Received: 20 February 2018 | Revised: 20 April 2018 | Accepted: 7 May 2018
DOI: 10.1002/qua.25675

WILEY International Journal of QUANTUM CHEMISTRY

REVIEW

Noncovalent interactions in inorganic supramolecular chemistry based in heavy metals. Quantum chemistry point of view

Lorena Barrientos[1] | Sebatian Miranda-Rojas[2] | Fernando Mendizabal[3]

[1]Facultad de Química, Centro de Investigación en Nanotecnología y Materiales Avanzados CIEN-UC, Pontificia Universidad Católica de Chile, Vicuña Mackenna 4860, Macul, Santiago de Chile, Chile

[2]Departamento de Ciencias Químicas, Facultad de Ciencias Exactas, Universidad Andres Bello, Avenida República 275, Santiago, Chile

[3]Departamento de Química, Facultad de Ciencias, Universidad de Chile, Casilla 653, Santiago, Chile

Correspondence
Fernando Mendizabal, Departamento de Química, Facultad de Ciencias, Universidad de Chile, Casilla 653, Santiago, Chile.
Email: hagua@uchile.cl

Funding information
Fondo Nacional de Desarrollo Científico y Tecnológico, Grant/Award Numbers: 1020141, 1060044, 1100162, 1140503, 1180158

Abstract

Complexity is a concept that is being considered in chemistry as it has shown potential to reveal interesting phenomena. Thus, it is possible to study chemical phenomena in a new approach called systems chemistry. The systems chemistry has an organization and function, which are regulated by the interactions among its components. At the simplest level, noncovalent interactions between molecules can lead to the emergence of large structures. Consequently, it is possible to go from the molecular to the supramolecular systems chemistry, which aims to develop chemical systems highly complex through intra- and intermolecular forces. Proper use of the interactions previously mentioned allow a glimpse of supramolecular system chemistry in many tasks such as structural properties reflecting certain behaviors in the chemistry of materials, for example, electrical and optical, processes of molecular recognition and among others. In the last time, within this area, inorganic supramolecular systems chemistry has been developed. Those systems have a structural orientation which is defined by certain forces that predominate in the associations among molecules. It is possible to recognize these forces as hydrogen bonding, π-π stacking, halogen bonding, electrostatic, hydrophobic, charge transfer, metal coordination, and metallophilic interactions. The presence of these forces in supramolecular system yields certain properties such as light absorption and luminescence. The quantum theoretical modeling plays an important role in the designing of the supramolecular system. The goal is to apply supramolecular principles in order to understand the associated forces in many inorganic molecules that include heavy metals for instance gold, platinum, and mercury. Relevant systems will be studied in detail, considering functional aspects such as enhanced coordination of functionalized molecular self-assembly, electronic and optoelectronic properties.

KEYWORDS

density functional theory, dispersion term, Post-Hartree-Fock, van der Waals forces
Grimme´s dispersion (D3)

1 | INTRODUCTION

The macroscopic and microscopic worlds that surround us are a complex systems. In daily life, each of us experiences this feeling of complexity: the Internet, the organization of cities, society, public transport, the human body, and countless of other good examples.[1,2] Thus, the word complexity depends on the context in which it is applied. Regardless of the context, *"the complex systems are more than just complicated; their complexity gives rise to many unique properties,"* as has been expressed by K. Mainzer.[3] These systems, built by the interactions of different components, generate a property that cannot emerge from the system's components acting in isolation.[4,5]

The research of complexity has been well developed in several areas of science such as mathematics, transport, communications, and so on.[1,2]. Since 1997, chemistry has started considering the research of complexity at the molecular scale, as it has shown potential to reveal interesting phenomena.[4,5] Consequently, nowadays it is possible to study chemical phenomena in a new approach called *systems chemistry*. Furthermore, there are three main characteristics of systems chemistry. First, its evolution is sensitive to the initial conditions. Second, the number of independent interacting components is large. Third, there are multiple pathways along which the systems can evolve.[6] Chemists have currently evolved from the manipulation of individual molecules to the description and manipulation of systems of molecules, giving origin to some fields such as the chemistry of materials, supramolecular chemistry, and nanochemistry. These emerging areas are related to other sciences such as physics, biology, biophysics, biotechnology, and materials science.[7,8] Moreover, with the aid of modeling, computational, and theoretical tools, the understanding of the behavior of systems chemistry is constantly increasing. Therefore, chemistry is gradually shifting from a reductionist approach to systems chemistry, studies that involve multiple variables simultaneously. Despite that research in this area is currently in its infancy, at present it is possible to recognize some examples in dynamic combinatorial, oscillating reactions, heterogeneous catalysis, atmospheric and environmental chemistry, and self-assembling systems.[5]

Systems chemistry has an organization and function which are regulated by the interactions between its components. As an example, at the simplest level, noncovalent interactions between molecules can lead to the emergence of large structures resulting in self-assembly processes.[5]. In the literature, we can find the description of how the structure obtained depends on the constituent molecules. This is the ability of chemists to design and create new molecules by using building block to achieve complicated talks. Extending this creativity from the isolated molecules to molecular networks give rise to new molecular systems with unique and exciting properties, which are absent in the isolated building blocks. A field where we can find these concepts applied corresponds to supramolecular chemistry, which focuses on noncovalent interactions between the constituent subunits that form the target complex chemical system.[6–8]

Supramolecular chemistry has been defined by the Nobel Prize in chemistry J.M. Lehn as "*Intermolecular chemistry, focusing on the structure and function of the entities formed by the association of two or more chemical species.*"[9] Supramolecular chemistry has provoked a substantial shift in chemistry from its interest in the molecule (atoms and bonds that form them) to focus on the association between the molecules or intramolecular interactions within a molecule.[10] The intra- and intermolecular term is a synonym of noncovalent. Then, the expression "noncovalent" implies the association type between two or more molecules (or certain regions within a molecule) that is not explained by the traditional chemical bond concept, for example, sigma bonds with two electrons.[11,12] Since most noncovalent interactions formed are relatively weak, they break without significant activation barriers; as a consequence, many supramolecular systems are under thermodynamic control.[6]

Noncovalent intra- and intermolecular interactions are characterized by acting at long distances, between 200 pm and 400 pm, as it has been expressed by A. Stone.[13] Thus, orbital overlapping is unnecessary.[10–12] The forces underlying the attraction among the subsystems are related to the electrical properties of the molecules that are associated. Noncovalent interactions originate from interactions between permanent multipoles, between a permanent multipole and an induced multipole, and last an instant multipole and an induced multipole.[14] The respective terms that contribute to the interaction energy are called electrostatic, inductive, repulsive Pauli-exchange and dispersion.[15] The total stabilization energy when molecules associate with themselves to form a supramolecular structure is between 1 and 100 kJ/mol per contact, considerably less than the energy of a covalent bond (400 kJ/mol)[16] (see Figure 1). Therefore, the description and study of the noncovalent interactions require precise methods of quantum chemistry that include the correlation and dispersion energies.

