable than AgH.

Table 3.4. Energy of formation (E_F) and cohesion energy (E_C) computed for the MH systems (M = Cu, Ag, Au) in the Wurzite structure-type. The values are given in eV and correspond to one MH formula unit.

MH	$E_{\rm F}$	E _C
CuH	0.273	-0.944
AgH	0.414	-0.372
AuH	0.700	-0.409

3.2.2 The molecular models.

The first molecular models that one could look at in a first step are the very simple and hypothetical MH (M = Cu, Ag, Au) molecules. Of course, such species have been already investigated at various levels of theory.⁴² Our aim was not to provide better data, but, calculating at the same DFT level than the other considered molecular models, our results can be considered as a reference for them. Our major computed data are gathered in Tables 3.5 and 3.6. Our optimized distances are in agreement with experiment.^{42a}

The longest MH distance and lowest vibrational frequency is found for M = Ag (Table 3.5). This is consistent with a weaker M-H bond in the case of silver. This is confirmed by the Morokuma-Ziegler EDA results given in Table 3.6. Although at the considered level of theory the calculated energies have to be taken with caution at their absolute scale, the comparison between the three metals is meaningful, at least a semi-quantitative level. Both homolytic and heterolytic fragmentations indicate weaker bonding in the case of silver.

Table 3.5. Relevant characteristic of the optimized MH (M = Cu, Ag, Au) models.

MH	$\Delta E_{\text{HOMO-LUMO}} (eV)$	d (Å)	Lowest freq. (cm ⁻¹)
CuH	2.67	1.454	2117
AgH	3.07	1.618	1720
AuH	3.26	1.538	2249

Compound	CuH	AgH	AuH
Fragmentation	Cu+H	Ag + H	Au + H
Pauli repulsion	6.52	6.66	10.24
Electrostatic interaction	-2.42	-2.70	-4.39
Orbital interaction	-8.35	-7.67	-10.33
Total bonding energy	-4.26	-3.71	-4.48
Compound	CuH	AgH	AuH
Fragmentation	$Cu^+ + H^-$	$Ag^+ + H^-$	$Au^+ + H^-$
Pauli repulsion	6.00	7.69	11.72
Electrostatic interaction	-13.52	-14.53	-18.88
Orbital interaction	-3.40	-3.00	-5.09
Total bonding energy	-10.92	-9.83	-12.25

Table 3.6. Energy decomposition analysis of the bonding energy in MH (M = Cu, Ag, Au). Top: Homolytic clivage. Bottom: Heterolytic clivage. All the energies are in eV.

We now move to a more realistic model. Among the copper and silver hydrides appearing in Scheme 3.1, the more emblematic are the $[M_8(\mu_8-H)L_6]^+$ (M = Cu, Ag; L = dithiocarbamate, dithiophosphate or diselenophosphate) reported by Liu and coworkers.⁴³ As for the hydride, L is a formally mono-anionic ligand. It follows that the metal is in its +I oxidation state. The hydride lies in the middle of a regular tetracapped tetrahedron described by the 8 metal cations which are held together by the bridging L ligands (no covalent metalmetal bonding). Each ligand possesses two chalcogen atoms, each of them bridging one edge of the M₈ tetracapped tetrahedron, in such a way that the ideal symmetry of the $[M_8(\mu_8-H)L_6]^+$ cluster is T_h (see Figure 3.1). These species are generally not considered to be superatoms since there are no metallic jellium electrons (M(+I)). However, assuming that the hydride is a full part of the cluster, then the H-centered cube can be viewed as a heteronuclear superatom bearing two jellium electrons (1S² configuration, provided by the two 1s(H) electrons).

We have in the followings analyzed the electronic structure and compared the stability of the $[M_8(\mu_8-H)L_6]^+$ species within the group 11 series (M = Cu, Ag, Au). The simplified ligand L considered in the calculations is the model S₂PH₂ (Figure 3.1) which has been shown in many cases to be a good approximation for the real dithiocarbamates or dichalcogenophosphates.⁴³

Relevant computed data for the optimized $[M_8(H)(S_2PH_2)_6]^+$ (M = Cu, Ag, Au) structures of T_h symmetry are given in Table 3.7. Whereas energy minima are found for Cu and Ag, in agreement with experiment, an imaginary vibrational frequency is found in the case of gold, indicating that this structure is not favorable for Au. We therefore concentrate again our analysis on the comparison between copper and silver.

cluster	ΔE_{H-L} (eV)	H-M _{tet} (Å)	M _{tet} -M _{tet} (Å)	M _{tet} -M _{cap} (Å)	M _{cap} -H (Å)	Freq (cm ⁻¹)
$[Cu_8(H)(S_2PH_2)_6]^+$	2.75	1.748	2.854	2.681	2.698	50
$[Ag_8(H)(S_2PH_2)_6]^+$	3.49	1.926	3.145	3.084	3.145	27
$[Au_8(H)(S_2PH_2)_6]^+$	2.35	1.928	3.149	2.975	3.149	-19

Table 3.7. Relevant computed datas for the $[M_8(H)(S_2PH_2)_6]^+$ systems.

In order to get a deeper understanding of the metal-hydride bonding, we have carried out a Morokuma-Ziegler EDA of the three $[M_8(H)(S_2PH_2)_6]^+$ clusters, considering the interaction between the $[M_8(S_2PH_2)_6]^{2+}$ and H⁻ fragments. The corresponding results are given in Table 3.8.

Again, the computed total bonding energy indicate stronger interaction in the case of copper hydride, as compared to silver. Interestingly, this ordering is driven by the E_{orb} component, indicating that in these clusters, the stronger Cu-H bonding is also the more covalent, the weaker Ag-H bonding being more ionic in character.

Table 3.8. Morokuma-Ziegler energy decomposition analysis (EDA) of the $[M_8(H)(S_2PH_2)_6]^+$ clusters. All values are in eV. E_{Pauli} = Pauli repulsion, E_{elstat} = electrostatic interaction, E_{orb} = orbital interaction. TBE = total bonding energy = $E_{Pauli} + E_{elstat} + E_{orb}$

cluster	$[Cu_8(H)(S_2PH_2)_6]^+$	$[Ag_8(H)(S_2PH_2)_6]^+$	$[Au_8(H)(S_2PH_2)_6]^+$
Fragmentation	$[Cu_8(S_2PH_2)_6]^{2+} + H^{-}$	$[Ag_8(S_2PH_2)_6]^{2+} + H^{-}$	$[Au_8(S_2PH_2)_6]^{2+} + H^{-}$
E _{Pauli}	24.75	21.88	31.89
Eelstat	-26.78	-27.13	-32.85
Eorb	-9.21	-5.76	-9.57
TBE	-11.24	-11.01	-10.53

Conclusion

All the calculations described above are consistent with a stronger M(I)-H bonding when M = Cu, as compared to M = Ag. The M = Au case is more difficult to interpret since it seems not to be inclined to form the same compounds as Cu and Ag. This is in line with the fact that Au(I) hydrides are scarce.⁴⁴ Let us suggest that the computed solid-state models are likely to be the best models for giant polyhydrides. They suggest that Cu(I) hydrides are much more stable than their Ag(I) counterparts. We can therefore conclude that, despite the fact that copper superatoms are more stable than their silver analogues (see Chapter 2), the particular stability of copper hydrides renders difficult to isolate superatoms (contrarily to silver) in the process described in Scheme 3.1. Copper hydrides appear to be a thermodynamic well in this process. This is why in order to get copper superatoms, the reaction conditions of Scheme 3.1 should be modified. A possibility should be to use ligands different from dichalcogenolates having the ability to compete with hydrides as coordinating species. In such a way, borohydride could be able to react as an electron donor, rather than a hydride donor.⁴⁵

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Chapter 4: Electronic and bonding properties of the tetrahedral clusters $[M_{16}Ni_{24}(CO)_{40}]^{4-}$ (M = Cu, Ag, Au) related to the pyramidal $[Au_{20}]$ cluster

Introduction

Since the beginning of this century, the chemistry of ligand-protected Group 11 superatoms^{1–3} has been tremendously developing, boosted in particular by the various potential applications of these atom- and electron-precise species.^{4,5} These clusters consist of a compact (generally pseudo-spherical) M_n core embedded in an outer protecting ("passivating") shell made of various stabilizing ligands, such as for instance thiolates, halogenides and/or phosphines.^{2,5–8} In the specific case of thiolates, additional peripheral M(I) atoms are also present in the protecting shell, in which they occupy bridging positions between sulfur atoms. As a result, metal-thiolato "stapples" are formed, which are anchored to the M_n core through the coordination of sulfur.^{9–11} Owing to the presence of formally anionic ligands on the outer shell, the inner metallic core is generally in a positive oxidation state ($[M_n]^{x+}$), giving rise to a non-integer averaged oxidation state [(n - x)/n)] lying between 0 and +1.

As developed in Chapter 2, The stability of superatoms is associated with "magic" electron numbers, which can be rationalized within the framework of a spherical jellium-type model and associated with closed-shell superatomic orbitals,^{5,12,13} ordering as $1S < 1P < 1D < 2S < 1F < 2P < 1G....^{1,6,12-17}$

Interestingly, the naked neutral [Au₂₀] tetrahedral cluster, obtained in the gas phase and further characterized by photoelectron spectroscopy,¹⁸ exhibits a closed-shell superatom configuration. It is characterized by a 20-electron "magic" number (the 5d(Au) electrons are not included in this counting). Its electronic structure, investigated by density functional calculations,^{18–23} exhibits a large HOMO–LUMO energy gap, in agreement with its remarkable stability and unique optical and catalytic properties.^{18,24–30} Its structure is that of a bulk face-centered cubic (fcc) gold fragment, in a finite nanosized cluster motif.^{18,26}

Efforts to bring $[Au_{20}]$ species into solution has been carried out since the last ten years,^{26,31–35} which resulted in structures and electronic structures completely different from that of the bare $[Au_{20}]$ cluster. Interestingly, in the beginning of the 90's, Dahl's group reported the stabilization of an octahedral Au₆ core from the reaction between the Longoni–Chini $[Ni_3(CO)_6]^{2-}$ cluster³⁶ as reducing agent of a Au(I) solution. The resulting $[Au_6Ni_{12}(CO)_{24}]^{2-}$ cluster^{37,38} was a first example of the capability of Group 11 cores to be embedded in an outer shell made of organometallic units, which can increase the versatility of the protecting layer. Later, the same approach was extended to achieve high-nuclearity counterparts employing Ag(OAc) and gold trichloride in modified conditions,³⁹ resulting in the formation of $[Ag_{16}Ni_{24}(CO)_{40}]^{4-}$ and $[Au_{16}Ni_{24}(CO)_{40}]^{4-}$, respectively, with the former characterized via single-crystal X-ray diffraction.³⁹

Both solid-state structures of [Au₆Ni₁₂(CO)₂₄]²⁻ and [Ag₁₆Ni₂₄(CO)₄₀]⁴⁻ exhibit an ideal T_d symmetry. At first sight, they can be viewed as made of a superatomic core, $([Au_6]^{2-}$ and $[Ag_{16}]^{4-}$, respectively) covered by four approximatively planar Ni₃(CO)₆ and Ni₆(CO)₁₀ units, respectively. However, a rationalization of the bonding between the superatom core and the nickel carbonyl units is not as straightforward as for thiolate- or phosphine-covered superatoms. Indeed, [:SR]⁻ or :PR₃ are two-electron ligands, making localized 2-electron/2center bonds with the metal core. In $[Ag_{16}Ni_{24}(CO)_{40}]^{4-}$ for example, each $Ni_6(CO)_{10}$ units has several bonding contacts with the cluster core (Figure 4.1), suggesting the possibility for delocalized bonding. Moreover, it is likely that the electron-donation is going in the opposite way as in the case of classical ligands, *i.e.*, from the core to the outer shell.⁴⁰ Therefore, the question of the outer nickel carbonyl shell being not to be considered as a protecting ligand but as a full part of the superatom entity arises. In any case, the role of the nickel carbonyl units in the overall stabilization of these species is particularly puzzling. Although DFT investigations of $[Ag_{16}Ni_{24}(CO)_{40}]^{4-}$ by Walter have recently appeared.¹³ they were not focused on the nature of the bonding between the nickel carbonyl groups and the Group 11 core, but to provide an analysis of the overall electronic structure.

Herein, we are interested in the role of the nickel carbonyl entity in the stabilization of the whole cluster, extending the exploration along the Group 11 triad in the series $[M_{16}Ni_{24}(CO)_{40}]^{4-}$ (M = Cu, Ag, Au). Both electronic and structural features are rationalized in terms of the superatom concept,^{6,10,13} showing a strong resemblance to the bare [Au₂₀], thus, proving that the synthesis in solution of a related passivated core is possible, which can be useful for further explorations of its physico-chemical properties towards building blocks for nanostructured materials.⁴¹ On the other hand, this allows the possibility to access towards

finite fcc fragments made of group 11 elements, for further understanding the size-dependent behavior and properties of a few atoms section of group 11 M(111) surfaces, which are widely employed as active supporting surfaces.^{42–46}



Figure 4.1. Molecular structure of $[Au_6Ni_{12}(CO)_{24}]^{2-}$ (left) and $[Ag_{16}Ni_{24}(CO)_{40}]^{4-}$ (right).

4.1. Computational details

All density functional theory calculations were carried out by using the Amsterdam Density Functional (ADF) program⁴⁷ and the zeroth-order regular approximation (ZORA) was applied to incorporate scalar relativistic effects in our calculations. The triple- ζ Slater basis set was employed, plus two polarization functions (STO-TZ2P) for valence electrons, within the generalized gradient approximation (GGA) according to the Becke-Perdew (BP86) exchange functional.^{48,49} The frozen core approximation was applied to the [1s²-4f¹⁴] inner electrons for Au, [1s²-4p⁶] for Ag, [1s²-3p⁶] for Cu, [1s²-3p⁶] for Ni, [1s²] for C and [1s²] for O, leaving the remaining electrons to be treated explicitly. A gradient convergence criterion of 10⁻⁵ and an energy convergence criterion of 10⁻⁸ were utilized to perform our geometry optimizations. Analyses of the interaction energy between fragments constituting the investigated clusters have been carried out within the Morokuma-Ziegler energy decomposition method.⁵⁰⁻⁵² Time-dependent DFT (TD-DFT) calculations were employed at the same level, but using the Perdew-Burke-Ernzerhof (PBE) exchange-correlation

of UV-Vis spectrum for related clusters.^{4,54–57}. It is worth mentioning that in the particular case of the investigated compounds, TD-DFT results at the BP86 level provided very similar results.

4.2. Results and discussion

4.2.1 The M₁₆ core

In $[Ag_{16}Ni_{24}(CO)_{40}]^{4-39}$, the T_d Ag_{16} core can be described in terms of two concentric shells, Ag'₄@Ag''₁₂, with two types of symmetry-equivalent metals. As said above, it can also be viewed as a compact piece taken out of a fcc metallic solid. Indeed, along anyone of its four 3-fold axes, the packing goes in three successive compact planes, as sketched in Figure 4.2: A (7 atoms), B (6 atoms) and C (3 atoms). Thus, the Ag₁₆ core has four 7-atom and four 3-atom faces. In $[Ag_{16}Ni_{24}(CO)_{40}]^{4-}$, each of the four 7-atom faces is capped by a $Ni_6(CO)_{10}$ unit. Previous calculations by Walter¹³ lead to describe this cluster core as a 20-ie $[Ag_{16}]^{4-}$ superatomic subsystem with the spherical jellium configuration $1S^2$ $1P^6$ $1D^{10}$ $2S^2$. At this point of the discussion, one should remind that in this type of clusters, only the 5s(Ag) electrons are considered participating to the bonding within the superatom core, and consequently to the jellium electron count. The fully occupied 4d(Ag) levels remain basically non-bonding and low-lying. Then the similarity between the $[Ag_{16}]^{4-}$ subsystem and $[Ag_{20}]$ (or [Au₂₀]) are striking. Indeed, the neutral unligated 20-je [Ag₂₀] (or [Au₂₀])^{18,21,23} adopts a tetrahedral structure that can be generated from the $[Ag_{16}]^{4-}$ subsystem by capping its four triangular faces with four Ag^+ . In these $[M_{20}]$ superatoms, the compact plane stacking goes as A (10 atoms), B (6 atoms), C (3 atoms) and A (1 atom). The alternative description of [M₂₀] in terms of concentric shells, M'4@M"12@M"'4, reveals three types of symmetry-equivalent metals.²² We have optimized the T_d - $[M_{16}]^4$ and T_d - $[M_{20}]$ (M = Cu, Ag, Au) species assuming T_d symmetry and found them to be closed-shell minima in these spatial configurations. Their major computed results are provided in Table 4.2. The relationship between their 20-je superatom electron configurations is evidenced by the plots of the $[Ag_{16}]^{4-}$ and $[Ag_{20}]$ Kohn-Sham jellium orbitals (Figure 4.3).



Figure 4.2. Illustration of the fcc packing (A, B and C planes) in Ag₂₀ (left) and the Ag₁₆ core of $[Ag_{16}Ni_{24}(CO)_{40}]^{4-}$ (middle) and with one Ni₆ plane (right). The red, yellow and black colors correspond to the symmetry-equivalent Ag', Ag'' and Ag''' atoms, respectively, in Ag₂₀ (Ag'4@Ag''₁₂@Ag'''₄) and the Ag₁₆ core (Ag'4@Ag''₁₂). The green color corresponds to Ni.



Figure 4.3. The Kohn-Sham jellium orbitals of $[Au_{16}]^{4-}$ and $[Au_{20}]$.

A Morokuma-Ziegler decomposition of the bonding energy^{50–52} between the $[M_{16}]^{4-}$ core and its $[M_4]^{4+}$ envelope in the $[M_{20}]$ equilibrium geometry has been performed (see Computational Details) and its components are given in Table 4.1. For the three metals, the total bonding energy between the two fragments is negative (stabilizing), with similar values for M = Cu and Au, whereas that corresponding to Ag is weaker. This is in phase with the computed cohesion energy of $[M_{20}]$ (Table 4.2) and with previous calculations on bare Group 11 metal clusters.⁵⁸ In fact, in such bare metal clusters Ag behaves always a bit differently than Cu and Ag, because the periodical trend is likely to be counterbalanced by the relativistic effects.⁵⁸ Among the three components of the bonding energy, the Pauli repulsion is, by

nature, positive. On the other hand, the two other components (electrostatic and orbital interactions) are stabilizing and more or less follow the same trend as the total bonding energy. The a_1 and t_2 components are dominating the orbital interaction energy. They result from the participation to the bonding of the valence (n + 1)s orbitals of M⁺, with some $(n + 1)p_{\sigma}$ contribution. Indeed, within the cluster T_d symmetry, the four valence s-type AOs combine into $a_1 + t_2$ and interact strongly with their 2S (a_1) and 1D $(t_2$ component) counterparts on the $[M_{16}]^{4-}$ fragment. As a consequence, the occupation after interaction of the M⁺ (n + 1)s orbital is substantial (~ 1.0 e, see Table 4.1), whereas that of its $(n + 1)p_{\sigma}$ AO remains lower than 0.1 e in the three clusters. The less important *e* and t_1 contributions of the capping atoms, are the trace of some bonding interaction of the M⁺ vacant $(n + 1)p_{\pi}$ combinations $(e + t_1 + t_2)$ with occupied $[M_{16}]^{4-}$ counterparts, as well as of the M⁺ nd occupied combinations $(a_1 + 2e + 2t_1 + 3t_2)$ with some vacant $[M_{16}]^{4-}$ MOs. In any case, the participation of the M⁺ (n + 1)p and nd AOs in the bonding with the $[M_{16}]^{4-}$ core remains minor.

Table 4.1. Decomposition of the bonding energy between the $[M_{16}]^{4-}$ core and its outer capping $[M_4]^{4+}$ fragment in the $[M_{20}]$ (M = Cu, Ag, Au) clusters of T_d symmetry and electron configuration of the four capping atoms. All energies are in eV.

Compound (T_d)	[Cu ₂₀]		[A	g ₂₀]	[Au ₂₀]		
Fragmentation	$[Cu_{16}]^{4-1}$	$+ [Cu_4]^{4+}$	$[Ag_{16}]^{4-1}$	$[Ag_{16}]^{4-} + [Ag_4]^{4+}$		$[Au_{16}]^{4-} + [Au_4]^{4+}$	
Pauli repulsion	23	.30	21	21.13		30.66	
Electrostatic interaction	-72	2.60	-64.79		-75	-75.02	
Orbital interaction decomposition	$ \begin{array}{c} a_1\\ a_2\\ e\\ t_1\\ t_2 \end{array} $	-4.24 -0.01 -1.41 -1.38 -9.33	$ \begin{array}{c} a_1\\ a_2\\ e\\ t_1\\ t_2 \end{array} $	-3.87 -0.01 -1.00 -0.89 -8.40	$ \begin{array}{c} a_1\\ a_2\\ e\\ t_1\\ t_2 \end{array} $	-5.63 -0.02 -1.23 -2.05 -12.45	
Total orbital interaction	-16	5.38	-14.17		-21.38		
Total bonding energy	-65	5.68	-57.83		-65.75		
Jellium electron configuration of the $[M_{16}]^{4-}$ fragment	$\frac{18^{1.95} 18^{5.79} 10^{7.83} 28^{0.79} 28^{0.24}}{18^{0.53}}$		1S ^{1.98} 1P ^{5.94} 1D ^{7.36} 2S ^{0.71} 2P ^{0.09} 1F ^{0.37}		1S ^{1.95} 1P ^{5.91} 1D ^{7.74} 2S ^{0.56} 2P ^{0.12} 1F ^{0.76}		
Electron configuration of the outer capping atoms	$3d^{9.81} 4s^{0.93} 4p^{0.22}$		$4d^{9.89}5s^{0.96}5p^{0.14}$		$5d^{9.71}6s^{1.14}6p^{0.19}$		

	Ec (kcal/mol)	$\Delta E_{H-L}(eV)$	M-M (Å)	M-M' (Å)	M'-M' (Å)	Lowest frequency
$[Cu_{16}]^{4-}$	-56.05	1.52	2.671	2.444	2.424-2.454	69 (<i>t</i> ₂)
$[Ag_{16}]^{4-}$	-53.18	1.40	3.023	2.820	2.806-2.828	$44(t_2)$
$[Au_{16}]^{4-}$	-46.99	0.65	3.911	2.831	2.737-2.738	35 (<i>t</i> ₂)
	Ec (kcal/mol)	$\Delta E_{H-L}(eV)$	M-M (Å)	M-M' (Å)	M'-M' (Å)	Lowest frequency
[Cu ₂₀]	-62.07	1.34	2.600	2.453	2.414-2.489	$67(t_{l})$
[Ag ₂₀]	-45.46	1.64	3.034	2.831	2.755-2.902	$41(t_{l})$
[Au ₂₀]	-56.34	1.81	3.131	2.817	2.674-2.946	$30(t_1)$

Table 4.2. Relevant computed data for $[M_{16}]^{4-}$ and $[M_{20}]$ clusters (M = Cu, Ag, Au).

4.2.2 The protecting Ni₆(CO)₁₀ units

Being centered on a C_3 axis of the tetrahedral $[M_{16}Ni_{24}(CO)_{40}]^{4-}$ cluster (Figure 4.1), each of the four Ni₆(CO)₃(μ -CO)₆(μ ₃-CO) units has local $C_{3\nu}$ symmetry. In fact, one can view the nickel atoms as part of the whole metal compact packing of the cluster (Figure 4.2, right side), which, along each of the C3 axis goes as C (M3), B (M6), A (M7) and B (Ni6). If, in a first step, we do not consider the central μ_3 -carbonyl ligand, the remaining Ni₆(CO)₉ fragment is almost planar, of idealized D_{3h} symmetry (Scheme 4.1). This approximately planar $Ni_6(CO)_9$ neutral fragment has $(6 \times 10) + (9 \times 2) = 78$ electrons in the metal coordination environment. This is the electron count that one would predict at first sight, assuming a localized 2-electron/2-center bonding scheme (nine 2-electron Ni-Ni bonds), with the six inplane coordinated metals satisfying the 16-electron rule $[(6 \times 16) - (2 \times 9) = 78]$. However, it appears from the nearly planar 6-fold connectivity of the three inner Ni atoms (Scheme 4.1) that a localized bonding scheme with 9 Ni-Ni bonds does not apply properly. Indeed, the inner Ni atoms have only 5 in-plane valence orbitals (s, p_x , p_y , d_{x2-y2} and d_{xy}) available for making 6 "bonds". Considering that the metal d_{x2-y2} and d_{xy} AOs are participating in 6 among the 12 Ni-(μ -CO) bonds (those involving the $\pi^*(CO)$ orbitals) and in all the Ni-Ni bonds, one is left with $(6 \times 2) - 6 = 6$ localized 2-electron/2-center Ni-Ni bonds. A reasonable Lewis description of the Ni₆(CO)₉ fragment would be to discard the three central Ni-Ni bonds in Scheme 4.1. This would leave the three inner metals with a 14-electron configuration, whereas the three outer ones would remain 16-electron centers. This electron-deficient and delocalized situation makes this Ni₆(CO)₉ fragment somewhat different from structurally related species, such as [Pt₃Fe₃(CO)₁₅]^{0/-/2-}, for example.^{59–62}

Adding now an out-of-plane μ_3 -CO on the central metal triangle of Ni₆(CO)₉ to complete the full Ni₆(CO)₁₀ organometallic unit reduces the electron deficiency of this triangle by 2 electrons and orientates the associated electron-accepting ability to the other side of the Ni₆ plane.



Scheme 4.1. Connectivity within a Ni₆(CO)₃(μ -CO)₆ fragment in [Ag₁₆Ni₂₄(CO)₄₀]⁴⁻.





The optimized geometry of the free Ni₆(CO)₁₀ unit (assuming $C_{3\nu}$ symmetry) and its Kohn-Sham MO diagram are shown in Figure 4.4. Its moderate out-of-planarity allows strengthening slightly the bonding around the metal centers by somewhat reducing their

electron deficiency. The Ni-Ni bond lengths, 2.594 Å (inner) and 2.431 Å (peripheral) are consistent with the above qualitative description of the bonding. The electron deficiency is evidenced by the existence of low-lying vacant orbitals. In particular the $39a_1$ LUMO has significant in-phase metal $4p_z$ AO's. The $16a_2$ HOMO has in-plane 3d-type character, whereas the $38a_1$ HOMO-1 is a $3d_{z^2}$ combination, as well as the low-lying $36a_1$. Contrarily to the HOMO, these two last occupied MOs have favorable directional properties to interact with the $[M_{16}]^{4-}$ core.

4.2.3 Interaction of a single $Ni_6(CO)_{10}$ with the $[M_{16}]^4$ core

The best way to analyze the role played by the outer organometallic shell in the bonding and stability of $[M_{16}(Ni_{24}(CO)_{40})]^{4-}$ is to first consider the interaction between one $Ni_6(CO)_{10}$ fragment and the $[M_{16}]^{4-}$ core. In this respect, we have undertaken a Morokuma-Ziegler decomposition of the bonding energy⁵⁰⁻⁵² between the $[M_{16}]^{4-}$ and $Ni_6(CO)_{10}$ fragments in an $[M_{16}(Ni_6(CO)_{10})]^{4-}$ model of C_{3v} symmetry, the structure of which (singlepoint calculation) being taken out of the optimized geometry of the $[M_{16}(Ni_{24}(CO)_{40})]^{4-1}$ tetrahedral parent. Its components are given in Table 4.3. For the three models, the orbital interaction energy is dominated by its a_1 and e components, in agreement with the fact that the directional properties of the Ni₆(CO)₁₀ orbitals of a_2 symmetry are unfavorable. Moreover, an analysis of the fragment orbital populations after interaction indicates that the $[M_{16}]^{4-}$ orbitals which are by far the most involved in the interaction are those which can be identified as the jellium-type MOs (Figure 4.3). Among them, the 1D and 2S orbitals, which are occupied in the isolated $[M_{16}]^{4-}$, are dominating the interaction (see their population in the $[M_{16}(Ni_6(CO)_{10})]^{4-}$ model in Table 4.3), whereas the 2P and 1F orbitals (lowest vacant levels in $[M_{16}]^{4-}$ interact in a lesser extent. Consistently, an examination of the occupation of the Ni₆(CO)₁₀ fragment after interaction (Table 4.3) indicates a major role played by the five lowest unoccupied organometallic MOs, in particular the 39a1 LUMO and the 51e LUMO+1 which are acting as strong accepting orbitals. The organometallic donor orbitals are principally of a_1 symmetry (d_{z2} combinations) and much less efficient. Thus, the Ni₆(CO)₁₀ acts mainly as a strong electron acceptor, as exemplified by its largely negative charge in the computed model (Table 4.3). Moreover, its frontier orbitals interact mostly with the jelliumtype orbitals of $[M_{16}]^{4-}$ core. Clearly, this is not the behavior of a 2-electron ligand which would be expected to act as an electron donor and interact with core surface orbitals, different from the delocalized jellium-type ones. Rather, the interaction of the $Ni_6(CO)_{10}$ fragment with

the $[M_{16}]^{4-}$ core resembles that of the four outer capping M⁺ atoms in the $[M_{20}]$ clusters (see above), despite of the fact they cap different faces of the $[M_{16}]^{4-}$ core.

Table 4.3. Decomposition of the bonding energy between the $[M_{16}]^{4-}$ and $Ni_6(CO)_{10}$ fragment in the $C_{3\nu}$ model $[M_{16}(Ni_6(CO)_{10})]^{4-}$ (M = Cu, Ag, Au) and population analysis of the fragment. All energies are in eV.

Compound $(C_{3\nu})$	[Cu ₁₆ Ni ₆	$(CO)_{10}]^{4-}$	[Ag ₁₆ Ni ₆	$(CO)_{10}]^{4-}$	$\left[Au_{16}N_{i6}(CO)_{10}\right]^{4-}$		
Fragmentation	$[Cu_{16}]^{4-} +$	$Ni_6(CO)_{10}$	$[Ag_{16}]^{4-} +$	$[Ag_{16}]^{4-} + Ni_6(CO)_{10}$		$[Au_{16}]^{4-} + Ni_6(CO)_{10}$	
Pauli repulsion	31	.57	24	24.90		26.17	
Electrostatic interaction	-29.87		-23.24		-24.21		
Orbital interaction decomposition	a_1 a_2 e	-5.34 -0.52 -7.90	a_1 a_2 e	-4.71 -0.42 -6.33	a_1 a_2 e	-4.43 -0.72 -6.69	
Total orbital interaction	-13	.77	-11.46		-11.85		
Total bonding energy	-12	.09	-9.79		-9.89		
Jellium electron configuration of the $[M_{16}]^{4-}$ fragment	$\frac{1 S^{1.88} 1 P^{5.83} 1 D^{8.78} 2 S^{1.49} 2 P^{0.28}}{1 F^{0.63}}$		$\frac{18^{1.90}1P^{5.58}1D^{8.52}2S^{1.53}2P^{0.27}}{1F^{0.48}}$		$\frac{18^{1.90}1P^{5.95}1D^{9.02}2S^{1.64}2P^{0.48}}{1F^{0.48}}$		
Occupation of selected Ni ₆ (CO) ₁₀ frontier MOs	$\frac{(36a_1)^{1.90}(38a_1)^{1.85}(16a_2)^{1.92}}{(39a_1)^{1.17}(51e)^{1.12}(52e)^{0.36}}$		$\begin{array}{c} (36a_l)^{1.87} (38a_l)^{1.88} (16a_2)^{1.92} \\ (39a_l)^{1.22} (51e)^{1.02} (52e)^{0.36} \end{array}$		$\begin{array}{c} (36a_1)^{1.88} (38a_1)^{1.79} (16a_2)^{1.86} \\ (39a_1)^{1.02} (51e)^{0.82} (52e)^{0.40} \end{array}$		
Ni ₆ (CO) ₁₀ Mulliken charge	-1.	64	-1.84		-1.43		

4.2.4 The [M₁₆(Ni₂₄(CO)₄₀)]⁴⁻ clusters

The geometries of the $[M_{16}(Ni_{24}(CO)_{40})]^{4-}$ (M = Cu, Ag, Au) clusters have been fully optimized (see computational details). Major structural data are provided in Table 4.4, together with the computed HOMO-LUMO gaps which are consistent with their closed-shell superatom nature. The optimized distances of the silver species are in good agreement with the reported corresponding experimental values.³⁹

Table 4.4. Relevant computed data for $[M_{16}Ni_{24}(CO)_{40}]^{4-}$ (M = Cu, Ag, Au) clusters. ΔE_{H-L} is HOMO-LUMO gap in eV. The two types of symmetry-equivalent group 11 atoms refer to the concentric spheres M'₄@M''₁₂ (see Section 4.2.1). The two types of symmetry equivalent Ni atoms are labeled Ni_A and Ni_B, the inner and outer metals in Ni₆(CO)₁₀, respectively (see Section 4.2.2). Distances are given in Å. Experimental values of Dahl's silver cluster taken from Ref. 39 are given in parenthesis.

Td	$[M'_4@M''_{12}@\{Ni_{24}(CO)_{40}\}]^{4-}$								
- 4	ΔE_{H-L}	M'-M'	M'-M"	M"-M"	M'-Ni _A	M"-Ni _A	M"-Ni _B	Ni _A -Ni _A	Ni _A -Ni _B
$[Cu_{16}Ni_{24}(CO)_{40}]^{4-}$	1.06	2.625	2.493	2.481-2.503	2.681	2.652	2.558	2.703	2.446
[Ag ₁₆ Ni ₂₄ (CO) ₄₀] ⁴⁻	0.83	2.995	2.865	2.832-2.897	2.838	2.973	2.731	2.703	2.449
	0.02	(2.97)	(2.83)	(2.84)	(2.80)	(2.93)	(2.69)	(2.67)	(2.42)
$[Au_{16}Ni_{24}(CO)_{40}]^{4-}$	0.88	3.067	2.872	2.847-2.893	2.780	2.935	2.699	2.743	2.485

Table 4.5. Decomposition of the bonding energy between the $[M_{16}]^{4-}$ core its $[Ni_{24}(CO)_{40}]$ envelope in the $T_d [M_{16}(Ni_{24}(CO)_{40})]^{4-}$ (M = Cu, Ag, Au) and population analysis of the fragment. All energies are in eV.