From this point of view, supramolecular chemistry offers applications in different fields such as medicinal chemistry and host-guest chemistry, catalysis, molecular electronics, self-assembly molecular channels, chemical sensors, among others.[17] The noncovalent interactions that can participate in the formation and stabilization of these supramolecular systems had been identified as hydrogen bonding, π-π stacking, electrostatic, hydrophobic, charge transfer, metal coordination, halogen bonding and metallophilic interactions.[18–21] This has led to the synthesis of supramolecular structures of different sizes, shapes, and functionalities. Another important aspect that must be considered is that when a pair of noncovalent interactions strengthen each other, it is called *cooperative*,[11] while when they weaken each other they are defined as operating in an *anticooperative* manner. A.S. Mahadevi and G.N. Sastry have well defined cooperativity as "*the sum of at least two interactions is larger than the*

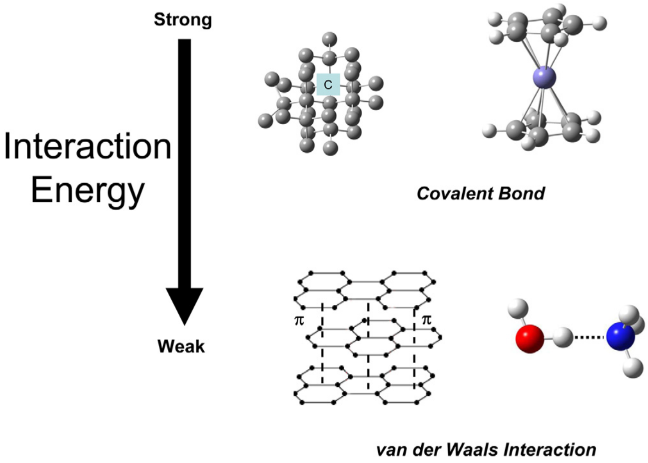

FIGURE 1 Schematic representations of the constituent materials with covalent and noncovalent networks

simple addition of the individual interactions."[11] Thus, the terms cooperative and anticooperative have different origins and meanings in different fields.

Within this broad field, we are interested in evaluating the ability of heavy metals, namely gold, platinum, mercury, and thallium for the formation of stable self-assembly and inorganic complexes.[22–25] Here, we will apply them in the context of supramolecular systems chemistry. As well as expressed by V. W.-W. Yam: *"to incorporate these attributes into the design and rational manufacture of supramolecular entities, it is necessary to understand the supramolecular forces and energies for the inorganic compounds of interest.*"[23] The understanding of these systems comes from the observation of structures and patterns, coupled with the theory and calculation of the energies of the intermolecular interactions and their rationalization.[26–30] Data on molecular structures and their interactions come from their crystalline phase. In this regard, our goal is to advance in the understanding of the supramolecular interactions of inorganic compounds studying at the theoretical level complexes that deployed such arrangements within the framework of systems chemistry.

2 | QUANTUM MECHANICS CALCULATIONS

2.1 | Interaction energy

This perspective involves the computational description of complex systems and properties that are determined by the electronic structure. High-level quantum chemistry calculations are performed using post-Hartree-Fock and DFT methods.[31–39] The specific level of calculation for a study will be chosen as a function of the system. The results of all the calculations made are compared with available experimental data (structure and spectroscopic information) and/or high-level quantum chemical calculations. The Turbomole version 7[40] and Gaussian[41] version 98 and 09 packages are used for the calculations. The simplest ab initio approaches considering electron correlation effects are the second-order Møller–Plesset perturbation theory (MP2) and the approximate of the Coupled-Cluster Single, Double and Triple (CCSDT) model.[31–33] In several cases as it will be pointed out bellow, ground-state calculations were performed at the MP2 or spin-component-scaled (SCS)-MP2 levels.[42] Also, density functional theory (DFT) calculations are used in the optimization of the ground-state molecular structures. PBE and TPSS have been used in the study of weak interactions.[43] These are the best functionals available without parameters fitted to experimental data. However, none of the existing functionals are optimal for evaluating the noncovalent interactions. Therefore, Grimme's dispersion correction will be used to incorporate a proper description of the weak forces when using those functionals, in what is nowadays known as the DFT-D3 level.[44,45]

The interaction energy (ΔE_{int}) for the systems under study is obtained with counterpoise correction for the basis-set superposition error (BSSE).[46,47] We will also use the local approximation at the post-Hartree-Fock and DFT levels to decompose the interaction energy (supermolecule approach). From the latter method, we have an idea of the origin of the dominant terms in the interaction between molecular units which are responsible for the final supramolecular structure. The magnitude of such interaction energy can be expressed as the sum of two energy terms: Hartree-Fock (HF) and electronic correlation (corr).[47,48] The electronic correlation term of the energy ΔE(corr) incorporates the stabilization due to weak interactions, and their removal is source of error. The effect of electronic correlation can be invoked at different post-Hartree-Fock levels (MP2, MP4, CCSD, CCSD(T)).[38,49,50] The most widely used option is the second-order Moller–Plesset (MP2).[49] A higher level of theory is Coupled Clusters (CC) methods at the CCSD and CCSD(T) levels. The MP2 method is applicable to extended complexes, although it is known that it exaggerates the interactions, but gives a good indication of their existence.[51,52] More precise post-Hartee-Fock methods are the SCS-MP2[53,54] and CCSD(T). The SCS-MP2 is considered as an accurate and efficient tool for incorporating electronic correlation for the study of large systems at a low computational cost.[54] As Professor Pekka Pyykkö said: "thus justifying SCS-MP2 as 'poor man's CCSD(T)'." [55]

On the other hand, until recently calculations on DFT for the description of weak attractions were not adequate because the interaction energy near the van der Waals minimum was unreliable. The main reason was related to the fact that the specific form of the correlation energy (virtual double-dipole excitations, leading to an R^{-6} power law) was not properly described.[56] This situation has been changing in recent years due to several attempts to incorporate a dispersion term by different means. As stated above, Grimme's group has been one of the first to succeed, including a correction to the DFT total energy.[35,42] They have obtained results comparable to the MP2 level. Other theoretical results in the literature at the DFT level were obtained using the SAPT (symmetry-adapted perturbation theory) method.[57] A few years ago, new methods were created incorporating the effect of dispersion to describe adequately the weak interactions (DFT-SAM, LC-ωPBE-XDM, M05-2X, M06-2X, etc).[58–61]

2.2 | Excitation and luminescence properties

DFT studies on electronically excited states can be performed using the linear-response time-dependent density functional theory (TDDFT) approach. The TDDFT calculations do not evaluate the spin-orbit splitting, and the values are averaged. The TDDFT approach provides an alternative to computationally demanding multireference configuration methods in the study of excited states. However, the DFT potential of most functionals has an incorrect asymptotic behavior at long distances implying that charge-transfer states become too low in energy.[62,63] The shape of the long-range DFT potential can be partly corrected by using hybrid and range-separated functionals.[64,65] At present, this has been overcame by the development of novel functionals with a physically better long-range potential description.