Compound (T_d)	$[Cu_{16}Ni_{24}]$	4(CO) ₄₀] ⁴⁻	[Ag ₁₆ Ni ₂	$_{24}(CO)_{40}]^{4-}$	$[Au_{16}Ni_{24}(CO)_{40}]^{4-}$		
Fragmentation	$[Cu_{16}]^{4-} + [$	Ni ₆ (CO) ₁₀] ₄	$[Ag_{16}]^{4-} +$	[Ni ₆ (CO) ₁₀] ₄	$[Au_{16}]^{4-} + [Ni_6(CO)_{10}]_4$		
Pauli repulsion	132	2.40	99	9.99	109.23		
Electrostatic interaction	-12:	5.13	-94	4.39	-102.49		
Orbital interaction	a_1 a_2	-6.52 -0.26	a1 a2	-5.22 -0.21	a_1 a_2	-4.65 -0.27	
decomposition	e t_1	-8.51 -7.53	e t_1	-6.84 -5.16	e t_1	-6.35 -8.05	
	t_2	-25.62	t_2	-22.36	t_2	-21.94	
Total orbital interaction	-48	.44	-39	9.78	-41.26		
Total bonding energy	-48	.45	-34	4.18	-34.51		
Ni ₆ (CO) ₁₀ Mulliken charge	-1.	.68	-1	.57	-1.12		

The Morokuma-Ziegler bonding energy decomposition^{50–52} between the $[M_{16}]^{4-}$ core and its complete $[Ni_{24}(CO)_{40}]$ envelope is provided in Table 4.5. Both total bonding energy and its orbital component indicate stronger interaction with copper, whereas silver and gold behave similarly. The a_1 , e, t_1 and (overall) t_2 components of the orbital interaction energy are dominating. From the results obtained on the $[M_{16}(Ni_6(CO)_{10})]^{4-}$ model (see above), one can

deduce that they result mainly from the participation of the p_z and d_{z2} combinations of the individual $[Ni_6(CO)_{10}]$ units (a_1 and e in local $C_{3\nu}$ symmetry). From the jellium electron configuration of the $[M_{16}]^{4-}$ and from the occupation of the frontier orbitals of a single $Ni_6(CO)_{10}$ fragment in the $[M_{16}(Ni_{24}(CO)_{40})]^{4-}$ cluster, it appears clearly that the major interactions between the $[M_{16}]^{4-}$ core and its $[Ni_{24}(CO)_{40}]$ envelope involves the occupied core jellium orbitals on one side and the accepting π -type orbitals (of substantial p_z character) of the $[Ni_6(CO)_{10}]$ unit on the other side. This result confirms that the behavior of the $[Ni_{24}(CO)_{40}]$ envelope is not that of a "passivating" ligand shell, but rather of a full part of the superatomic entity.



Figure 4.5. Kohn-Sham orbital diagram of $[Ag_{16}Ni_{24}(CO)_{40}]^{4-}$. The MO localization (in %) is given as follows: $Ag_{16}/Ni_{24}/(CO)_{40}$.

The Kohn-Sham MO diagram of $[Ag_{16}Ni_{24}(CO)_{40}]^{4-}$ is shown in Figure 4.5. Those of the Cu and Au relatives (not shown) are similar. The highest occupied levels can be

assimilated to the 2S (65*a*₁) and 1D (81*e* and 145*t*₂) jellium levels. The lowest unoccupied levels correspond to a mixture of the 1F and 2P jellium orbitals with $\pi^*(CO)$ combinations.

4.2.5 Optical properties

From the heterometallic nature of the title clusters, interesting optical properties may be anticipated. This is why a TD-DFT analysis has been undertaken in order to simulate their UV-vis spectra which are shown in Figure 4.6 allowing estimating characteristic patterns for further possible experimental realization. They exhibit similar features with four major absorption bands. The relevant associated electronic transitions are listed in Table 4.6 in the case of M = Ag. One can see these transitions exhibit a MLCT character for all $[M_{16}(Ni_{24}(CO)_{40})]^{4-}$ (M = Cu, Ag, Au) clusters. The low-energy transitions are also associated with some core-ligand charge transfer character. The results show a sizable blue-shift of the main peaks for $[Au_{16}Ni_{24}(CO)_{40}]^{4-}$ in relation to its copper and silver counterparts, revealing strong differences between the expected optical patterns along the series.



Figure 4.6. TD-DFT-simulated UV-vis absorption spectra of $[M_{16}Ni_{24}(CO)_{40}]^{4-}$ (M=Cu, Ag and Au).

Table	4.6.	Major	computed	electronic	absorption	for	$[Ag_{16}Ni_{24}(CO)_{40}]^{4-}$.	The	MO
localiza	ations	(in %) a	re given in	parentheses	as follows: A	$Ag_{16}/2$	Ni ₂₄ /(CO) ₄₀ .		

Photon	%	Major components of the transition
Energy (eV) ^a		
1.70 (0.13)	26	$145t_2 (23/60/17) \longrightarrow 66a_1 (24/37/39)$
	13	$65a_1(59/21/20) \longrightarrow 148t_2(17/29/54)$
2.02 (0.11)	23	$102t_1(5/77/18) \longrightarrow 104t_1(23/35/42)$
	22	$81e(32/48/20) \longrightarrow 148t_2(17/29/54)$
	15	$144t_2 (3/50/47) \longrightarrow 105t_1 (0/33/67)$
	12	$103t_1 (6/70/24) \longrightarrow 82e (0/36/64)$
2.72 (0.09)	27	$142t_2 (8/83/9) \longrightarrow 147t_2 (15/29/55)$
	26	$76e (4/86/10) \longrightarrow 104t_1(23/35/42)$
3.23 (0.06)	21	$134t_2 (7/85/6) \longrightarrow 146t_2 (16/31/53)$
	18	$142t_2 (8/83/9) \longrightarrow 83e (8/25/67)$
	13	$97t_1 (4/91/5) \longrightarrow 82e (0/36/64)$

^a Values in parenthesis correspond to oscillator strengths.

4.2.6 Bonding considerations

So far, the closed-shell 20-je $[M_{16}]^{4-}$ superatom has not been reported, even as a ligand-passivated species, and one may wonder whether it is sufficiently stable for being isolated. Indeed, apart from its somewhat large negative charge, its 2S HOMO contains an antibonding interaction between the M₄ inner core and its outer M₁₂ cage, depicting a radial node. Despite its bonding nature within each individual M₄ and M₁₂ sphere, this orbital is likely lacking bonding character. A way to reinforce the 2S bonding is to add a third concentric sphere, made of 0-electron capping units having empty σ -type frontier orbitals, the in-phase combination of which being able to stabilize the 2S HOMO, whereas in addition the other combinations would also contribute to somewhat stabilize the 1D and 1P orbitals. This is what happens in [M₂₀] (M'₄@M''₁₂@M₄'''), but also in [M₁₆Ni₂₄(CO)₄₀]⁴⁻ ([M'₄@M''₁₂@{Ni₂₄(CO)₄₀]⁴⁻). In the latter cluster, the four Ni₆(CO)₁₀ fragment, which pack to the M₁₆ core in a compact fashion, are mainly interacting with the occupied jellium orbitals by using their vacant σ -type frontier orbitals.

This behavior is different from that of a 2-electron ligand (thiolate, halogenide, phosphine, etc...) which is expected to have its occupied frontier orbital to interact with a coreaccepting orbital localized on the superatom surface. Both situations are sketched in a schematic manner in Figure 1.7. Although very simplified, this description illustrates most of the differences between ligands and outer fragments belonging to the superatom core. The real situation is of course somehow more complex. In particular, significant mixing often occurs between the surface accepting orbitals of the superatomic core and the vacant antibonding jellium-type orbitals, which makes the distinction between them difficult. This is what happens for 1F and 2P MOs of the $[M_{16}]^{4-}$ cores considered in this paper, which exhibit more accepting character than expected at first sight. Also, secondary bonding interactions occur between occupied MOs (mainly jellium-type) of the jellium core and vacant p-type of the supplementary superatom fragment.



Figure 4.7. Simplified MO interaction diagram illustrating the difference between an outer sphere atom belonging to the superatom entity (right side) and a (neutral or anionic) 2-electron ligand (left side).

Conclusion

In summary, our calculations indicate that $[Ag_{16}Ni_{24}(CO)_{40}]^{4-}$ and $[Au_{16}Ni_{24}(CO)_{40}]^{4-}$ are strongly related to bare tetrahedral $[Ag_{20}]$ and $[Au_{20}]$ clusters, showing a $1S^21P^61D^{10}2S^2$ closed-shell configuration. In addition, the $[Cu_{16}Ni_{24}(CO)_{40}]^{4-}$ counterparts is shown to be thermodynamically more stable than its Ag and Au relatives, thus, it should be possible to characterize it experimentally, similarly to its silver and gold counterparts. Hence, the insolution stabilization of the inner FCC-like M₁₆ kernel motif as basic structure observed in the Au₂₀ golden pyramid, allows to further explore the physico-chemical characteristics towards tetrahedral building blocks for nanostructured materials with novel properties. In addition, such structures represent a minimal model of four faces representing a (111) surface of a face-centered cubic unit cell in order to study catalytic activity, among other properties. We expect versatile chemistry on the basis of the potential modifications in the surface of the M₁₆ core.

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Chapter 5: On the possibility to stabilize bare tetrahedral 16-atom metallic architectures

Introduction

Since the beginning of this century, the chemistry of atom-precise nanoclusters of group 11 metals has been developing tremendously.¹⁻⁵ As largely discussed in the preceding chapters, the stability and structure of such species is generally well understood within the framework of the superatom model^{6,7} based on the spherical jellium formalism.⁸ In these superatoms, the average metal oxidation state is generally lower than +I and larger or equal to 0. In most of them, it is larger than 0 and therefore the cluster superatomic core is polycationic. The neutrality of the whole molecule is then generally met (or approached) by the presence of a "passivating" outer shell of coordinated anionic ligands, such as thiolates, halides or hydrides.



Figure 5.1. The fcc-derived structure of the T_d [Au₂₀] cluster with ABCA packing. The green, yellow and grey colors correspond to the symmetry-equivalent Au', Au" and Au" atoms, respectively (Au'4@Au"12@Au"'4). Removing the four grey atoms generates the M₁₆ framework (M'4@M"12) discussed in this chapter.

An emblematic neutral superatom is the $[Au_{20}]$ tetrahedral cluster, obtained in the gas phase and further characterized by photoelectron spectroscopy.⁹ This naked cluster is an unique example of a stable group-11 superatom in which the metal oxidation state is 0. Density functional theory (DFT) calculations,¹⁰⁻¹⁴ have confirmed its 1S² 1P⁶ 1D¹⁰ 2S² closedshell jellium configuration.⁸ Its structure (Figure 5.1) is that of a bulk face-centered cubic (fcc) gold fragment, in a finite nanosized cluster motif.^{9,15} Indeed, along anyone of its four 3fold axes, the packing goes in four successive compact planes, as sketched in Figure 5.1: A (10 atoms), B (6 atoms), C (3 atoms) and A (1 atom). Thus, the [Au₂₀] tetrahedron has four 7atom faces. Within T_d symmetry, there are three types of symmetry-independent atoms, Au', Au" and Au" arranged in concentric shells going as per Au'₄@Au"₁₂@Au"'₄ (Figure 5.2). Removing the four external Au" atoms, one is left with an M₁₆ structure which has been shown to exist in $[Ag_{16}Ni_{24}(CO)_{40}]^{4-}$ (see Chapter 4).¹⁶ In this cluster, the four 7-atom faces of the truncated tetrahedral Ag₁₆ kernel are covered by Ni₆(CO)₁₀ raft-type units. Although one is tempted at first sight to view this compound as made of a 20-je [Ag₁₆]⁴⁻ superatom passivated by four Ni₆(CO)₁₀ organometallic ligands, we have show in Chapter 4 that the Ni₆(CO)₁₀ raft units are full part of the superatomic entity and should not be considered as external ligands. Similarly, $[Au_{20}]$ can be described as made of an $[Au_{16}]^{4-}$ superatom capped on its four 3-atom faces by four Au⁺ ions, in spite of the fact that the capping Au⁺ ions are not ligands but full parts of the superatomic structure. Thus, the question which arises is: can an $[M_{16}]^{4-}$ (M = Cu, Ag, Au) be enough stable for being isolated (as a salt for example) or does such a 20-je (je = jellium electron) species need an additional atom sphere, such as the Ni₂₄ sphere in $[Ag_{16}Ni_{24}(CO)_{40}]^{4-}$ or the $[Au_4]^{4+}$ outer sphere in $[Au_{20}]$? It is noteworthy that the average M oxidation state in a hypothetical $[M_{16}]^{4-}$ species would be negative, an unprecedented situation in Group 11 superatoms. In the case $[M_{16}]^{4-}$ species would not be viable,¹⁷ an additional question is: could it be possible to stabilize it in some ways without adding a supplementary outer sphere of metal atoms? In the followings, we investigate some possibilities through a change in the electron count or some atom substitution and/or inclusion. Thus, our major concern in this work is to find potentially viable¹⁷ species based on a tetrahedral M₁₆ fragment and adopting a closed-shell superatom configuration.

5.1. Computational details

All density functional theory calculations were carried out by using the Amsterdam Density Functional (ADF) program¹⁸ and the zeroth-order regular approximation (ZORA) was applied to incorporate scalar relativistic effects in our calculations. The triple- ζ Slater basis set was employed, plus two polarization functions (STO-TZ2P) for valence electrons, within the generalized gradient approximation (GGA) according to the Becke-Perdew (BP86) exchange functionals.^{19,20} The frozen core approximation was applied to the [1s²-4f¹⁴] inner electrons for Au, [1s²-4p⁶] for Ag, [1s²-3p⁶] for Cu, leaving the remaining electrons to be treated variationally. A gradient convergence criterion of 10⁻⁵ and an energy convergence criterion between 10⁻⁵ and 10⁻⁸ were utilized to perform our geometry optimizations. The solvent effect was used through a polarizable continuum model, which consists of a conductor-like screening treatment through the COSMO module,²¹ it was used in order to get positive HOMO values and we choose dimethyl formamide (DMF), which is usually employed in the coinage metal nano- cluster synthesis.

5.2. Results and discussion

5.2.1 Homonuclear M₁₆ anions

Unsurprizingly, the optimized T_d geometries (fully characterized as energy minima) of $[M_{16}]^{4-}$ (M = Cu, Ag, Au) in vacuum yielded HOMO's with positive energies. Such a result is not uncommon when computing highly charged anions without considering any cationic environment. Mimicking somehow this environment by introducing the effect of a polar solvent (DMF) through the COSMO²¹ dielectric model (see Computational Details) led to T_d energy minima with negative HOMO energies. Some relevant computed data are given in Table 5.1, where E_C is the cohesion energy per atom defined as $E_C = \{E([M_{16}]^{4-}) - 12 \times E(M) - 4 \times E(M^-)\}/16$. The data computed with solvent effect are not that much different from those considering the isolated tetra-anions, except for the cohesion energy, the absolute value of which increasing substantially in DMF environment. As a whole, these results strongly suggest that the $[M_{16}]^{4-}$ species is unlikely to exist, except perhaps in the environment of a strong field of cationic charges.

Table 5.1. Relevant results computed for the hypothetical 20- and	d <i>18-je</i> [M ₁₆] ⁴	and $[M_{16}]^2$	(M = Cu)	, Ag, Cu) clusters	$(T_d \text{ symmetry})$	in
vacuum and in DMF.						