2.3 | Pseudopotentials

In the systems proposed, there are heavy atoms such as Pt, Au, Hg, and Tl. Thus, the relativistic effects are important for a proper description and must be taken into account. These effects arise when considering the speed of light as a constant quantity. These effects start to became relevant from the middle of the periodic table (z > 55), as it explains many anomalies presented by these elements.[26] From the viewpoint of chemistry, relativistic effects are manifested in a splitting of the orbital, generating spin-orbital effect on the shell: p ($p_{1/2}$, $p_{3/2}$), d ($d_{5/2}$, $d_{3/2}$) yf ($f_{7/2}$, $f_{5/2}$).[66] As a consequence of these phenomena, some properties are changed such as bond distances and orbital energies. Also, it affects the ionization energy, electronic affinity, electronegativity and polarizability.[49] These properties are very important when studying the reactivity and interaction of a system. From a quantum mechanical point of view, the Dirac equation provides a correct treatment of relativistic effects.[26] However, as all these variables make the calculation very complex for systems, an alternative and less expensive approach to replace the orbital wave functions of core electrons by an effective internal potential. This substantially reduces the number of equations to just calculate the orbitals were functions of the valence electrons. A way to implement this approach and reduce the numbers of electrons maintaining the accuracy at the ab initio level is to use the technique of pseudopotentials (PP). It implicitly includes the quasi-relativistic and relativistic effects at scalar levels,[67,68] which is very important for the case of heavy metals (Au, Pt, Hg, Tl). Thereby, the use of pseudopotentials maintains the accuracy of ab initio calculations and allow including the spin-orbital effect in the description of electronic structure. PPs of the Stuttgart/Cologne type[69] will be used for heavy metals (Au, Pt, Hg, Tl). Two *f*-type and *3f2g* polarization functions will be used on metals. Light atoms like C, N, O, F, S, Se, and others are treated with PPs and/or through the augmented correlation-consistent valence-triple-zeta (aug-cc-pVTZ) basis sets.[70]

3 | DISPERSION INTERACTIONS IN MATERIALS BASED ON HEAVY METALS

In the literature, it is possible to find an increasing interest in the supramolecular chemistry of organic molecules.[71,72] However, the self-assemblies of inorganic complexes have been relatively less explored than those related to the organic framework. In particular, inorganic molecular assemblies based on d^8, d^{10}, and s^2 transition metal complex systems represent an important class, based on the exotic geometries obtained from various types of noncovalent interactions.[22–25] The versatility of the coordination modes of the heavy metals has enabled wide structure and topology variations of the complexes. The self-assembly of molecules with gold atoms involves inter- and/or intramolecular interactions that

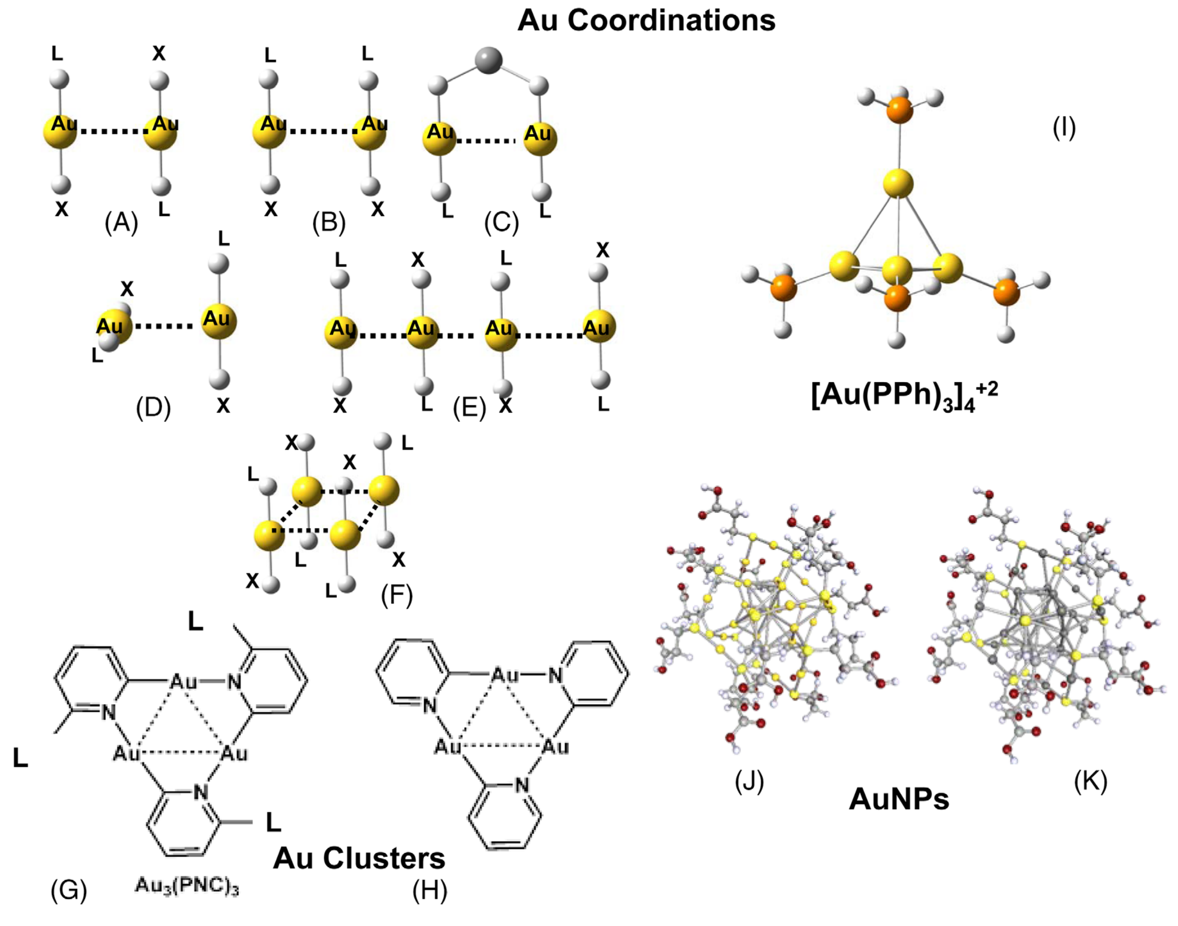

FIGURE 2 Intra- and Intermolecular interactions of different supramolecular inorganic systems: (a-f) dimers, oligomers, chains, sheets, (g-i) clusters, and (j-k) nanoparticles

lead to the formation of dimers, oligomers, chains, sheets, clusters, and nanoparticles (see Figure 2), allowing the generation of systems of high complexity.[73–86] In addition to the aforementioned noncovalent interactions, metal–metal and representative-atom-metal interactions in the complexes have also been found to be associated with the direct formation of this type of self-assemblies.[87] Moreover, this wide range of structures has made available a diversity of excited states that have enriched these complexes with interesting electronic and luminescence properties.[23,88]

It is well established that there are metal-metal attractive interactions between cations with d^8, d^{10}, and s^2 configurations at both intra- and intermolecular levels.[26] This phenomenon is known as metallophilic interaction, and in the particular case of gold as "aurophilic interaction."[51,52,66,89–96] These closed-shell interactions are estimated to be energetically similar to hydrogen bonds (20–50 kJ/mol) in the case of gold(I) and to be weaker for other metals such as silver(I), copper(I), thallium(I), mercury(II), and platinum(II).[22–25,97–100] The aurophilic Au—Au interaction has been determined experimentally via solid state X-ray diffraction[101–107] and NMR measurements.[108,109] From a theoretical point of view, the aurophilic attraction has been understood as the contribution of two terms to the equilibrium distance: dispersion and ionic.[89] The relativistic effects in the metallophilic interaction contribute among 20% and 30% to the interaction energy associated to this intermolecular interaction.[66] Moreover, a significant number of studies have discussed the metallophilic interactions coexisting with hydrogen bonding, halogen bonding, M–π or π-π attractions, all of which are able to participate in the process of generating supramolecular systems chemistry.[110–115] The experimental results in many studies are explained by theoretical models described at the Post-Hartree-Fock (MP2, SCS-MP2, CCSD(T)) and DFT-D3 levels. In the case of bigger systems, the DFT-D3 method is often used.

From a theoretical standpoint, the mechanism behind the metallophilic interaction is a dispersion-type (van der Waals) contribution, with the additional allowance for virtual charge-transfer terms.[89,113–115] The dispersion interaction is recovered in the electronic correlation. However, it has been stated that all dispersions are electronic correlations, but not all electronic correlations are dispersions.[20] Furthermore, not all the localized orbitals involved are purely metal orbitals, as the ligands have an important contribution. There is a significant amount of experimental and theoretical studies containing interactions with centers of gold and other heavy metal complexes and clusters reported in the literature.[116,117] In this work, we will describe complexes depending on the type of interaction: intra- or intermolecular. Due to a large number of structures reported in the literature, we decided to limit some systems that best represent the ideas described above of which we have been authors and co-authors during the last two decades. Some of these works have been produced together with the research groups of the Professors Pekka Pyykkö (University of Helsinki, Finland) and Antonio Laguna (University of Zaragoza, Spain).

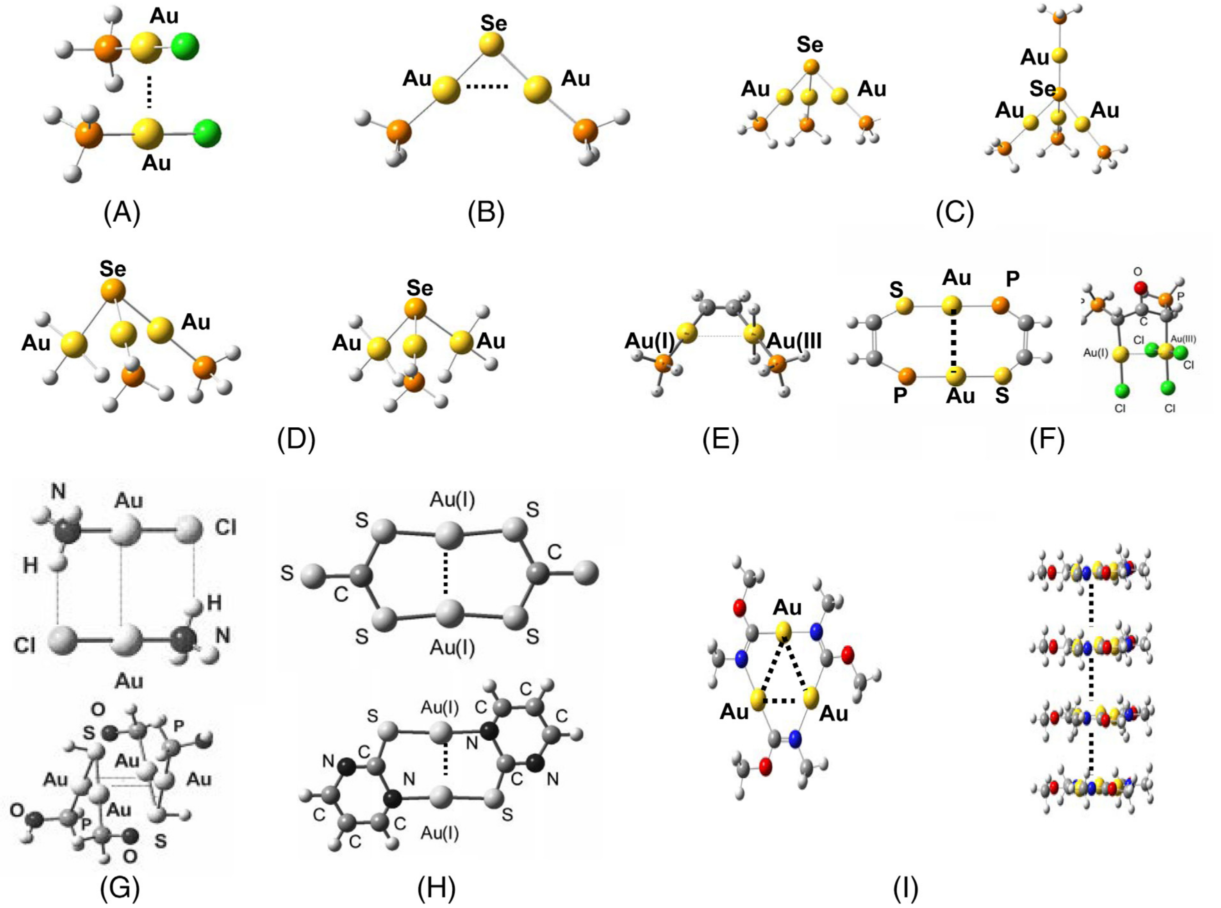

FIGURE 3 Aurophillic Interactions in complexes (a) $[ClAuPH_3]_2$, (b) $[S(AuPH_3]_2]$, (c) $[Se(AuPH_3)_n]^{(n-2)+}$ (n = 2-6), (d) $[Se(AuPH_3)_2\,(AuR_3)]$, $[Se(AuPH_3)(AuR_3)_2]^-$ (R = −H, $-CH_3$), (e) $[PH_3Au(I)C(L) = C(L)Au(III)(R)_2PH_3]$, (f) $[Au_2\,(HP(C_2H_2\text{-}S\text{-}2)_2)_2]$ and $[Au_2AuCl_3(CH(PH_3)_2CO)]$, (g) $[(AuNH_3Cl)_2]$ and $[H_2P(OH)AuPH_2(O)]_2$, (h) $[Au_2(CS_3)_2]^{-2}$ and $[Au_2(pym\text{-}2\text{-}S)_2]$ (pym = pyrimidethiolate), (i) $[Au_3(CH_3N = COCH_3)_3]_n$ (n = 1-4)

TABLE 1 Intermolecular distance Au-Au (pm) and interaction energy, $V(R_e)$, in kJ/mol for the $[AuClPH_3]_2$ model with counterpoise (CP) correction Basis set on gold is *3f2g*