	[Cu	6] ⁴⁻	[Agı	6] ⁴⁻	[Au	6] ⁴⁻	[Cu1	6] ²⁻	[Ag ₁	6] ²⁻	[Au	16] ²⁻
Environment	Vacuum	DMF ^a	Vacuum	DMF ^a	Vacuum	DMF ^a	Vacuum	DMF ^a	Vacuum	DMF ^a	Vacuum	DMF ^a
6 x M'-M' (Å)	2.618	2.671	3.011	3.080	3.080	3.911	3.641	3.627	4.223	4.195	4.447	4.206
24 x M'-M'' (Å)	2.467	2.444	2.854	2.820	2.836	2.831	2.483	2.482	2.876	2.866	3.071	2.851
12 x M''-M'' (Å)	2.484	2.424	2.868	2.806	2.833	2.737	2.377	2.381	2.753	2.747	2.954	2.733
6 x M''-M'' (Å)	2.447	2.454	2.837	2.828	2.831	2.738	2.336	2.338	2.703	2.696	2.903	2.667
$\rho = (C-M'')/(C-M')^{b}$	1.80	1.75	1.81	1.80	1.76	1.33	1.24	1.25	1.24	1.24	1.26	1.23
$\Delta E_{\text{HOMO-LUMO}}(eV)$	1.32	1.53	1.30	1.41	1.22	0.65	1.02	1.21	1.26	1.45	1.55	1.63
E _{HOMO} (eV)	7.66	-2.98	6.78	-3.03	6.98	-3.14	1.58	-4.05	1.18	-4.08	0.54	-4.97
E _C (kcal/mol)	-39.1	-58.1	-24.6	-41.7	-31.6	-48.0	-58.8	-60.1	-42.8	-43.8	-52.6	-53.0
Lowest vibrational frequencies (cm ⁻¹)	76 (<i>t</i> 1)	69 (<i>t</i> ₂)	$45(t_1)$	44 (<i>t</i> ₂)	20 (<i>t</i> ₂)	35 (<i>t</i> ₂)	77 (e)	76 (e)	47 (e)	46 (<i>e</i>)	33 (t_1)	33 (<i>t</i> ₁)

^a Solvent effect considered through the COSMO model (see Computational details). ^b C = center of the cluster.

This hypothesis is in line with what one can get through a qualitative Hückel approach and considering a system made of 16 (n + 1)s interacting AOs. Within this very simple model, the four highest occupied orbitals are antibonding, with positive energies. 2S lies at α + 0.46| β | and the t₂ component of 1D at $\alpha + 0.29|\beta|$. This led us to investigate the 18-je $[M_{16}]^{2-1}$ clusters, with the 1S² 1P⁶ 1D¹⁰ closed-shell jellium configuration. The major DFT-computed data are provided in Table 5.1. Whereas the HOMOs of the isolated anions have positive energies, the corresponding values are much smaller than for their tetraanion relatives. Consistently, calculations with and without solvent effect provide similar cohesion energies. A critical difference with the $[M_{16}]^{4-20-je}$ series lies in the M'-M' distances. In the dianions these distances are very long, whereas, in the tetra-anions they are within bonding contacts, consistently with their ABC fcc packing mode (Figure 5.1). In other words, in an ideal piece of a fcc crystal, M' lies exactly in the same plane as its six M'' neighbours, constituting the 7atom A plane of Figure 5.1. In the $[M_{16}]^{2-}$ series, M' lies significantly outside this plane, making the 16-atom framework describing a hollow polyhedron. The deviation from compacity in these M_{16} T_d frameworks can be evaluated by looking at the ratio of the distances between M' and M" and the center of the tetrahedron C. Assuming an ideal fcc packing, this ratio $\rho = (C-M^{2})/(C-M^{2})$ is equal to $(11/3)^{1/2} = 1.91$. For comparison, in the 20*je* $[M_{20}]$ series, it is computed to be 1.81, 1.80 and 1.73 for M = Cu, Ag, Au, respectively, indicating fairly compact nature. The isoelectronic tetraanions exhibit similar p values (Table 5.1), except for $[Au_{16}]^{4-}$ in DMF. The ρ values of the *18-je* dianions (~ 1.25) indicate severe distortion away from compacity. Taking into account this distortion within the abovementioned Hückel model (no M'-M' bonding contact) opens a large HOMO-LUMO gap for the 18-je count. Due to its nodal properties, the 2S LUMO (a_1 symmetry) is strongly destabilized. This effect was previously noted by Häkkinen et al.²² More importantly, two occupied t_2 levels are also stabilized, due to their nodal properties: the 1P level and the t_2 component of the 1D subshell. It is noteworthy that within this simple Hückel approach and for this electron count, none of the occupied orbitals of the "distorted" non-compact structure have a positive Hückel energy (the now degenerate 1D $(t_2 + e)$ HOMOs lie at $\alpha + 0|\beta|$) and this structure is found to be more stable than the fcc-derived one by $0.69|\beta|$. This qualitative picture is confirmed by DFT calculations, as exemplified by the Kohn-Sham orbital diagrams of $[Ag_{16}]^{4-}$ and $[Ag_{16}]^{2-}$ shown side by side in Figure 5.2.

Chapter 5



Figure 5.2. Kohn-Sham frontier orbital diagrams of $[Ag_{16}]^{4-}$ and $[Ag_{16}]^{2-}$. Their *31e* levels have been aligned for the sake of comparison. The jellium labels are given on the right side.

5.2.2 Heterometallic M₁₆ species

A way to get rid of the large negative charge in the 20-je $[M_{16}]^{4-}$ (M = group 11 element) is to "dope" them by four group 12 elements. The major results obtained for the 20-je neutral T_d models $[M'_4M''_{12}]$ (M' = Zn, Cd, Hg; M'' = Cu, Ag, Au) are given in Table 5.2. Among the nine computed models, only $[Hg_4Au_{12}]$ is not found to be a minimum for the considered T_d symmetry. Although all the HOMOs of the computed models have now negative energies, the computed HOMO-LUMO gaps have moderate values. Moreover, most of them exhibit also an HOMO-HOMO-1 gap of similar order (Table 5.2), suggesting the possibility for a stable 18-je situation. The low values of most of the ρ parameters (Table 5.3) is also in line with a preference for a lower electron-count.

Table 5.2.	Relevant results	computed	for the	e hypothetical	20-је	[M'4M'	12]	(M' =	Zn,	Cd,	Hg;	M''	= Cu,	Ag,	Au)	clusters	of	T_d
symmetry.																		

	[Zn4Cu12]	[Cd4Cu12]	[Hg4Cu12]	[Zn4Ag12]	[Cd4Ag12]	[Hg4Ag12]	[Zn4Au12]	[Cd4Au12]	[Hg4Au12]
6 x M'-M' (Å)	3.073	3.743	4.692	2.936	3.451	3.944	1.759	3.417	4.667
24 x M'-M'' (Å)	2.471	2.621	2.773	2.750	2.854	2.906	2.720	2.820	2.973
12 x M''-M'' (Å)	2.462	2.581	2.399	2.759	2.855	2.865	2.755	2.795	2.733
6 x M''-M'' (Å)	2.417	2.425	2.367	2.736	2.800	2.778	2.683	2.793	2.715
4 x C-M' (Å)	1.882	2.292	2.873	1.798	2.114	2.415	1.759	3.092	2.858
12 x C-M'' (Å)	2.858	2.927	2.793	3.223	3.313	3.304	3.192	3.276	3.193
$^{a}\rho = (C-M'')/(C-M')$	1.52	1.28	0.97	1.79	1.57	1.37	1.81	1.06	1.12
$\Delta E_{\text{HOMO-LUMO}}(eV)$	1.22	0.63	0.82	1.75	1.19	0.82	1.69	0.98	0.44
$E_{\Delta E_{HOMO-HOMO-1}}(eV)$	0.93	1.51	1.06	0.28	0.93	1.28	0.30	1.06	1.37
^c E _C (kcal/mol) ^a	-48.9	-45.6	-42.8	-36.6	-35.0	-31.6	-46.9	-44.7	-39.3
Lowest vibrational = frequency (cm ⁻¹)	49 (<i>t</i> ₂)	39 (<i>t</i> ₂)	19 (<i>t</i> ₂)	$28(t_1)$	28 (t ₂)	27 (a_1)	$17(t_1)$	27 (<i>t</i> ₂)	-32 (<i>t</i> ₂)

^a cohesion energy = $E_C = \{E([M'_4M''_{12}]) - 4 \times E(M') - 12 \times E(M'')\}/16.$

Table 5.3. Rel	evant results	computed	for the	hypothetical	18 - je	[M'4M'	'12] ²⁺	(M' =	Zn,	Cd,	Hg;	M''	= Cu,	Ag,	Au)	clusters	of T_d
symmetry.																	

	$[Zn_4Cu_{12}]^{2+}$	$[Cd_4Cu_{12}]^{2+}$	[Hg4Cu12] ²⁺	$[Zn_4Ag_{12}]^{2+}$	[Cd4Ag12] ²⁺	[Hg4Ag12] ²⁺	$[Zn_4Au_{12}]^{2+}$	[Cd4Au12] ²⁺	[Hg4Au12] ²⁺
6 x M'-M' (Å)	3.667	4.276	4.147	2.837	4.238	4.200	3.717	4.197	4.307
24 x M'-M'' (Å)	2.524	2.684	2.671	2.798	2.908	2.917	2.755	2.872	2.901
12 x M''-M'' (Å)	2.416	2.439	2.472	2.750	2.787	2.807	2.726	2.758	2.761
6 x M''-M'' (Å)	2.390	2.433	2.458	2.678	2.745	2.767	2.641	2.701	2.716
4 x C-M' (Å)	2.246	2.619	2.539	2.350	2.595	2.572	2.276	2.570	2.638
12 x C-M'' (Å)	2.819	2.856	2.888	3.186	3.246	3.270	3.151	3.204	3.214
$\rho = (C-M'')/(C-M')$	1.26	1.09	1.14	1.36	1.25	1.27	1.38	1.25	1.22
$\Delta E_{H-L} (eV)$	1.94	1.75	1.54	1.67	1.90	1.49	1.55	1.91	1.62
E _C (kcal/mol) ^a	-68.4	-63.4	-64.3	-56.7	-53.2	-54.2	-64.7	-61.1	-59.6
Lowest vibrational frequency (cm ⁻¹)	69 (e)	60 (<i>t</i> ₂)	48 (<i>t</i> ₂)	9 (<i>a</i> ₂)	41 (e)	40 (e)	$-28(a_2)$	$28(t_1)$	21 (t_1)

^a E_c = cohesion energy = {E([M'₄M''₁₂]²⁺) - E(M'²⁺) - 3 x E(M') - 12 x E(M'')}/16.

As a matter of fact, the $[M'_4M''_{12}]^{2+}$ cations (see Table 5.3) have larger HOMO-LUMO gaps than their neutral homologs (except for $[Zn_4Ag_{12}]^{2+}$ and $[Zn_4Au_{12}]^{2+}$, which incidentally are associated with small positive or imaginary frequencies, respectively) associated with much larger cohesion energies. Clearly, as for the homometallic series discussed above, the best electron count for a 16-atom tetrahedral arrangement is 18.

5.2.3 Centered X@M₁₆ species

A possible way of stabilizing the 2S HOMO of the 20-je M₁₆ framework is to provide the cluster with a supplementary AO of a_1 symmetry in the molecular T_d architecture. This can be done by encapsulating a supplementary element in the middle of the M₁₆ tetrahedron. In the case where M is a group 11 metal, neutrality of a 20-je [X@M₁₆] species is reached for X belonging to group 14. The major results obtained for M = Cu, Ag, Au and X = C, Si, Ge, Sn, Pb are gathered in Table 5.4. At this point of the discussion, one should recall that we are restricting our analysis to the potential stability of tetrahedral (T_d) frameworks and that other authors have found that $[XAu_{16}]^-$ (X = Si, Ge, Sn) 21-je anions have a global minimum structure adopting a low-symmetry exohedral structure, showing a preference of the maingroup element for lower connectivity.²³ A similar result was found by others on the 20-je [SiAu₁₆].²² This is in line with the fact that several of our models have imaginary frequencies in T_d symmetry (Table 5.4) and therefore are not true minima. Some of these minima of lower symmetry are described in the annex of this chapter. Nevertheless, 7 among the 15 tested models are found to be true minima. In spite of the fact they may not be global minima on the potential energy surface, it is very likely that they present higher kinetic stability than the above-mentioned predicted global minima. Indeed, in the latter the group 14 element occupies an unsaturated exohedral position exposed to incoming reagents. It is noteworthy that these computed minima have substantial HOMO-LUMO gaps and no significant HOMO-HOMO-1 gap, as the result of the stabilization of the 2S cluster orbital through the participation of the ns AO of the encapsulated X atom. Additionally, the occupied t_2 levels are also somewhat stabilized by the np AOs of X. The Sn- and Pb-centered clusters appear to be the most likely to be observed.

Table 5.4. Relevant results computed for the hypothetical 20-	$-je [X@M_{16}] (X=C,$	Si, Ge, Sn, Pb; $M = Cu$, Ag	g, Au) clusters of T_d symmetry.

	[CCu16]	[SiCu16]	[GeCu16]	[SnCu ₁₆]	[PbCu ₁₆]	[CAg16]	[SiAg16]	[GeAg ₁₆]	[SnAg16]	[PbAg16]	[CAu ₁₆]	[SiAu16]	[GeAu16]	[SnAu16]	[PbAu ₁₆]
6 x M'-M' (Å)	3.186	3.867	4.002	4.172	4.252	3.579	4.205	4.384	4.596	4.708	3.492	4.068	4.278	4.512	4.644
24 x M'-M'' (Å)	2.476	2.534	2.574	2.625	2.657	2.860	2.891	2.917	2.965	2.996	2.834	2.865	2.888	2.935	2.966
12 x M"-M" (Å)	2.438	2.384	2.399	2.415	2.431	2.842	2.765	2.759	2.766	2.775	2.805	2.770	2.757	2.758	2.761
6 x M''-M'' (Å)	2.427	2.341	2.352	2.365	2.383	2.800	2.737	2.718	2.715	2.720	2.801	2.730	2.702	2.695	2.692
4 x X-M' (Å)	1.951	2.368	2.451	2.555	2.604	2.191	2.575	2.685	2.815	2.883	2.138	2.491	2.620	2.763	2.844
12 x X-M'' (Å)	2.852	2.773	2.788	2.805	2.825	3.306	3.227	3.213	3.217	3.225	3.287	3.227	3.204	3.200	3.201
$\rho = (X-M'')/(X-M')$	1.46	1.17	1.14	1.10	1.08	1.49	1.25	1.20	1.14	1.12	1.54	1.30	1.22	1.16	1.13
$\Delta E_{\text{HOMO-LUMO}}(eV)$	0.72	1.89	1.88	1.91	2.02	0.75	1.49	1.55	1.82	1.88	0.94	1.89	1.98	2.01	1.94
E _C (kcal/mol) ^a	-63.6	-64.7	-65.1	-61.8	-60.0	-46.1	-47.1	-46.8	-46.3	-45.7	-56.7	-58.0	-57.4	-56.7	-56.0
Lowest vibrational frequency (cm ⁻¹)	-122 (<i>t</i> ₂)	53 (t ₂)	-216 (<i>t</i> ₂)	47 (<i>t</i> 1)	54 (<i>t</i> ₁)	36 (<i>t</i> ₂)	-70 (t ₂)	-41 (<i>t</i> ₂)	17 (<i>t</i> ₂)	24 (<i>t</i> ₂)	35 (<i>t</i> ₁)	-24 (<i>t</i> ₂)	20 (<i>t</i> ₂)	14 (<i>t</i> ₁)	-11 (<i>t</i> _l)

^a E_c = cohesion energy = E_C = {E([XM₁₆]) – E(X) - 16 x E(M)}/17.

Table 5.5. Relevant results computed for the hypothetical 18-*je* [X@M₁₆] (X= Be, Mg, Ca, Sr, Ba; M = Cu, Ag, Au) clusters of T_d symmetry.

	[BeCu 16]	[MgCu16]	[CaCu16]	[SrCu16]	[BaCu16]	[BeAg ₁₆]	[MgAg ₁₆]	[CaAg16]	[SrAg16]	[BaAg16]	[BeAu ₁₆]	[MgAu16]	[CaAu16]	[SrAu16]	[BaAu16]
6 x M'-M' (Å)	3.773	4.076	4.234	4.329	4.434	3.991	4.499	4.731	4.850	4.970	3.842	4.389	4.635	4.764	4.883
24 x M'-M'' (Å)	2.502	2.571	2.632	2.674	2.728	2.843	2.919	2.980	3.023	3.075	2.826	2.891	2.946	2.986	3.032
12 x M''-M'' (Å)	2.370	2.377	2.408	2.434	2.473	2.756	2.739	2.753	2.770	2.802	2.767	2.736	2.740	2.753	2.775
6 x M''-M'' (Å)	2.323	2.314	2.345	2.373	2.415	2.721	2.677	2.680	2.699	2.731	2.724	2.670	2.662	2.673	2.696
4 x X-M' (Å)	2.311	2.496	2.593	2.651	2.715	2.444	2.755	2.897	2.970	3.044	2.353	2.688	2.838	2.917	2.990
12 x X-M'' (Å)	2.754	2.754	2.790	2.821	2.869	3.213	3.178	3.189	3.211	3.248	3.222	3.173	3.171	3.186	3.211
$\rho = (X-M'')/(X-M')$	1.19	1.10	1.08	1.06	1.06	1.31	1.15	1.10	1.08	1.07	1.37	1.18	1.12	1.09	1.07
$\Delta E_{\text{HOMO-LUMO}}(eV)$	0.82	1.28	1.88	1.95	1.98	0.39	1.00	1.85	1.98	2.06	0.89	1.51	1.90	1.91	1.89
E _C (kcal/mol) ^a	-62.5	-60.6	-61.8	-60.0	-58.7	-44.1	-44.5	-47.5	-46.7	-46.6	-55.9	-55.9	-58.6	-57.6	-57.0
Lowest vibrational frequency (cm ⁻¹)	-44 (<i>t</i> ₂)	73 (<i>t</i> ₁)	58 (<i>t</i> ₁)	50 (<i>t</i> ₁)	$40(t_1)$	-118 (<i>t</i> ₂)	36 (<i>t</i> ₂)	28 (a ₂)	20 (<i>a</i> ₂)	10 (<i>a</i> ₂)	11 (<i>t</i> ₂)	35 (<i>t</i> ₁)	-12 (<i>a</i> ₂)	-23 (<i>a</i> ₂)	-29 (<i>a</i> ₂)

^a E_c = cohesion energy = E_C = { $E([XM_{16}]) - E(X) - 16 \times E(M)$ }/17.