System	Method	Au-Au	$V(R_e)$
$[AuClPH_3]_2$	MP2 [52]	304.4	−33.6
	SCS-MP2 [52]	323.1	−20.8
	CCSD(T) [52]	327.9	−19.9
	PBE [52]	347.4	−7.51
	TPSS [52]	348.3	−4.09
	B97D [52]	436.4	−1.12
	PBE-D3 [52]	334.2	−27.9
	TPSS-D3 [52]	329.9	−34.2
	B97D-D3 [52]	332.0	−35.1
	M06L [52]	319.9	−23.4
	M06 [52]	314.9	−27.0
	M06HF [52]	320.2	−22.8
	M062X [52]	328.3	−24.1
	M05 [52]	348.1	−10.8
	M052X [52]	317.5	−24.4
	PW91 [52]	325.2	−14.1
	CAM-B3LYP [52]	343.6	−6.68
	LC-ωPBE [52]	316.8	−21.9
	MP2 [115]	300.0	−37.0
	LMP2 [115]	303.0	−34.8
$[AuCl(PPh_3)]_2$	Exp. [52]	344.0	
$[AuCl(PMe_3)]_2$	Exp. [52]	333.8	
$[AuCl(PEt_3)]_2$	Exp. [52]	361.5	
$[AuCl(PMe_2Ph)]_2$	Exp. [52]	323.0	

3.1 | Aurophillic interactions

In the classic $[ClAuPH_3]_2$ dimer (see Figure 3A), the intermolecular aurophilic interaction has been studied using ab initio post-Hartree-Fock and DFT methodologies.[51,52] The post-Hartree-Fock methods provide results closer to the experimental data than DFT-based methods. Among the former methods, it is important to highlight the accuracy of the results obtained by the SCS-MP2 and CCSD(T) methods for the description of this

TABLE 2 Intramolecular Au-Au distance (pm) by the $[S(AuPH_3)_2]$ model. Basis set on gold is *2f*

System	Method	Au-Au	S-Au	Au-P	AuSAu°
$[S(AuPH_3)_2]$	MP2 [52]	290.2	228.6	227.5	78.8
	SCS-MP2 [52]	296.6	229.8	226.4	80.3
	CCSD(T) [52]	299.5	232.0	232.1	80.4
	PBE [52]	321.6	230.3	226.3	88.8
	TPSS [52]	310.4	230.9	226.9	88.5
	B97D [52]	330.4	231.7	227.5	90.9
	PBE-D3 [52]	326.6	230.4	226.1	90.3
	TPSS-D3 [52]	326.4	230.9	226.5	89.9
	B97D-D3 [52]	336.0	232.1	226.5	92.7
	M06L [52]	306.8	231.8	233.0	82.8
	M06 [52]	316.7	231.9	235.9	86.1
	M06HF [52]	332.5	229.2	218.5	93.0
	M062X [52]	333.7	231.8	228.6	92.1
	M05 [52]	320.4	232.6	236.2	87.0
	M052X [52]	330.1	230.4	227.7	91.5
	PW91 [52]	317.5	230.8	229.9	86.9
	CAM-B3LYP [52]	330.5	230.2	230.7	91.8
	LC-ωPBE [52]	318.7	228.4	228.2	88.5
$[S(AuPPh_3)_2]$	Exp. [52]	301.8	215.9	213.5	88.7

type of interaction. It was found that the aurophilic interaction is driven by the induction and dispersion terms. When DFT is used, the best results of geometry and interaction energy are obtained with the PW91 level. We found that the incorporation of PBE-D3, TPSS-D3, M06HF, M06L, M06 M062X, M052X, CAM-B3LYP, and LC-ωPBE provided results of similar accuracy as MP2, as shown in Table 1.

In order to describe the intramolecular auropphillic interaction, we have used the $[S(AuPH_3)_2]$ molecule (Figure 3B) as a model.[52] The post-Hartree-Fock results based on the Au-Au distance and Au-S-Au angle are in concordance with the experimental values used as reference[118] and to other theoretical results that have been published.[119,120] As seen in Table 2, MP2 overestimates the Au-Au and Au-S-Au stabilization reflected by the shorter distance and angle, while SCS-MP2 and CCSD (T) were very close to the crystal structure, remarking again the high accuracy achieved by these methods.

Also, intramolecular aurophillic interaction has been studied using the $[Se(AuPH_3)_n]^{(n-2)+}$ (n = 2–6) models at the HF and MP2 levels (Figure 3C).[121] There is a good agreement between experimental and theoretical geometries, since these models show unusual geometries with short gold-gold interactions. With the latter method, the gold-gold distances are close to 300 pm. Only theoretical calculations at the MP2 level are in agreement with experimental geometries. Other selenium compounds have been modeled to study the intramolecular interactions Au(I) and Au(III), d^{10}-d^8. The selected compounds were $[Se(AuPH_3)_2(AuR_3)]$, $[Se(AuPH_3)(AuR_3)_2]^-$ (R = -H, $-CH_3$) and $[\{Se(AuPH_3)\}_2\{Au(CH_3)_2\}_2]$ (Figure 3D).[122] The MP2 calculations were in good agreement with experimental geometries. Here the electronic correlation is reflected at the MP2 level, although this method overestimates the aurophillic interaction.[51]

At this level of the describe gold contacts, we have carried out an ab initio study designed to shed some light on the aurophilic attractions between Au(I) and Au(III) in the $[PH_3Au(I)C(L){=}C(L)Au(III)(R)_2PH_3]$ (where R = –H, $–CH_3$; L = –H, $–CH_3$) model (Figure 3E). Calculations carried out at the MP2 level revealed important facts such as the presence of an intramolecular aurophilic interaction in the cis-complexes that stabilizes them with respect to the trans-isomer.[123] Using models to study the intermolecular interaction between Au(I) and Au(III), we have been able to estimate an interaction energy between 21 and 25 kJ/mol at the MP2 level of calculation. Moreover, we have corroborated this type of interactions Au(I)-Au(III) in other models as $[Au_2(HP(C_2H_2\text{-}S\text{-}2)_2)_2]$ and $[Au_2AuCl_3(CH(PH_3)_2CO)]$ at the MP2 level (Figure 3F).[124] The Au(I)-Au(III) distance in the systems studied are in a range of 320 to 340 pm, greater than the Au(I)-Au(I) distances.

The experimental and theoretical work showed the coexistence of aurophilic interaction and hydrogen bonding (HB). These interactions participate as building forces in the supramolecular structures. We have studied both interactions in the model systems: $[(AuNH_3Cl)_2]$, $[(AuNH(CH_3)_2Cl)_2]$, $[\{Au_2(u\text{-}SH)(PH_2O)(PH_2OH)\}_2]$, $[H_2P(OH)AuCl]_2$ and $[H_2P(OH)AuPH_2(O)]_2$ at the HF and MP2 levels[112,114] (Figure 3G). It was determined that the aurophilic interaction has the same magnitude of a hydrogen bonding. HB increased its strength by the presence of an aurophilic contact. As shown in Table 3, both interactions produce a synergistic effect when they are present in the same system.