When X is a group 2 element, *18-je* neutral X@M₁₆ (M = group 11) species can be considered. The results obtained for X = Be, Mg, Ca, Sr, Ba and M = Cu, Ag, Au are gathered in Table 5.5. Due to the high energy of the group 2 valence ns AO, the cluster 2S orbital is destabilized and the computed X@M₁₆ *18-je* models have significant HOMO-LUMO gaps, especially in the case of X = Ca, Sr and Ba. As a whole, the results of Table 5.5 suggest that these three element are likely to provide viable species when combined with Cu and Ag.

Another way to obtain neutrality for a 20-je species X@M₁₆ (M = group 11) is to encapsulate group 4 metals, then the new species are labeled as A@M₁₆ (A = Ti, Zr, Hf). Our calculations on the series corresponding to A = Ti, Zr, Hf and M = Cu, Ag, Au (Table 5.6) led to small HOMO-LUMO gaps, with imaginary vibrational frequencies for the two gold derivatives as well as for [TiAg₁₆]. Despite the small ρ value in these compounds, the 2S HOMO is not enough stabilized due to the relatively high energy of the valence (n +1) s AO of the group 4 atoms. Interestingly, the corresponding HOMO-HOMO-1 gaps are much larger, strongly suggesting stability of such transition-metal species for the count of *18-je* (see below). With the same idea, the neutrality for a *16-je* species A@M₁₆ (M = group 11) is also possible by incorporating one A atom from group 12. The results computed for the series, corresponding to A = Zn, Cd, Hg and M = Cu, Ag, Au are given in Table 5.7. Again, for as the previous *20-je* species, relatively small HOMO-LUMO gaps are obtained,

To conclude this section, it appears that *20-je* species are best favored when encapsulating a group 14 element and *18-je* species when encapsulating an atom from group 2.

Table 5.6. Relevant results computed for the hypothetical 20-je $[A@M_{16}]$ (A = Ti, Zr, Hf; M = Cu, Ag, Au) clusters of T_d symmetry. No convergence for $[TiAu_{16}]$ in T_d symmetry.

	[TiCu16]	[ZrCu ₁₆]	[HfCu ₁₆]	[TiAg16]	[ZrAg16]	[HfAg16]	[TiAu16]	[ZrAu16]	[HfAu16]
6 x M'-M' (Å)	3.985	4.116	4.131	4.385	4.544	4.538	-	4.447	4.4404
24 x M'-M'' (Å)	2.553	2.598	2.600	2.900	2.936	2.932	-	2.918	2.908
12 x M''-M'' (Å)	2.369	2.382	2.383	2.732	2.734	2.736	-	2.721	2.726
6 x M''-M'' (Å)	2.331	2.356	2.349	2.697	2.698	2.689	-	2.718	2.712
4 x X-M' (Å)	2.440	2.521	2.530	2.685	2.782	2.779	-	2.723	2.697
12 x X-M'' (Å)	2.758	2.779	2.776	3.185	3.186	3.183	-	3.189	3.189
$\rho = (X-M'')/(X-M')$	1.13	1.10	1.10	1.19	1.15	1.15	-	1.17	1.18
$\Delta E_{HOMO-LUMO} (eV)$	0.37	0.45	0.65	0.07	0.45	0.80	-	0.29	0.45
ΔЕномо-номо-1 (eV)	1.74	1.94	1.71	1.69	1.92	1.60	-	1.89	1.75
E _C (kcal/mol) ^a	-67.5	-69.0	-69.4	-49.9	-52.0	-52.2	-	-63.0	-63.2
Lowest vibrational frequency (cm ⁻¹)	61 (<i>t</i> ₁)	$68(t_1)$	58 (t ₂)	-31 (<i>t</i> ₂)	33 (<i>t</i> ₂)	$33(t_1)$	-	-40 (<i>t</i> ₂)	-21 (<i>t</i> ₂)

^a E_c = cohesion energy = E_C = { $E([XM_{12}]) - E(X) - 16 \times E(M)$ }/17.

Table 5.7. Relevant results computed for the hypothetical	$18 - je [A@M_{16}] (A = Z_{16})$	n, Cd, Hg M = Cu, Ag, Au) clust	ters of T_d symmetry. No
convergence for [HgAg ₁₆] in T_d symmetry.			

	[ZnCu ₁₆]	[CdCu ₁₆]	[HgCu ₁₆]	[ZnAg16]	[CdAg ₁₆]	[HgAg ₁₆]	[ZnAu ₁₆]	[CdAu16]	[HgAu ₁₆]
6 x M'-M' (Å)	3.981	4.166	4.184	4.314	4.560	-	4.218	4.488	4.498
24 x M'-M'' (Å)	2.549	2.610	2.620	2.888	2.939	-	2.868	2.918	2.924
12 x M''-M'' (Å)	2.375	2.399	2.351	2.745	2.747	-	2.750	2.744	2.750
6 x M''-M'' (Å)	2.319	2.341	2.406	2.693	2.685	-	2.689	2.676	2.681
4 x X-M' (Å)	2.438	2.551	2.562	2.642	2.792	-	2.583	2.748	2.754
12 x X-M'' (Å)	2.755	2.782	2.792	3.192	3.188	-	3.192	3.182	3.188
$\rho = (X-M'')/(X-M')$	1.13	1.09	1.09	1.21	1.14	-	1.24	1.16	1.16
$\Delta E_{LUMO-LUMO+1} (eV)$	0.09	0.06	0.07	0.19	0.14	-	0.18	0.12	0.13
$\Delta E_{HOMO-LUMO}(eV)$	0.71	0.89	0.52	0.15	0.45	-	0.81	1.14	0.64
E _C (kcal/mol) ^a	-58.5	-57.0	-73.0	-41.5	-41.4	-	-52.8	-52.3	-49.5
Lowest vibrational frequency (cm ⁻¹)	65 (e)	63 (<i>t</i> ₁)	58 (t ₂)	-57 (<i>t</i> ₂)	18 (<i>t</i> ₂)	-	-36 (<i>t</i> ₂)	17 (<i>t</i> 1)	16 (<i>t</i> 1)

^a E_c = cohesion energy = E_C = {E([XM₁₆]) – E(X) - 16 x E(M)}/17.

Conclusion

Our DFT calculations strongly indicate that M_{16} tetrahedral group 11 architectures are unlikely to exist when bearing 20-*je*. Beside of the large anionic charge required by this electron count, the intrinsic antibonding nature of the 2S HOMO renders this electron count particularly unfavorable. There are two possibilities to avoid this situation in keeping the T_d symmetry. One is to reduce the electron count to 18-*je*, which is also a "magic" superatomic electron number. In this regard, the heterometallic series $[M'_4M''_{12}]^{2+}$ (M' =group 12; M'' = group 11) offers good opportunities for obtaining stable species.

The other alternative for stabilizing the 20-*je* species is to stabilize its 2S HOMO in adding a supplementary AO of a_1 symmetry by incorporating an additional atom at the center of the cluster. Some neutral [X@M₁₆] clusters with X = group 14 and M = group 11 appear to be the best candidates, in spite of the fact that their T_d energy minimum might not always be the global minimum. Interestingly, some neutral [X@M₁₆] clusters with 18-*je* in which X = group 2 and M = group 11 are also susceptible to be observed.

The conclusions drawn above are based on the computed vibrational frequencies, comparison of cohesion energies and the HOMO-LUMO gaps. The latter can be compared to real systems computed at the same level of theory (see Chapters 2 and 4). For example, the HOMO-LUMO gaps obtained for the $[M_{16}Ni_{24}(CO)_{40}]^{4-}$ systems are in the range 0.83-1.06 eV. They are in the range 1.34-1.81 eV for the $[M_{20}]$ systems. These values compare well with that of the clusters investigated in this current chapter, which are, for example, in the range 1.49-1.94 eV for the heterometallic *18-je* $[M'_4M''_{12}]^{2+}$ (Table 5.2) 0.72-2.02 eV for the *20-je* X@M₁₆, (Table 5.4) and 0.39-2.06 eV for the *18-je* X@M₁₆ (Table 5.5).

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ANNEX: Low-symmetry structures of true minima found for some of the investigated X@M₁₆ clusters

As mentioned in Chapter 6, some of our computed models are not true minima in T_d symmetry since they are associated with imaginary vibrational frequency we have looked for minima of lower symmetry by following the atomic displacements associated with these imaginary frequencies. Only the structures where it was possible to obtain a convergence and a lack of imaginary frequency are presented below. Indeed for [CCu₁₆], [BeCu₁₆], [BeAg₁₆], [TiAg₁₆], [HfAu₁₆] and [ZrAu₁₆], the minimum could not be reached, so far. The main structures of the energy minima that we obtained are presented in Figure 5.A1.



Figure 5.A1. Different structures corresponding to characterized true energy.

Table 5.A1. Energy minima obtained for some of the hypothetical *20-* and *18-je* centered M_{16} clusters which do not adopt the T_d symmetry. In parenthesis the difference in kcal/mol between E_{Td} and $E_{new symmetry.}$

Structure	D_{4d}	$C_{3\nu}$	C _{5v-1}	C _{5v-2}
		[SrAu ₁₆] (5.4), [CaAu ₁₆] (0.0)		
Clusters	[GeCu ₁₆]	$[ZnAu_{16}]$ (1.9), $[PbAu_{16}]$ (4.1),	[SiAu ₁₆] (7.5),	[BaAu ₁₆]
	(122.2)	[GeAg ₁₆] (3.0), [HgAg ₁₆],	[SiAg ₁₆] (0.0)	(11.1)
		$[ZnAg_{16}](7.1)$		

The characterized energy minima that we were able to obtain are summarized in Table 5.A1 and relevant corresponding computed values are provided in Tables 5.A2 and 5.A3.

Table 5.A2. Relevant results computed for the hypothetical 20-*je* centered M₁₆ clusters in their low symmetry energy minima.

	[GeCu ₁₆]	[SiAg ₁₆]	[GeAg ₁₆]	[SiAu ₁₆]	[PbAu ₁₆]
	(D_{4d})	(C_{5v})	$(C_{3\nu})$	(C_{5v})	$(C_{3\nu})$
M-M (Å)	8*2.352 16*2.456 8*2.488 8*2.617	10*2.766 10*2.784 5*2.785 5*2.845 5*2.856 5*3.010	6*2.761 6*2.799 6*2.820 3*2.824 6*2.840 3*2.842 3*2.848 3*2.848 3*2.869 3*2.885	10*2.737 10*2.765 5*2.780 5*2.802 5*2.806 5*3.097	6*2.725 6*2.775 3*2.802 6*2.810 6*2.848 3*2.890 3*2.908 3*2.914 3*2.966
X-M (Å)	8*2.602 8*2.843	5*2.668 5*2.833	3*2.624 6*2.860	5*2.665 5*2.849	1*2.948 6*2.973 3*3.080 3*3.329 3*3.371
$\Delta E_{\text{HOMO-LUMO}} (eV)$	1.03	1.45	1.65	1.69	1.93
Ec (kcal/mol)	-64.62	-47.14	-46.99	-57.58	-56.26
Lowest vibrational frequencies	36 (<i>e</i> ₂)	31 (<i>e</i> ₂)	17 (<i>a</i> ₂)	15 (e ₂)	$24(e_1)$

Table 5.A3. Relevant results computed for the hypothetical -je centered M₁₆ clusters in their low symmetry energy minima.

	$\begin{bmatrix} CaAu_{16} \\ (C_{3\nu}) \end{bmatrix}$	$[\operatorname{SrAu}_{16}] \\ (C_{3\nu})$	[BaAu ₁₆] (C _{5v})	$\begin{bmatrix} ZnAg_{16} \end{bmatrix} \\ (C_{3\nu})$	$\begin{bmatrix} ZnAu_{16} \\ (C_{3\nu}) \end{bmatrix}$	[HgAg ₁₆] (C _{3v})
M-M (Å)	6*2.701 6*2.738 3*2.770 6*2.800 6*2.832 3*2.870 3*2.902	6*2.709 6*2.754 3*2.794 6*2.816 6*2.846 3*2.919 3*2.944 3*2.965 3*3.020	5*2.795 10*2.799 5*2.801 10*2.816 5*2.890	6*2.747 3*2.748 3*2.750 6*2.806 3*2.834 6*2.845 3*2.853 6*2.854 3*2.859	6*2.730 3*2.756 3*2.772 6*2.783 6*2.784 3*2.799 3*2.811 3*2.816 6*2.836	6*2.754 3*2.813 6*2.821 3*2.836 3*2.841 3*2.872 6*2.873 3*2.877 6*2.918
X-M (Å)	1*2.899	6*3.035 1*2.959	5*3.179 5*3.198 5*3.199	3*2.600 6*2.775	3*2.650 6*2.771 1*3.273	3*2.818 6*2.831 1*3.360
$\Delta E_{\text{HOMO-LUMO}} (eV)$	1.84	1.86	1.60	0.50	0.99	0.24
E _c (kcal/mol)	-58.8	-58.0	-57.9	-42.0	-52.9	-39.5
Lowest vibrational frequenecies	22 (<i>e</i> ₁)	15 (<i>e</i> ₁)	23 (e ₂)	20 (<i>a</i> ₂)	12 (<i>a</i> ₂)	23 (<i>e</i> ₁)

Chapter 6: Symmetry lowering by cage doping of $[W@Au_{12}]$. Evaluation of electronic and optical properties in the *18-je* clusters $[W@Au_{12}Pt_n]$ (n = 0-4)

Introduction

Gold nanostructures are a fundamental concern in nanoscience, owing to their potential to serve as useful building blocks towards the design of novel materials with variable sizes displaying novel properties for catalysis, nanoelectronics and biological diagnostics,¹⁻⁷ among other applications.⁷⁻¹⁰ The efficiency in catalysis for carbon monoxide oxidation unraveled for discrete clusters is a relevant example of the differences between the inert bulk and clusters with precise numbers of gold atoms.¹¹⁻¹³ The current synthetic control to achieve nanoparticles¹⁴⁻²² with selected atomic precision provides valuable opportunities to gain deeper knowledge of the structure-property relationship at regimes involving a few metallic atoms.