To conclude this section, we have explored the relationship of the electronic structure and spectroscopic properties of $[Au_2(CS_3)_2]^{-2}$, $[Au_2(pym\text{-}2\text{-}S)_2]$ (pym = pyrimidethiolate), $[Au_2(dpm)_2]^{+2}$ (dpm = bis(diphosphino)methane), $[Au(CN)_2]_n^{-n}$ (n = 1-3) and $[Au_3(CH_3N = COCH_3)_3]_n$ (n = 1-4), which were studied using DFT[125–127] (Figure 3H,I). The absorption spectrum of these binuclear gold(I) complexes $[Au_2(CS_3)_2]^{-2}$, $[Au_2(pym\text{-}2\text{-}S)_2]$ and $[Au_2(dpm)_2]^{+2}$ was calculated by single excitation time-dependent (TD) method at the B3LYP level.[125] All complexes showed a $^1(5d\sigma^* \rightarrow 6p\sigma)$ transition associated with a metal–metal charge transfer (MMCT), which is strongly interrelated with the gold–gold distance. Similar results are obtained for the clusters $[Au(CN)_2]_n^{-n}$ (n = 1-3) at the TD-B3LYP level, showing a $^1(5d\sigma^* \rightarrow 6p\sigma)$ transition associated with MMCT that is strongly interrelated with gold-gold contacts.[126] Finally, the $[Au_3(CH_3N = COCH_3)_3]_n$ (n = 1-4) were studied at the MP2, B3LYP and PBE.[127] In Figure 4 are depicted the MMCT for three complexes. Theoretical calculations at the MP2 level are in agreement with experimental geometries and aurophillic attraction, and to a lower extent with PBE. In all models, the values calculated by theoretical methods are in agreement with experimental range.

TABLE 3 Au-Au distances and hydrogen bonding (HB) geometries for complexes at the HF and MP2 levels. Distances in pm, interactions energies, $V(R_e)$, in kJ/mol. Donor (D) and acceptor (A) atoms refer to the HB

System	Method	Au-Au	D-A	H-A	AMMA°	$V(R_e)$
$[(AuNH_3Cl)_2]$ [112]	MP2	238.8	329.5	233.9	180°	−90.3
	HF	352.3	352.9	257.3	180°	−86.2
$[(AuNH(CH_3)_2Cl)_2]$ [112]	MP2	314.1	338.1	274.4	146.5°	−74.6
	HF	366.9	387.7	325.9	145.5°	−37.3
$[\{Au_2(u\text{-}SH)(PH_2O)(PH_2OH)\}_2]$	MP2	296.1	249.6	154.4	55.4°[a]	−273.9
	HF	327.8	256.9	165.2	51.7°[a]	−231.8
$[H_2P(OH)AuCl]_2$ [114]	MP2	310.3	314.4	218.5	180°	−93.6
	HF	348.2	344.5	249.1	180°	−54.8
$[H_2P(OH)AuPH_2(O)]_2$ [114]	MP2	316.8	269.5	181.6	180°	−110.7
	HF	353.4	301.0	219.8	180°	−67.9

[a] P-O—O-P.

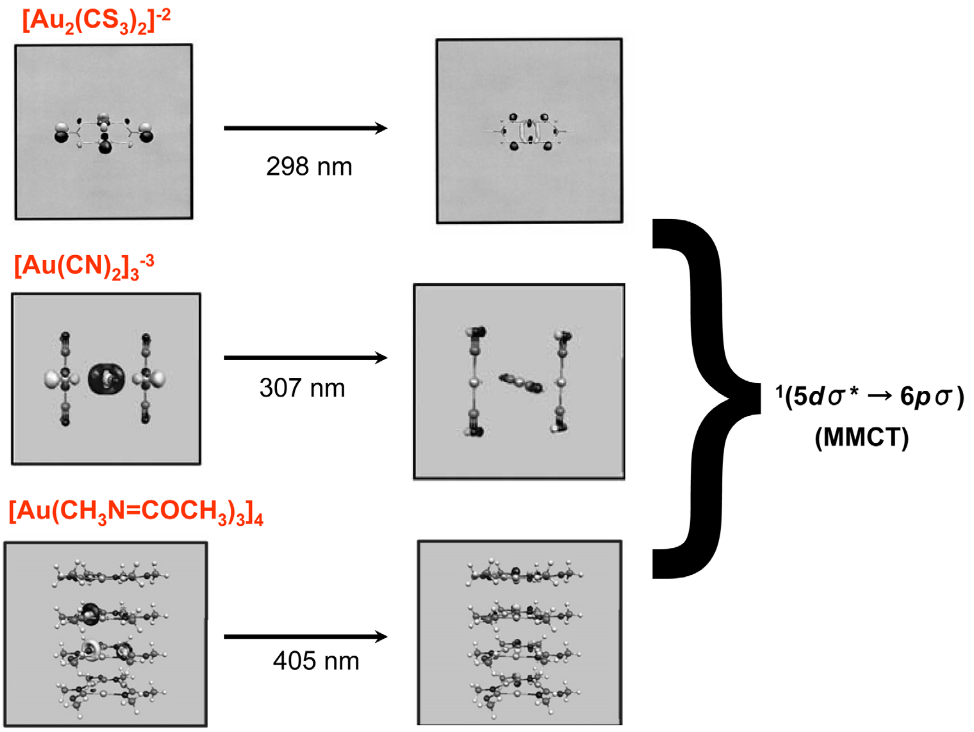

FIGURE 4 Principal electronic transition in the same complexes: $^1(5d\sigma^* \rightarrow 6p\sigma)$ metal–metal charge transfer (MMCT)