Gold chemistry possesses a rich structural diversity owing to the particular role of relativistic effects,²³⁻²⁸ resulting in unusual structures, highlighting the tetrahedral Au_{20} cluster²⁹⁻³² and the hollow Au_{32} cage cluster.³³⁻³⁵ Furthermore, the doping of heteroatoms into the gold skeletal structure allows us to modify the physical and chemical properties achieving the potential tune of the molecular properties, where the influence of a doping atom is of special importance to the field of catalysis.^{2,6,36-38}

In this concern, the icosahedral [W@Au₁₂] cluster remains as one of the most prominent examples of bare endohedral clusters depicting highly stable closed-shell electronic and geometrical structure. This emblematic 18-jellium electron (*18-je*) superatom was initially predicted from density functional theory (DFT) calculations by Pyykkö and Runeberg^{39,40} and subsequently characterized experimentally by Li et al.⁴¹ showing in addition the appearance of related isoelectronic species.⁴² The *18-je* count ensures an electronic and structural stability owing to a specific electronic shell filling accounted by a $1S^{2}1P^{6}1D^{10}$ spherical jellium configuration.^{28,43,44} Such shell description resembles that of isolated atoms, from where comes the concept of superatom developed by Jena and Khana.⁴⁴⁻

⁴⁸ Several clusters have been evaluated in analogy to this cluster taking advantage of the superatom model,⁴⁹⁻⁵⁹ where the nature of the endohedral and cage atoms allows to modulate the total number of valence electrons.^{42,51,54,58}

Particularly, the doping of the cage results in a loss of the high icosahedral symmetry (symmetry lowering), which has been employed towards the enhancement of optical properties,^{60,61} among other features. Our interest relies in the exploration of the cage doping, allowing the access to viable 18-je clusters related to [W@Au₁₂], introducing a decrease in symmetry by the inclusion of a heteroatom in the cage which does not contribute formally to the overall electron count. Herein, we propose a new series of neutral clusters adopting the closed-shell 18-je superatom count, namely $[W(a)Au_{12}Pt_n]$ with n = 0, 1, 2, 3 and 4. Indeed, Pt contributes to zero electron to the superatom electron count (in a first approximation 5d AO's do not participate to bonding). On the other hand, adding one or several Pt atoms to the [W@Au₁₂] framework should induce less symmetrical structures with cages involving a larger number of vertices. These species are evaluated by using relativistic density functional methods. In addition, their optical properties computed by time-dependent DFT (TD-DFT) calculations are discussed to provide valuable information for a possible experimental characterization, a possible broadening of the absorption peaks in less symmetrical structures will be discussed. In addition, the variation of the molecular electrostatic potential $(V(\mathbf{r}))$ along the series is studied in order to evaluate the variation of the most catalytically active sites given by cluster corners,⁶² as has been recently reported by Stenlid and Brinck.⁶³

6.1. Computational details

Relativistic DFT calculations⁶⁴ were carried out by using the ADF code⁶⁵, incorporating scalar corrections via the zeroth-order regular approximation (ZORA) Hamiltonian⁶⁶. All calculations were done employing all-electron triple- ζ Slater quality basis set, plus two polarization functions (STO-TZ2P), within the generalized gradient approximation (GGA) according to the Becke-Perdew (BP86) exchange-correlation functionals.^{67,68} The frozen core approximation was applied to the [1s²-4f¹⁴] core electrons for W, Pt and Au, leaving the remaining electrons to be treated explicitly, where the nuclear coordinates does not alter the core electrons defined by a fixed core potential. Geometry optimizations were performed without any symmetry constraint, via the analytical energy gradient method implemented by Versluis and Ziegler⁶⁹ followed by the respective vibrational

analysis obtained from analytical second derivatives.^{70,71} Analyses of the interaction energy between fragments constituting the investigated clusters were carried out within the Morokuma-Ziegler energy decomposition method.⁷²⁻⁷⁴ Time-dependent DFT (TD-DFT) calculations were employed at the same level, but using the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional^{75,76} owing to its good performance in the description of optical properties of gold-based clusters at a relative low computational cost, allowing further comparisons to other computational studies.⁷⁷⁻⁸¹

The molecular electrostatic potential is a well-established tool to provide a quantitative analysis of the molecular charge distribution, which has been shown to be connected to the catalytic activity in gold clusters,⁸⁴ This quantity can be evaluated according to the formula,

$$V(\mathbf{r}) = \sum_{A} \frac{Z_{A}}{|\mathbf{R}_{A} - \mathbf{r}|} - \int \frac{\rho(\mathbf{r})d\mathbf{r}}{|\mathbf{r}' - \mathbf{r}|}$$

where, V(r) is a scalar function owing to the potential created by the nuclear and electronic density of the charge density, in atomic units. Z_A is the charge on nucleus located at R_A , given by the atomic number of atom A, and $\rho(r)$ is the electronic density. The sign and strength of V(r) is given by the predominance of nuclei (positive) or electronic (negative) effects on different molecular regions. The surface was set to 0.001 a.u. (electrons/Bohr³), as contour of the electronic density accounting for van der Waals surface of the molecule.^{85,86}

6.2. Results and discussion

In the followings, the various $[WAu_{12}Pt_n]$ (n = 0-4) optimized structures are noted Pt_n according to the number of Pt atoms. The n = 0 case (Pt₀) corresponds to the reference $[W@Au_{12}]$ icosahedral cluster calculated at the same level of theory. In the case of Pt₃ where several isomers of low energy were found, they are associated with a letter **a**, **b**, **c**..., depending on the increasing order of their relative energy (Pt₂-**a** is the most stable Pt₂ isomer). We discuss here only the most stable isomers, *i.e.* those lying in a relative energy range of 15 kcal/mol. They are shown in Figure 6.1. The stability of these BP86 results is supported by different comparison to GGA and GGA-Hybrid calculations of gold cluster properties.^{49,81-83} The structure of $[WAu_{12}]$ (n = 0) is also shown for comparison. Relevant computed data are given in Tables 6.1 and 6.2.

The global minimum of [WAu₁₂Pt], **Pt**₁, can be described as a W@Au₁₁Pt icosahedron of which one triangular face is capped by an Au atom. However, one of the edges of the

capped face is open (Au...Au = 3.38 Å). The next isomer of **Pt**₁ lies 19.7 kcal/mol above, and therefore is not reported in Table 6.1. It depicts a W@Au₁₂ icosahedron face-capped by a Pt atom.

In **Pt2-a** W is encapsulated into a rather regular $Au_{10}Pt_2$ icosahedron, an edge of which being made of the two Pt atoms. The two faces sharing this edge are capped by two Au atoms which are bonded to each other. The resulting structure is quite compact. **Pt2-b** is of the same $C_{2\nu}$ symmetry as **Pt2-a** and can be derived from it by the permutation of two Pt with two Au. However, the $Au_{10}Pt_2$ skeleton in **Pt2-b** is missing a bond on its Au-Au edge common to its two capped faces. In **Pt2-c** W is encapsulated in a fairly unsymmetrical $Au_{10}Pt_2$ polyhedron having 11 triangular and 4 distorted square faces, two square faces being capped by Au atoms.

Only one low-energy isomer having 3 Pt atoms, Pt_3 , was found. Indeed, the next isomer was computed lying 27.6 kcal/mol above. Pt_3 has a fairly unsymmetrical structure which can be viewed as a simple packing of three "hexagonal compact planes": $Au_5/WAu_3Pt_3/Au_4$.

The only low-energy isomer having 4 Pt atoms was found to be of T_d symmetry (the next one was found 26.1 kcal/mol above). Actually, the Au₁₂Pt₄ polyhedron in which W is encapsulated in **Pt4-a** has the same structural feature than that found previously for the $[Au_{16}]^{4-}$ anion⁸⁷⁻⁹⁰ and related Au₁₆ clusters encapsulating various elements.^{37,91-93} It is composed of an Au₁₂ truncated tetrahedron, the four hexagonal faces of which being capped by the four Pt atoms which in fact are situated close to the centers of the faces.



Figure 6.1. The low-energy optimized structures of the $[W@Au_{12}Pt_n]$ (n = 1, 4) clusters.

	$\mathbf{Pto}\left(I_{h} ight)$	$\mathbf{Pt}_{1}\left(C_{s}\right)$	$\mathbf{Pt_{2-a}}(C_{2\nu})$	$\mathbf{Pt_{2-b}}\left(C_{2\nu}\right)$	$\mathbf{Pt_{2-c}}(C_s)$	Pt ₃ (C_l)	$\mathbf{Pt_4}(T_d)$
ΔE (kcal/mol)	0.0	0.0	0.0	4.7	13.5	0.0	0.0
n(W-Au)	12	11	10	10	9	9	12
n(W-Pt)	0	1	2	2	2	3	4
W-Au range (Å)	2.773-2.773	2.712-2.828	2.766-2.880	2.752-2.849	2.655-2.952	2.793-3.076	3.224-3.224
W-Pt range (Å)	-	2.485	2.510-2.510	2.477-2.477	2.452-2.475	2.438-2.507	2.404-2.404
Au-Au range (Å)	2.874-2.874	2.756-2.933	2.747-2.978	2.784-2.954	2.730-3.158	2.742-3.017	2.722-2.773
Au-Pt range (Å)	-	2.655-3.010	2.716-3.081	2.651-3.000	2.661-2.966	2.651-2.853	2.839-2.839
Pt-Pt range (Å)	-	-	3.144	-	2.889	-	-

Table 6.1. Major computed data for the isomers of lower energy (ΔE : isomer relative energy; n: number of bonding contacts.

The **Pt**_n (n = 1, 3) structures have in common to maintain the maximum of compacity, and keeping the total number of W-metal bonding contacts equal to 12 (or close to), with all the Pt atoms bonded to W. For n = 1 and 2, this is achieved in approaching icosahedral geometry as much as possible. For larger n values, the icosahedral environment of W starts to be problematic to satisfy. The n = 4 case is particular for it allows the Au₁₂Pt₄ cage to adopt a very symmetrical arrangement, derived from an fcc compact structure (ABC stacking with 7, 6 and 3 atoms respectively), but dilated in such a way that it can offer a sufficient space in its center into which W can settle. The number of W-metal "bonds" in **Pt**₄ is particularly large (16), but the 12 W-Au contacts are quite long (3.224 Å), whereas in the other species reported in Table 6.1 they do not exceed 3.08 Å. On the other hand, the 4 W-Pt distances are particularly short (2.404 Å).

In order to evaluate more quantitatively the strength of the bonding between W and its host in the different Pt_n structures, we have performed a Morokuma-Ziegler energy decomposition analysis (EDA) relative to this interaction. The results obtained for the four global minima are given in Table 6.2, together with that corresponding to the reference compound [W@Au₁₂], Pt₀.

Table 6.2. Energy decomposition analysis, HOMO-LUMO gaps (ΔE_{H-L}), per atom cohesion energy (E_c), adiabatic electron affinities (AEA) and adiabatic ionization potentials (AIP) of the **Pt**_n (n = 0-4) global minima.

Compound	$\mathbf{Pto}\left(I_{h}\right)$	$\mathbf{Pt}_1(C_s)$	$\mathbf{Pt}_{2-\mathbf{a}}(C_{2v})$	$\mathbf{Pt}_{3}(C_l)$	$\mathbf{Pt}_{4}(T_{d})$
Fragmentation	$W + Au_{12}$	$W + Au_{12}Pt$	$W + Au_{12}Pt_2$	$W + Au_{12}Pt_3$	$W + Au_{12}Pt_4$
Pauli repulsion	68.06	68.37	69.32	67.66	71.82
Electrostatic interaction (eV)	-41.17	-42.04	-42.80	-42.17	-45.43
Orbital interaction (eV)	-40.41	-39.72	-39.71	-39.88	-41.76
Total bonding energy (eV)	-13.52	-13.38	-13.19	-14.39	-15.37
Ec (kcal/mol)	-66.1	-69.3	-72.7	-74.9	-79.1
ΔE _{H-L} (eV)	1.79	1.08	0.99	0.65	1.09
AEA (eV)	1.87	2.55	2.73	3.05	2.93
AIP (eV)	7.28	7.05	6.61	6.88	7.12

Following its orbital interaction component, the total bonding energy between W and its host decreases slowly in absolute value when going from n = 0 to n = 2, and then starts to increase again. **Pt**₃ and **Pt**₄ have a stronger bonding interaction than **Pt**₀. The cluster per atom cohesion energy is defined as $E_c = E(Pt_n) - [E(W) - 12 \times E(Au) - n \times E(Pt)]/(13 + n)$. It increases in absolute value with the number of Pt atoms; therefore the cluster cohesion is stronger for **Pt**₄. Looking at the HOMO-LUMO gaps which are indicative of kinetic stability and stiffness of the structure, all the Pt-doped clusters have smaller HOMO-LUMO gaps than the **Pt**₄ reference, **Pt**₁ and **Pt**₄ being the most favored on this criterion. Adiabatic electron affinities (AEAs) and ionization potentials (AIPs) are related to chemical stability. AEAs of the Pt-doped species are all larger than that of **Pt**₀, **Pt**₃ and **Pt**₄ being the most stable with respect to reduction. On the other hand, the AIPs of the Pt-doped species are slightly lower than that of **Pt**₀. From this criterion, **Pt**₁ and **Pt**₄ appear to be the most stable with respect to oxidation.

The inclusion of Pt atoms in the golden cage leads to a decrease in symmetry, which vary along the series as $Pt_0(I_h) \rightarrow Pt_1(C_s) \rightarrow Pt_{2-a}(C_{2v}) \rightarrow Pt_3(C_l) \rightarrow Pt_4(T_d)$, and leads to a sizable splitting of the frontiers shells. In Figure 6.2, the 1D-HOMO goes from a five-fold

shell in the classical [W@Au₁₂] cluster ($Pt_0(I_h)$) to five non-degenerate levels in $Pt_1(C_s)$, $Pt_{2-a}(C_{2v})$ and $Pt_3(C_1)$, with larger splitting in the Pt_{2-a} cluster owing to the less symmetrical structure. For the [WAu₁₂Pt₄] cluster ($Pt_4(T_d)$), the tetrahedral symmetry splits the 1D shell in two set of three- and two-fold levels with a lesser splitting as observed for Pt_2 and Pt_3 (Figure 6.2). Along the series, the LUMO vary from an orbital of the 2D* shell to a 2S* orbital in Pt_3 and Pt_4 .



Figure 6.2. Representation of the frontier orbitals for $Pt_0(I_h)$, $Pt_1(C_s)$, $Pt_{2-a}(C_{2v})$, $Pt_3(C_l)$, and $Pt_4(T_d)$, depicting representative isosurfaces of the frontier orbitals.

In order to provide insights of characteristic fingerprints of the optical properties in the low-energy region, which have been well reported for gold nanoclusters,⁷ the optical absorption spectra in the range from 0.0 to 4.5 eV was calculated (Figure 6.3). In these *18-je* clusters despite the similar electronic structure, the symmetry lowering away from the icosahedral point group of $[W@Au_{12}]$ (Pto(*I_h*)) frontier orbitals splits the 3-peak pattern below 4.5 eV, into several peaks owing to the loss of degeneracy of the frontier 1D shell and 2D* shell. In $[WAu_{12}]$ the first peak at 2.743 eV (A) is attributed to a 1D \rightarrow 1F transition, the second peak at 3.194 eV (B), concerns a mix between "5d-block" \rightarrow 2D* and "5d-block" \rightarrow 2S* transitions. The third peak at 4.002 eV (C), is originating from a 1D \rightarrow 2P* transition.

For $Pt_1(C_s)$, the first peak A spread into three new peaks owing to the latter splitting of the 1D shell, the second peak (B) appears as a new signal and a shoulder due to the splitting of the 2D* band, whereas the peak C is slightly red-shifted in relation to Pt_0 , showing a 2-

peak pattern. In $Pt_{2-a}(C_{2v})$, the first peak (A) of $1D \rightarrow 1F$ character, leads to several peaks in the range between 2.0 - 3.0 eV, where the peak B appears as a single shoulder and two peaks between 3.0 - 3.7 eV, similarly to peak C, which is shown as a 2-peak pattern. Similarly in $Pt_3(C_1)$, the peak A appears as a broad signal from 2.4 to ~ 3.0 eV, whereas peak B is a broader signal in comparison to the parent Pt_0 cluster. Lastly, peak C appears slightly blue shifted. Moreover, for $Pt_4(T_d)$, a more defined peak pattern is observed where peak A splits in two absorption bands, similarly to peak B, owing to the splitting of the 1D shell into a set of two- and three-fold levels. Particularly the peak related to the parent peak C in $[W@Au_{12}]$ ($Pt_0(I_h)$) is obtained as a peak with a shoulder associated with a larger oscillator strength, denoting a larger transition dipole moment.

These results illustrate the variation of the optical behavior in related clusters retaining a similar superatomic electronic configuration and stability, suggesting that related properties can be modified by the inclusion of different elements which are able to lower the symmetry of the clusters. This approach can be useful for further design of broad black-absorbers, allowing to absorb light in a wide range, thus able to enhance the efficiency of thin film solar cells.^{94,95}



Figure 6.3. Calculated optical absorption spectrum for $Pt_0(I_h)$, $Pt_1(C_s)$, $Pt_{2-a}(C_{2\nu})$, $Pt_3(C_1)$ and $Pt_4(T_d)$. The increase in the range of the A transition is denoted by a black line behind the respective region.

Furthermore, the surface representation of the molecular electrostatic potential $(V_s(\mathbf{r}))$ was investigated, in order to evaluate the variation of the most catalytically active sites given by cluster corners,⁶² in function of the charge redistribution along the series. This work was done in the group of Pr. Alvaro Muñoz-Castro at the Universidad Autónoma de Chile (Santiago). Recently, Stenlid and Brinck,⁸⁴ gave an intuitive description based on $V_s(\mathbf{r})$ for atomically precise gold and platinum clusters, where sites with positive potential are located over catalytic relevant sites, with maximum values (Vs,max) at atoms with low-coordinated sites and negative potential at bonding regions. In addition, they showed a direct correlation between values of V_{s,max} and interaction energies towards CO and H₂O, unraveling the capability of V_{s,max} to locate and quantify catalytic active sites within a molecular cluster. The surface representation of the molecular electrostatic potential ($V_s(\mathbf{r})$) for $Pt_0(I_h)$, $Pt_1(C_s)$, Pt_2 $a(C_{2\nu})$, Pt_{2-b}($C_{2\nu}$), Pt₃(C_l) and Pt₄(T_d), is given on Figure 6.4, indicating variation along the series. For the parent [W@Au₁₂] cluster ($Pt_0(I_h)$), a more polarized V_s(**r**) is observed in comparison to the icosahedral Au₁₃ reported by Stenlid and Brinck,⁸⁴ suggesting an enhanced catalytic activity for the Au vertices in the icosahedral Au_{12} cage, and more negative regions in the respective edges accounting for Au-Au bonds. When one Pt atom is incorporated to the Au₁₂ cage ($Pt_1(C_s)$), a gold atom is exposed as a low-coordinated site, enhancing selectively the catalytic activity to a specific site, where the region of the Pt atom is a smaller positive region in $V_s(\mathbf{r})$. Similarly, for the case with two Pt atoms (Pt_{2-a}($C_{2\nu}$) and Pt_{2-b}($C_{2\nu}$)), a pair of low-coordinated gold sites are generated, suggesting a more active site in such regions, with Pt atoms leading to a smaller positive region in $V_s(\mathbf{r})$. Lastly, for the case with three Pt atoms (Pt₃(C_1)), a gold site shows a smaller value on V_s(**r**), recovering in part the observed V_s(**r**) for the parent cluster.