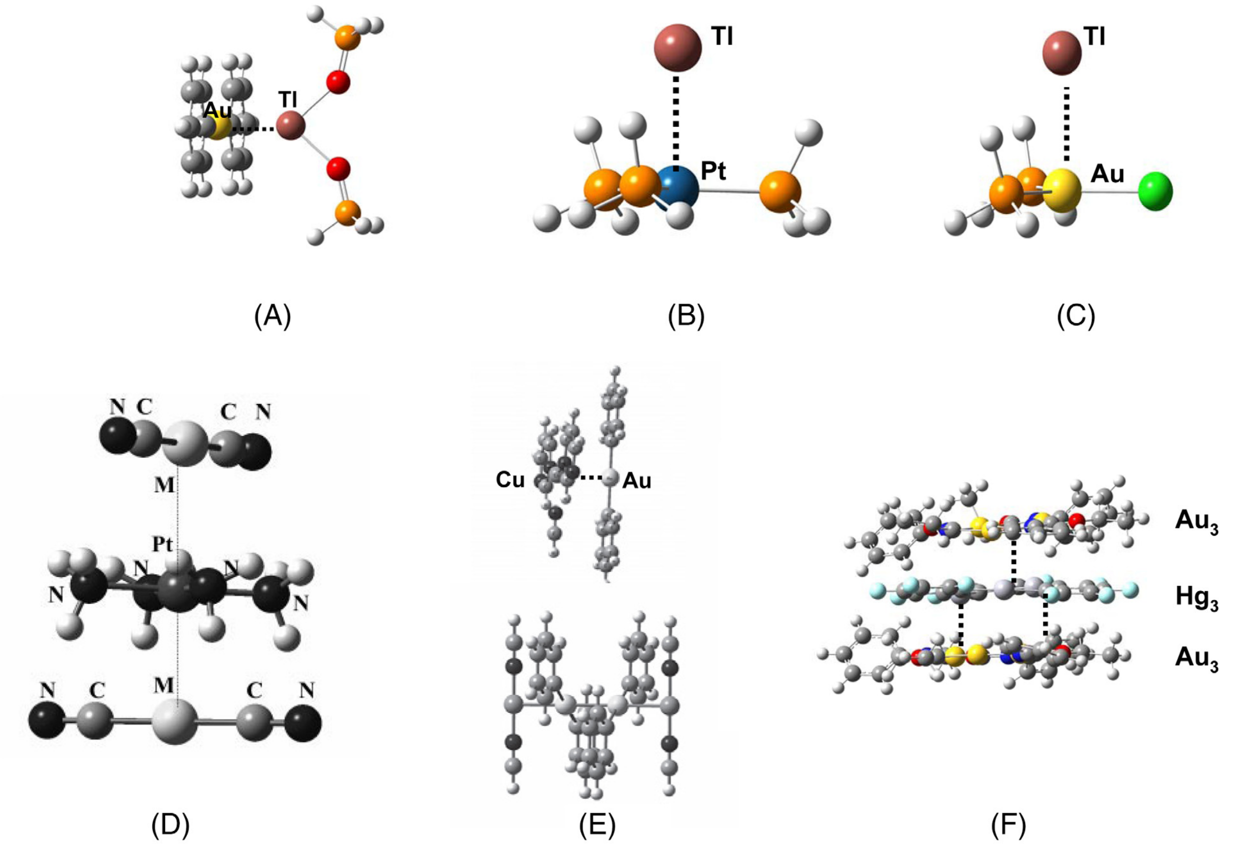

FIGURE 5 Metallaphillic interactions in systems (a) $[Au(C_6H_5)_2][Tl(OPH_3)_2]$, (b) $[Pt(PH_3)_3Tl]^+$, (c) $[AuCl(PH_3)_2]Tl^+$, (d) $[Pt(NH_3)_4][Au(CN)_2]_2$, (e) $[Au(C_6H_5)_2][Cu(py)_2(NCH)]$ and $[Cu(NCH)_2][Au(C_6H_5)_2]$–$[Cu(NCH)_2][Au(C_6H_5)_2]$, (f) $[Hg_3(o\text{-}C_6F_4)_3]$-$\{Au_3(\mu\text{-}C(OEt) = NC_6H_4CH_3)_3\}$

TABLE 4 Optimized M-M´ metallophillic interactions. Distance R_e in pm and interaction energy $V(R_e)$ in kJ/mol

System	Method	M-M´ (R_e)	$V(R_e)$
$[Au(C_6Cl_5)]_2[Tl(OPPh_3)]$ [97]	MP2(QR)[a]	302.8	−275.7
	HF(QR)	336.2	−227.4
	MP2(NR)[b]	313.1	−217.0
	HF(NR)	400.3	−159.5
$[Pt(PH_3)\text{-}Tl]^{+}$ [128]	HF	279.9	−134.1
	MP2	266.9	−202.6
	MP3	281.3	−136.1
	MP4	275.6	−205.5
	CCSD	279.2	−171.6
	CCSD(T)	277.3	−203.6
$[AuCl(PH_3)_2]\text{-}Tl^{+}$ [129]	HF	316.3	−36.8
	MP2	285.1	−97.7
	MP4	286.6	−96.6
	CCSD(T)	292.7	−80.8

[a] Quasi-relativistic (QR).
[b] Non-relativistic (NR).

3.2 | Metallophilic interactions

One of the first systems involving metallophilic interactions that we studied was the complex $[Au(C_6Cl_5)]_2[Tl(OPPh_3)]$ with a d^{10}-s^2 Au(I)-Tl(I) unsupported contact.[97,98] For this purpose, we used a reduced model of the type $[Au(C_6H_5)_2][Tl(OPH_3)_2]$ at the HF and MP2 levels (Figure 5A). Quasirelativistic (QR) and nonrelativistic (NR) calculations were performed to study the nature of the intermetallic Au(I)-Tl

TABLE 5 Optimized M-M´ distance, R_e, in pm and interaction energies ($V(R_e)$), in kJ/mol

System	Method	M-M´(R_e)	$V(R_e)$
$[Au(C_6H_5)_2]\cdots[Cu(py)_2(NCH)]$ [131]	MP2	259.1	−216.5
	HF	271.6	−189.2
$[Au(C_6H_5)_2]\cdots[Cu(NCH)_2]$ [131]	MP2	272.2	−348.8
	HF	311.5	−333.2
$[Cu(NCH)_2][Au(C_6H_5)_2]\cdots[Au(C_6H_5)_2][Cu(NCH)_2]$ [131]	MP2	274.0	−64.9
	HF	[a]	
$[Cu(NH_3)_2][AuH_2]\cdots[AuH_2][Cu(NH_3)_2]$ [131]	MP2	297.4	−2.6
	HF	[a]	
$[Cu(NH_3)_2][AuH_2]\cdots[Cu(NH_3)_2][AuH_2]$ [131]	MP2	296.6	−36.6
	HF	370.3	−23.3
$[AuH_2][Cu(NH_3)_2]\cdots[Cu(NH_3)_2][AuH_2]$ [131]	MP2	[a]	
	HF	[a]	
$[Hg_3(C_6F_4)_3]\cdot\{Au_3(\mu\text{-}C(OEt){=}NC_6H_4CH_3)_3\}$ [132]	HF	396.3	−8.4
	MP2	329.5	−265.5
	SCS-MP2	331.6	−118.2
	PBE	362.5	−26.6
	PBE-D3	336.9	−200.4
	TPSS	347.0	−17.2
	TPSS-D3	327.6	−251.4
$[Hg_3(C_6F_4)_3]\cdot\{Au_3(\mu\text{-}C(OEt){=}NC_6H_4CH_3)_3\}_2$ [132]	HF	406.9	−15.9
	MP2	325.4	−456.3
	SCS-MP2	330.5	−175.8
	PBE	363.5	−13.9
	PBE-D3	337.9	−381.6
	TPSS	347.2	−22.7
	TPSS-D3	328.5	−446.3

[a] No minimum.