In sharp contrast, the T_d -[W@Au₁₂Pt₄] exhibits regions with smaller value of V_s(**r**), leading a very site-specific region expected for catalytic activity located at the center of each Au(111)-like face, where each Pt atom is located. This situation is comparable to the recent prediction of the efficient catalytic activity of a Mo doped Au(111)-gold-surface, leading to a promising low-temperature N₂ dissociation towards NH₃ production which can have a deep impact in a new generation of the Born-Haber Process.⁹⁶ Thus, T_d -[W@Au₁₂Pt₄] can be a useful model to explore the catalytic activity of different clusters retaining a high gold/dopant ratio. Further evaluation of interaction energies can be informative to correlate these observations to catalytic activities of the here discussed clusters.



Figure 6.4. Surface representation of the molecular electrostatic potential (V_s(**r**)) for $Pt_0(I_h)$, $Pt_1(C_s)$, $Pt_{2-a}(C_{2v})$, $Pt_{2-b}(C_{2v})$, $Pt_3(C_1)$ and $Pt_4(T_d)$.

Conclusion

We investigated geometries and energies of a series of viable *18-je* clusters related to $[W@Au_{12}]$, introducing a decrease in symmetry with the inclusion of Pt heteroatoms in the golden cage, where W remain as an endohedral atom and strong cluster compacity is maintained. Along the $[W@Au_{12}Pt_n]$ series, with n = 0, 1, 2, 3 and 4, a resulting loss of symmetry from the parent icosahedral symmetry is induced. The calculated cohesion energy shows a relative stability of the proposed clusters in relation to the parent cluster $[W@Au_{12}]$ experimentally characterized. Moreover, the obtained values of HOMO-LUMO gap, adiabatic electron affinities (AEAs) and ionization potentials (AIPs), indicate **Pt**₁ and **Pt**₄, as the most stable with respect to oxidation.

The induced symmetry lowering by the favorable inclusion of Pt atoms in the cage, results in a sizable splitting of the frontier superatomic shells, which in turn effectively modify the optical properties relatively to $[W@Au_{12}]$. The simulated absorption spectra show an interesting broadening effect of the absorption peaks particularly for **Pt**₁, **Pt**₂ and **Pt**₃, thus

likely to be useful for further design of broad black-absorbers, which are able to absorb light in a wider range, with potential capabilities to enhance the efficiency of thin film solar cells and photocatalysis processes, among other aapplications.

In addition, the catalytic activity of each specific site is evaluated through the surface representation of the molecular electrostatic potential ($V_s(\mathbf{r})$), denoting interesting variations along the series, leading to the selectivity of a few catalytic sites, which can be useful as model, towards more selective catalysts. Interestingly, for T_d -[W@Au₁₂Pt₄] very site specific regions are obtained, which are located at the center of each Au(111)-like face, where each Pt atom is allocated. Thus, such cluster can be a useful model to explore the catalytic activity of different clusters retaining a high gold-dopant ratio in a closed-shell molecular Au(111) model.

The discussed approach to include heteroatoms within the external cage, can be further developed to modify molecular properties of similar superatomic clusters displaying stable geometrical structures, by the inclusion of well-chosen elements inducing lower symmetries thus permitting to tune and improve the desired properties.

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Chapter 7: Bonding analysis of pseudo 2-electron trigonal bipyramidal organometallic Cu/Zn clusters

Introduction

Despite brass is one of the most common alloys found in everyday's live and has been used for millennia, molecular bimetallic Zn/Cu compounds remain almost unknown. This is somewhat surprising, because copper and zinc can be mixed to form a broad range of uniform solid solutions with different Zn/Cu ratios, making brass a highly homogeneous material. This is very useful since it allows fine-tuning of the alloy properties, in particular the mechanical and electrical properties as well as the resistance to corrosion.

To our knowledge, on the molecular level only two types of clusters are known so far, exhibiting a $[Zn_xCu_y]$ core in which Cu-Zn bonding is present. All these compounds were reported by the group of R. Fischer in Münich. The first type, namely the two strongly related clusters $[(ZnCp^*)_4(Cu({}^{BuNC}))_4]$ and $[(ZnCp^*)_3(ZnCp)(Cu({}^{BuNC}))_4]$,¹ display a tetracapped tetrahedral $[Cu_4Zn_4]$ geometry (see Figure 7.1). This motif is also found in γ -brass, though the arrangement of an inner zinc tetrahedron being surrounded by an outer copper tetrahedron is inversed with respect to the molecular species. These compounds have been described as 8electron superatoms. The other type is exemplified by the σ -aromatic triangular $[Zn_2CuCp^*_3]$,² (see Figure 7.2) which is an isolobal analogue of the D_{3h} $[H_3]^+$ ion. The compounds have been defined as molecular and embryonic brass, respectively.^{1,2} According to the group in Münich, $[Zn_2CuCp^*_3]$ can be expected to be useful as a building block for the bottom-up synthesis of larger deltahedral clusters, as a trigonal M₃ (M = metal) unit is the fundamental feature of such species.²



Figure 7.1. Tetracapped tetrahedral geometry displayed by the $[Cu_4Zn_4]$ core of $(ZnCp^*)_4(Cu(^tBuNC))_4$ (left). Its total structure (right).

It turns out that very recently, two new clusters, namely $[Zn_4Cu_3Cp^*_5]$ (1) and $[Zn_5Cu_2Cp^*_5]^+$ (2) were isolated and fully characterized in the Münich group. These two isoelectronic compounds are actually found as impurities in the product of the reaction of the $[Zn_2CuCp^*_3]$ synthesis. This latter compound, is obtained from the treatment of Cu(OAc) with an equimolar amounts of $[Zn_2Cp^*_2]$ in benzene at room temperature for three days.² Compounds 1 and 2(OAc) were extracted as byproducts from the resulting insoluble dark red suspension containing the triangular $[Zn_2CuCp^*_3]$ cluster as the major component. Despite their weak yields, they could be isolated and fully characterized,³ their X-ray molecular structures are shown in Figure 7.3 and relevant corresponding metrical data are given in Table 7.1.



Figure 7.2. Representation of the [Zn₂CuCp*₃] structure.

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Figure 7.3. Molecular structure of $[Cu_3Zn_4Cp_{5}]$ (1) (left) and $[Cu_2Zn_5Cp_{5}]^+$ (2) (right). The trigonal bipyramids are highlighted. Orthogonal view on the Cu1, Cu2, Cu3 plane showing the Cu1, Cu2, Cu3, Zn3/2 tetrahedrons of 1 (bottom, left). Orthogonal view on the Cu1, Cu2, Zn3 plane showing the Cu1, Cu2, Zn3, Zn2/4 tetrahedrons of 2 (bottom, right).

Table 7.1. Selected averaged experimental (X-ray) and optimized (DFT) distances for 1, 1', 2 and 2' (in Å). The corresponding averaged computed Wiberg indices are given in parenthesis for 1' and 2'. The Zn' and Zn" labels designate the zinc atom bonded to Cp*/Cp and that belonging to the Cu₂Zn triangle in 2/2', respectively.

	1 (X-ray)	1' (DFT)	1 (DFT)
Cu-Cu	2.440	2.414 (0.270)	2.426
Cu-Zn	2.445	2.470 (0.091)	2.432
Zn-Zn'	2.318	2.345 (0.600)	2.314
	2 (X-ray)	2' (DFT)	2 (DFT)
Cu-Cu	2.415	2.385 (0.339)	2.401
Cu-Zn	2.487	2.490 (0.074)	2.437
Cu-Zn''	2.400	2.399 (0.268)	2.401
Zn-Zn'	2.311	2.338 (0.606)	2.299
Zn-Zn''	2.717	2.872 (0.025)	2.682

In both clusters, the metal atoms are arranged in a trigonal bipyramidal fashion, the apical positions of which being occupied by $ZnZnCp^*$ units. The Zn_2Cu_3 trigonal bipyramid in **1** is very close to D_{3h} symmetry. In the case of **2**, the bipyramid is distorted due to the heterometallic nature of the $ZnCu_2$ triangle, but the connectivity is basically the same as in **1**. However, the capping Zn atoms in **2** are are much closer to the Cu atoms than to Zn3, as exemplified by Cu_{triangle}-Zn2 (avg. 2.463 Å) and Cu_{triangle}-Zn4 (avg. 2.487 Å) which are significantly shorter than Zn3-Zn2 (2.745(6) Å) and Zn3-Zn4 (2.688(7) Å).

Cluster geometries are strongly related to their electronic structure, associating specific cluster shapes with specific numbers of electrons.^{4,5} Stable closed-shell organometallic clusters most often obey the Wade-Mingos electron-counting rules.⁵ These rules state that the number of skeletal electron pairs (SEPs) associated with cluster bonding is equal to the number of vertices of the deltahedron in which the cluster is inscribed, plus one. Accordingly, the trigonal bipyramidal skeletons of **1** and **2**, should be associated with 5 + 1 = 6 SEPs. **1** can be formally considered a constituted of five fragments, three CuCp* and two Zn-ZnCp* units. Assuming first that, as generally admitted, the Cu and Zn 3d electrons are not significantly involved in the bonding, CuCp* and Zn-ZnCp* are 0- and 1-electron donor moieties, respectively. One thus ends up with only 1 SEP for **1**, as for its isoelectronic relative **2**. This makes **1** and **2** highly electron-deficient with respect to the Wade-Mingos rules. It should be however kept in mind that these rules assume that the fragments constituting the cluster participate to cluster bonding with 3 frontier orbitals, one of σ type and two of π type.⁵

non-bonding $4p_{\pi}$ frontier orbitals as well as one 4s/4p hybrid of σ type (the other sp hybrid is involved in the Zn-Zn single bond). On the other hand, the case of the CuCp* (or [ZnCp*]⁺) fragment is different since it is generally considered as participating to the bonding with only one frontier orbital of σ type (a 4s/4p hybrid) the occupied low-lying 3d-block being, as said above, discarded. Thus, the Wade-Mingos standard "reference" should be considered with caution when dealing with 1 and 2. To clear out this situation, we have performed density functional (DFT) calculations on these two clusters as well as on several cluster models (see Computational Details). For the sake of simplicity we have first replaced the pentamethylcyclopentadienyl (Cp*) ligands in 1 and 2 by simple cyclopentadienyls (Cp). The calculations reported below have been made in collaboration with Julius Harnung from the Fischer group in Munich.

7.1. Computational details

The computations were performed by using the Amsterdam Density Functional $(ADF)^6$ and the Wiberg indices⁷ were computed with the NBO 6.0 program.⁸ In these ADF caculations, we employed the triple- ζ Slater basis set, plus two polarization functions (STO-TZ2P) for valence electrons, within the generalized gradient approximation (GGA) according to the Becke–Perdew (BP86) exchange functional.^{9,10} London dispersion corrections were included through the pairwise Grimme approach (Grimme-D3).¹¹ The frozen core approximation was applied to the $[1s^2-3p^6]$ for Cu, $[1s^2-3p^6]$ for S, and $[1s^2]$ for C leaving the remaining electrons to be treated variationally. Geometry optimizations were performed without any symmetry restrain, via the the analytical energy gradient method implemented by Verslius and Ziegler¹². A gradient convergence criterion of 10^{-6} were utilized to perform our geometry optimizations. Analyses of the interaction energy between fragments constituting the investigated clusters have been carried out within the Morokuma-Ziegler energy decomposition method.¹³

7.2. Results and discussion

The optimized geometries of the $[Zn_4Cu_3Cp_5]$ (1') and $[Zn_5Cu_2Cp_5]^+$ (2') were found to be energy minima for C_s symmetry, with their symmetry plane containing the Cu₃ and ZnCu₂ triangle, respectively. However, the $[Zn_4Cu_3]$ metallic core of 1' was found to be very

close to D_{3h} , as in the X-ray structure of **1**. The lowering of symmetry to C_s is obviously due to the mismatch of the D_{3h} 3-fold symmetry with the 5-fold symmetry of the Cp ligands. The optimized metrical data of **1'** and **2'** (Table 7.1) are consistent with their experimental counterparts in **1** and **2**. The Zn₄Cu₃ metal framework of **1'** is very close to D_{3h} symmetry. Its Kohn-Sham orbital diagram is shown in Figure 7.4. The large HOMO-LUMO gap is consistent with the stability of **1**. In order to get a better insight into its bonding, a Morokuma-Ziegler energy decomposition analysis (EDA)¹³ was carried out, considering the interaction between two fragments: $[Cu_3Cp_3]^{2-}$ triangular unit¹⁴ and its bi-capping $[(CpZn_2...Zn_2Cp]^{2+}$ "dimeric" unit. The formal fragment charges were chosen for closed-shell simplicity and also considering that $[Cu_3Cp_3]^{2-}$ is isostructural and isoelectronic to the known $[Zn_2CuCp*_3]^2$ (see above), which can be viewed as an isolobal¹⁵ analogue of H₃⁺ (σ -aromatic 2-electron/3-center bonding). A similar fragmentation has been suggested for the cluster $[{Pd(C_6H_4F)}_3(\mu_2-SC_6H_4Cl)_3Ag(H_2O)_2][BF_4]_2$ implying that an aromatic $[Pd_3]^+$ triangle acts as a donor ligand to a Ag⁺ ion.¹⁴ Our EDA results are given in Table 7.2.

Unsurprisingly, with such a formal fragment partitioning in 1', the electrostatic interaction component dominates the total bonding energy. Representing 44% of the former, the orbital interaction component is, however, not negligible. Its *a*' and *a*'' components, respectively of σ - and π -type with respect to the Cu₃ plane, are of similar order, the *a*' interaction being the strongest. A detailed analysis of the 1' Kohn-Sham orbital compositions based on its fragment orbitals allowed us to describe the covalent component of the bonding interaction through the simplified qualitative interaction orbital diagram sketched in Figure 7.5, considering D_{3h} pseudo-symmetry.

Table 7.2. Morokuma-Ziegler energy decomposition analysis (EDA) of **1**' and **2**'. All values in eV. E_{Pauli} = Pauli repulsion; E_{elstat} = electrostatic interaction; E_{Orb} = orbital interaction. TBE = total bonding energy = E_{Pauli} + E_{elstat} + E_{orb} + E_{disp} .

	1' (C_s)		2' (C_s)	
Fragmentation	$[Cu_3Cp_3]^2 + [CpZn_2Zn_2Cp]^{2+}$		$[ZnCu_2Cp_3]^- + [CpZn_2Zn_2Cp]^{2+}$	
E_{Pauli}	14.92		10.37	
Eelstat	-24.53		-14.15	
E _{orb} decomposition	a'	-6.30	<i>a</i> '	-4.30
	<i>a</i> ''	-4.55	<i>a</i> ''	-3.48
E_{orb}	-10.85		-7.78	
E_{disp}	-1.24		-1.16	
TBE	-21.70		-12.72	

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Figure 7.4. Kohn-Sham orbital diagram of **1**'. The levels are labelled according to C_s symmetry (in black) and D_{3h} pseudo-symmetry (in blue). The C_s symmetry plane contains the Cu₃ triangle.

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Figure 7.5. Simplified orbital diagram associated with the interaction of the $[Cu_3Cp_3]^{2-}$ and $[(CpZn_2...Zn_2Cp]^{2+}$ fragments in **1**' (D_{3h} pseudo-symmetry assumed). The occupied 3d(Zn) and (most of) the 3d(Cu) combinations, not involved in the interaction, are not represented.

The $[Zn_4Cp_2]^{2+}$ "dimer" has six accepting frontier orbitals, the in-phase and out-ofphase combinations of the three accepting orbitals on the terminal Zn of each $[Zn_2Cp]^+$ "monomer" (see above). In the D_{3h} pseudo-symmetry of **1**', the sp(Zn) hybrids give rise to a'_1 and a''_2 combinations, whereas the $4p_{\pi}(Zn)$ AO's lead to e' and e'' combinations (see left side of Figure 7.5). On the other hand, the $[Cu_3Cp_3]^{2-}$ unit has no accepting orbitals. Its highest occupied levels are the $\pi(Cp)$ and 3d(Cu) combinations, among which is buried the strongly bonding a'_1 orbital, principally of 4s/4p composition, which contains the 3-center bonding electron pair of this fragment. This $Cu_3 a'_1$ orbital interacts strongly with the a'_1 LUMO of the $[Zn_4Cp_2]^{2+}$ "dimeric" fragment, giving rise to a fully in-phase, strongly

bonding, combination which contains the unique SEP that one would consider if no 3d(Cu) orbitals were involved (see above). But in fact 3d(Cu) combinations of proper symmetry interact with the other accepting orbitals of the $[Zn_4Cp_2]^{2+}$ fragment. This can be traced by the occupation of it's a''_2 , e' and e'' frontier orbitals, which is 0.54, 2 x 0.10 and 2 x 0.11, respectively. For comparison, the a'_1 occupation is 1.02. The 3d(Cu) counterparts are of $3d_{\pi}$ (a''_2 and e'') and $3dz^2$ (e') character. Counting the resulting bonding pairs, one ends up with 6 SEPs, all of the proper symmetry (a'_1 , a''_2 , e' and e'') as in clusters satisfying the Wade-Mingos rules. Thus, to some extent, **1** satisfies the Wade-Mingos rules, despite not all, but only specific, $3d_{\pi}$ and $3dz^2$ combinations are involved. Moreover, the e' and e'' interactions are not very strong, because of the relatively poor energy match between 4p(Zn) and 3d(Cu). On the other hand, some second-order participation to the bonding (not represented in Figure 7.5) and involving the a'_1 and a''_2 combinations associated with the Zn-Zn bonding pairs can also be traced. This tends to weaken somewhat the strength of the Zn-Zn bonds at the expenses of Zn-Cu bonding, as exemplified by the computed Zn-Zn Wiberg index in **1'** (0.600), significantly weaker than in CpZnZnCp (0.811).

To summarize the above MO analysis, the bonding within the Cu₃Zn₂ trigonal bipyramidal skeleton in **1** can be viewed as intermediate between that of an hypothetical electron-deficient 1-SEP cluster and that of a regular Wade-Mingos 6-SEP species. It should be pointed out that, although not preponderant, the role of the $4p_{\pi}(Zn)$ AOs in the framework stability is crucial. This can be shown by replacing in **1**' the $[CpZnZn]^+$ capping units by $[CpZn]^+$ fragments which, assuming η^5 -Cp coordination, do not possess $4p_{\pi}$ accepting frontier orbitals. Indeed, the optimized geometry of the $[Zn_2Cu_3Cp_5]$ cluster exhibits (η^1 -Cp)Zn units, thus leaving the $4p_{\pi}(Zn)$ orbitals available for bonding within the Zn₂Cu₃ trigonal bipyramidal skeleton. With such a low coordination mode associated with the rather electron-poor character of the Zn₂Cu₃ skeleton, the hypothetical $[Zn_2Cu_3Cp_5]$ cluster appears unlikely to be isolable.

The optimized geometry of **2'** is also in good agreement with the X-ray structure of **2** (see Table 7.1). In particular it shows a rather long Zn(apical)-Zn"(equatorial) bond of 2.872 Å. It is noteworthy that when the dispersion corrections are not included in the calculations, the Zn-Zn" distance is elongated to 3.019 Å, a no-bond value. Thus, despite the small E_{disp} component in the fragment energy decomposition of Table 7.2, the dispersion forces appear to play a significant role in the overall cluster structure. The weak covalent Zn-Zn" bonding is also exemplified by its low Wiberg index (0.025). It can be explained by the fact that the

highest 3d-type combinations of the $[Cp_3Cu_2Zn]^-$ fragment have little Zn participation (3d(Zn) levels are lower) and therefore interact with the $4p_{\pi}(Zn)$ combinations of the $[Zn_4Cp_2]^{2+}$ "dimer" primarily through the copper atoms.

The real methylated compounds **1** and **2** have also been optimized and were found to be of C_1 symmetry, slightly distorted away from C_s due to the steric effect of the methyl groups. Their selected metrical data reported in Table 7.1 are in good agreement with that of the X-ray structure. For these compounds, it was not possible to perform a 2-fragment EDA analysis similar to that carried out for the **1'** and **2'** models. As a matter of fact, it was not possible to converge the $[(Cp*Zn_2...Zn_2Cp*]^{2+}$ unit in the proper closed-shell configuration. However, a 3-fragment analysis in which this "dimeric" unit is split into two $[Zn_2Cp*]^+$ fragments was possible. The corresponding results, together with that obtained in a similar way for **1'** and **2'** are provided in Table 7.3. It appears clearly that the 2- and 3-fragment EDA analyses of **1'** and **2'** are fully consistent and indicate negligible interaction between the two capping $[Zn_2Cp^*]^+$ units.

Table 7.3. 3-fragment Morokuma-Ziegler energy decomposition analysis (EDA) of **1**' and **2**', **1** and **2**. All values in eV. E_{Pauli} = Pauli repulsion; E_{elstat} = electrostatic interaction; E_{Orb} = orbital interaction. TBE = total bonding energy = E_{Pauli} + E_{elstat} + E_{orb} + E_{disp} .

	1'	2'	1	2
Fragmentation	$[Cu_3Cp_3]^{2-}+2$	$[ZnCu_2Cp_3]^- + 2$	$[Cu_3Cp*_3]^{2-}+2$	$[ZnCu_2Cp*_3]^-+2$
	$[Zn_2Cp]^+$	$[Zn_2Cp]^+$	$[Zn_2Cp^*]^+$	$[Zn_2Cp^*]^+$
E_{Pauli}	13.42	9.37	16.43	13.09
Eelstat	-21.28	-11.21	-21.41	-12.93
Eorb	-10.16	-7.42	-11.78	-9.18
Edisp	-1.30	-1.21	-2.64	-2.57
TBE	-19.32	-10.48	-19.40	-11.58

In Table 7.3, the results obtained for of 1 and 2 with that of 1' and 2' indicate that the bonding analysis carried out for the non-methylated models applies to the real methylated compounds. Among the changes upon ligand methylation, one can note an increase of the absolute value of the E_{orb} component by ~ 1.6/1.8 eV due a the destabilization of the Cu₃ or Cu₂Zn 3d(Cu) block. The E_{disp} component is also doubled upon methylation, due to methyl...methyl van der Waals interactions. However, with an absolute value increase of ~ 1.3/1.4 eV, its contribution to the total bonding interaction remains relatively small (7-10% of the sum of the stabilizing components).

Conclusion

The trigonal bipyramidal clusters 1 and 2 are at first glance with 1 SEP highly electron deficient with regard to the Wade-Mingos rules, owing to the fact that the basal MCp* units lack $4p_{\pi}$ frontier orbitals. However, according to our EDA analysis of the models **1**' based on the fragments $[Cu_3Cp_3]^{2-}$ and $[CpZn_2\cdots Zn_2Cp]^{2+}$ not only 4s/p orbitals of the trigonal M₃ basal unit are involved in skeletal bonding, but even, if to at a lower extend, also $3d_{\pi}$ and $3d_{\tau^2}$ combinations. The latter provide frontier orbitals of proper symmetry and five additional SEPs to satisfy the Wade-Mingos rules for trigonal bipyramidal clusters. In spite of the fact that some of these additional SEPs have only moderate bonding character, the metal skeletons of 1 and 2 do not need the help of μ_2/μ_3 ligands for maintaining their unbridged bipyramidal trigonal structures. Dispersion interactions between the Cp* protecting ligands provide additional stabilization to the structures. This is a specific property of Cp* as a ligand,¹⁶ among others, such as its flexible coordination mode $(\eta^1 \dots \eta^5)$ and its steric bulk which allows the ligands forming a compact protecting shell around the metal skeleton. Such Cu/Zn clusters are on the borderline between electron deficient and regular Wade-Mingos species and therefore are likely to be highly reactive and should allow further cluster expansion reactions, eventually reaching compositions predicted by the superatom model.

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Chapter 8: General conclusion

The work reported in this thesis manuscript is focused on the application of quantum chemistry methods to the study of different types of inorganic transition-metal compounds, all of them made of or containing group 11 elements. Most of these compounds are clusters which can be described as superatoms within the framework of the spherical jellium theory. A new family of organometallic clusters which at first sight violate the Wade-Mingos rules is also analysed, as well as a series of solid-state and molecular hydrides. Our aim was to provide a rationalization of the stability and structure of the investigated species. Properties, mainly optical, are also analyzed in relationship with the electronic structure.

After a general introduction to electron counting rules in chemistry, a series of bare superatomic clusters of Cu, Ag and Au are investigated with the help of DFT calculations. Our results indicate that copper superatoms are almost as stable as gold clusters and more stable than their silver counterparts, in spite of the fact that reported characterized copper superatoms are so far scarce as compared to their silver and gold homologs. TD-DFT calculations show that with an increase of the cluster core nuclearity, the absorption bands are redshifted, allowing differentiating between the clusters types. Moreover, the optical properties of the silver cores are somewhat different from that of their Cu and Au relatives.

The fact that copper superatoms are scarce could result from the general methods of synthesis of the coinage metal superatoms which starts with metal(I) species. The use of borohydride as a reducing agent seems, in the case of copper, to lead preferentially to the stabilization of copper(I) polyhydrides. We then have compared the stability of various coinage metal hydrides, based on DFT calculations on simple extended and molecular models. Our results indicate that copper hydrides are significantly more stable than their silver and gold counterparts. To conclude the two preceding chapters, one can say that copper superatoms are more stable than silver superatoms. However, copper hydrides are even more stable than silver hydrides. This is why chalcogenolate-protected copper superatoms are so scarce. To avoid the thermodynamical well of hydrides, ligands different to chalcogenolates and able to compete with hydrides should be used in the case of copper.

In the next chapter we investigate the electronic structure of Dahl's $[Ag_{16}Ni_{24}(CO)_{40}]^{4-}$ cluster, as well as its Cu and Ag relatives, in relationship with the emblematic known $[Au_{20}]$

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superatom (and its Cu and Ag relatives). Indeed, both series of compounds have a tetrahedral architecture and contain the same $[M_{16}]^{4-}$ central core with a $1S^2 \ 1P^6 \ 1D^{10} \ 2S^2$ jellium configuration. In the case of $[Au_{20}]$, the $[Au_{16}]^{4-}$ core is capped by four Au⁺ ions, whereas in $[M_{16}Ni_{24}(CO)_{40}]^{4-}$ it is capped by four Ni₆(CO)₁₀ units. Our DFT calculations showed that in both cases, the capping entities are a full part of the superatom entity, where it appears that the free (uncapped) $[M_{16}]^{4-}$ core must be capped for further stabilization. It follows that the Ni₆(CO)₁₀ units in $[M_{16}Ni_{24}(CO)_{40}]^{4-}$ should not be considered as external ligands as their bonding with the $[M_{16}]^{4-}$ core is mainly associated with a delocalization of the 20 jellium electrons onto the Ni atoms. Thus, the $[M_{16}Ni_{24}(CO)_{40}]^{4-}$ species can be seen as the solution version of tetrahedral M_{20} clusters, encouraging experimental efforts to further develop the chemistry of such complexes as M(111) finite surface section structures, with M = Ag and Au and, particularly promising, with M = Cu. Furthermore, optical properties were simulated by TD-DFT to assist future experimental characterization.

Following the general idea of an unstable $[M_{16}]^{4-}$ (M = group 11 metal) tetrahedral unit, in the next part we have tried to find ways to stabilize it by various (often combined) ways: Substituting some of the group 11 atoms by other metals, encapsulating a supplementary atom at the center of the cluster, reducing the electron count from 20 to 18. Our DFT results indicate that M₁₆ tetrahedral group 11 core are unlikely to exist when bearing 20-*je*. In addition to the large anionic charge required by this electron count, the intrinsic antibonding nature of the 2S HOMO makes this electron count particularly unfavorable. There are two possibilities to avoid this situation in keeping the T_d symmetry. One is to reduce the electron count to 18-*je*, which is also a "magic" superatomic electron number. The second one for the 20-*je* species is to stabilize its 2S HOMO in adding a supplementary AO of a_1 symmetry by incorporating an additional atom at the center of the cage.

In Chapter 6, we investigate the possibility of doping Pyykkö's famous icosahedral $[W@Au_{12}]$ cluster by adding supplementary 0-electron Pt atoms. DFT calculations on the isoelectronic (18 jellium electrons) models $[W@Au_{12}Pt_n]$ (n = 0-4) indicate that the doped clusters with n = 1 and n = 4 are the most stable, in particular with respect to oxidation. The symmetry lowering away from the icosahedral symmetry caused by doping induces a sizable energy splitting of the frontiers orbitals, which in turn modify the optical properties of the calculated clusters, as observed from the TD-DFT-calculated optical properties. The simulated absorption spectra show an interesting broadening effect of the absorption peaks, which appears as a useful approach for further design of broad black-absorbers. In addition,

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the variation of expected catalytic sites along the series is accounted through the surface representation of the molecular electrostatic potential.

The last chapter concerns a very recently characterized family of organometallic clusters. These compounds are constituted of Zn and Cu metals, describing a trigonal bipyramidal cluster which is protected by five Cp* ligands. Using the classical Wade-Mingos electron counting rules, these species have only one skeletal bonding pair, whereas six are expected for such compounds to be stable. In fact our DFT calculations have shown that these compounds can be regarded as being intermediates between highly electron deficient clusters (one skeletal electron pair) and regular six-electron pairs systems if the participation to the bonding of some of the 3d(Cu) electrons is considered. Such participation is generally discarded in the classical Wade-Mingos approach, because it is negligible. In our case, this participation is significant, although not very strong. Moreover, the dispersion forces existing between the Cp* ligands bring additional stabilization to the whole architecture.

Résumé

Les travaux décrits dans ce mémoire portent sur le calcul de la structure électronique de clusters homo- ou hétéronucléaires de métaux du groupe 11, afin d'en interpréter leur stabilité, leur structure et éventuellement leurs propriétés. Nous nous sommes tout d'abord intéressés au fait que, contrairement à leurs homologues de l'or et de l'argent, les superatomes de cuivre sont très rares. Nos calculs montrent que ces derniers sont plus stables que les superatomes d'argent. Néanmoins, les méthodes de synthèse de superatomes par réduction de complexes de Cu(I) par le borohydrure conduisent préférentiellement à la formation de polyhydrures de Cu(I) en raison de leur grande stabilité. Nous nous sommes de plus intéressés à la stabilité de clusters contenant un cœur tétraédrique M₁₆, analogue à celui contenu dans le cluster emblématique [Au₂₀]. Notre étude des clusters organométalliques à 20 électrons $[M_{16}Ni_{24}(CO)_{40}]^{4-}$ (M = groupe 11) indiquent que les quatre entités périphériques $Ni_{6}(CO)_{10}$ font partie intégrante du superatome, suggérant que $[M_{16}]^{4-}$ n'est pas viable. Des calculs sur plusieurs séries de systèmes homo- ou hétéro-nucléaires nus proposent de contourner cet écueil soit en réduisant le nombre d'électrons à 18, soit en incorporant un élément encapsulé au centre de l'entité tétraédrique. Dans une autre étude, nous avons exploré la possibilité de dopage du cluster icosaèdrique à 18 électrons [WAu12] par des atomes de platine (donneurs de 0 électron), soit $[WAu_{12}Pt_x]$ (x = 1-4). Le calcul indique que certains isomères sont viables et présentent un large spectre d'absorption UV-vis leur conférant des applications potentielles. Enfin, nous avons étudié la structure électronique de clusters organométalliques apparemment très déficitaires en électrons, [Cu₃Zn₄Cp*₅] et $[Cu_2Zn_5Cp^*_5]^+$ et montré que ce déficit n'est aussi important qu'il n'apparaît.

Abstract

The work described in this manuscript concerns electronic structure calculations of homo- and hetero-nuclear clusters made of group 11 metals, in order to rationalize their stability, structure and in some cases properties. We have first looked at the fact that copper superatoms are very scarce, contrarily to their gold and silver counterparts. Our calculations indicate that copper superatoms are more stable than silver superatoms. However, the synthetic process based on the reduction of Cu(I) complexes bv borohydride leads preferentially to the formation of very stable Cu(I) polyhydrides. On the other hand, we have looked at the stability of clusters containing a tetrahedral M₁₆ core similar to the one contained in the $[Au_{20}]$ cluster. emblematic Our investigation of the 20-electron organometallic clusters [M₁₆Ni₂₄(CO)₄₀]⁴⁻ (M = group 11) showed that the four peripheral Ni₆(CO)₁₀ units are full part of the superatom entity, suggesting that the $[M_{16}]^{4-}$ entity is not viable. Calculations on several homo- and hetero-nuclear series of bare species indicate that this instability can be avoided either in reducing the electron count to 18, or in incorporating a supplementary element in cluster center. In another investigation, we explored the possibility of doping the icosahedral 18electron [WAu₁₂] cluster by 0-electron donor platinum atoms, namely [WAu₁₂Pt_x] (x = 1-4). Calculations indicate that some isomers are stable and have a large spectrum of UV-vis absorption, providing them potential applications. Finally, we have investigated the electronic structure of organometallic clusters, [Cu₃Zn₄Cp*₅] and $[Cu_2Zn_5Cp_5]^+$, which are apparently extremely electron-deficient and showed that this deficiency is not as large as it appears.