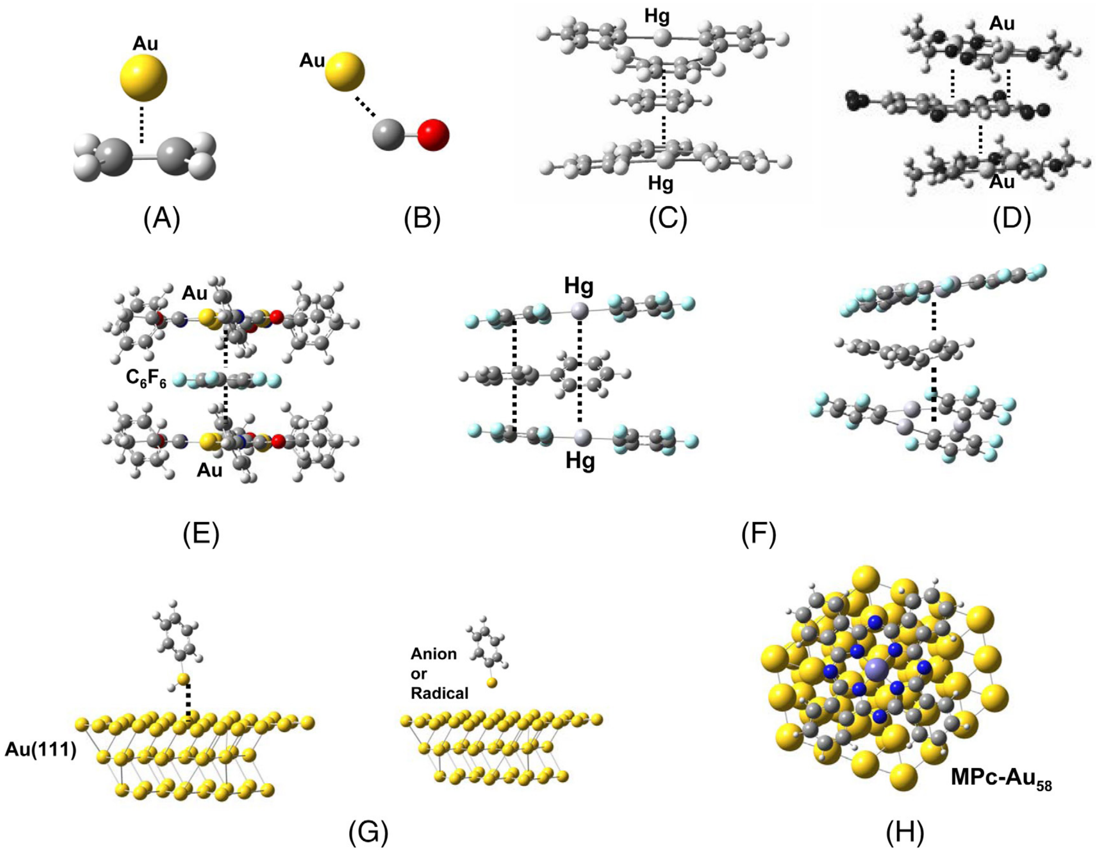

FIGURE 6 Interaction between molecule and heavy metal (a) Au(0)-CO, (b) Au(0)-Ethylene, (c) $[Hg_3(o\text{-}C_6F_4)_3]_n$ {benzene} (n = 1,2), (d) $\{Au_3(CH_3N = COCH_3)_3\}$n{2,4,7-trinitro-9-fluorenone} (n = 1,2), (e) $[Au_3(\mu\text{-}C(OEt) = NC_6H4CH_3)_3]_2\text{-}(C_6F_6)$, (f) $[Hg(C_6F_5)_2]_2$-{L}, $[Hg_3(o\text{-}C_6F_4)_3]_2${L} (L = naphthalene, biphenyl, fluorene), (g) thiophenols-gold(111) interaction, (h) MPc-Au$_{58}$ (M = Fe,Co)

(I) interactions, which were consistent with the presence of a high ionic contribution (80%) and dispersion-type (van der Waals) interaction with a charge-transfer contribution (20%) when relativistic effects were taken into account (see Table 4). The TD-B3LYP calculations are in agreement with the experimental excitation spectra for the complex and confirm the excitation behavior as a function of the Tl(I) geometrical environment.

To complement the about present studies, two additional complexes with d^{10}-s^2 interactions were analyzed by our group. These were $[Pt(PH_3)_3Tl]^+$ and $[AuCl(PH_3)_2]Tl^+$ complexes,[128,129] which were modeled by methods HF, MPn (*n* = 2-4), CCSD and CCSD(T) (see Figure 5B,C). We found that the changes in the geometry in both models are sensitive to the electron correlation energies. It is interesting to note in Table 4, the obtained interaction energy differences in the equilibrium distance (Pt-Tl and Au-Tl) range from 134 a 205 kJ/mol and 37 to 98 kJ/mol, respectively. In both models was verified that mainly the charge-induced dipole and dispersion terms predominate, being the charge-induced dipole term (R^{-4}) the principal contribution to the stability of the complexes. The dispersion interaction (R^{-6}) is smaller, but not negligible.

Also, we have studied other heavy metals (Ag(I), Pt(II), Pd(II), etc.) containing heterometallic systems in which short closed-shell metal–metal interactions of the type d^{10}-d^8 and d^8-d^8. The electronic structure and the spectroscopic properties of $[Pt(NH_3)_4][Au(CN)_2]_2$, $[Pt(NH_3)_4][Ag(CN)_2]_2$, $[Pt(CNCH_3)_4][Pt(CN)_4]$, and $[Pt(CNCH_3)_4][Pd(CN)_4]$ (see Figure 5D) were studied at the HF, MP2, B3LYP, and PBE levels.[130] In all the complexes, it was found that the nature of the intermetal interactions (metallophilicity) is consistent with the presence of a high-ionic contribution (90%) and a dispersion-type interaction (10%). The absorption spectra of these complexes were calculated by the single-excitation TD-DFT method at the HF, B3LYP, and PBE levels. The $[Pt(NH_3)_4][M(CN)_2]_2$ (M = Au, Ag) complexes showed a $^1(d\sigma^* \rightarrow p\sigma)$ transition associated with a metal–metal charge transfer. On the other hand, the $[Pt(CNCH_3)_4][M(CN)_4]$ (M = Pt, Pd) complexes showed a $^1(d\sigma^* \rightarrow \pi^*)$ transition associated with a metal-to-metal and ligand charge transfer (MMLCT). The values obtained theoretically are in concordance with the experimental range.

To conclude this section, we present the discussion of systems with the d^{10}-d^{10} type of interaction between Au(I) and Cu(I) or Hg(II) which we have described in different systems.[131] In this context, model compounds are normally used to study the metallophilic attraction between gold and copper atoms. Then, ab initio calculations on dimers and tetramers in different distributions of the simplified ligands were analyzed.[131] Table 5 summarizes the geometric parameters and interaction energies for these systems. We included reduced models of dimers and tetramers with the general formula: $[Au(C_6H_5)_2][Cu(py)_2(NCH)]$, $[Au(C_6H_5)_2][Cu(NCH)_2]$, $[AuX_2][Cu(NH_3)_2]$ (X = H,Cl), $[Cu(NCH)_2][Au(C_6H_5)_2]$–$[Cu(NCH)_2][Au(C_6H_5)_2]$, $[Cu(NH_3)_2][AuH_2]$–$[AuH_2][Cu(NH_3)_2]$, $[Cu(NH_3)_2][AuH_2]$–$[Cu(NH_3)_2][AuH_2]$ and $[AuH_2][Cu(NH_3)_2]$–$[Cu(NH_3)_2][AuH_2]$ (see Figure 5E). An attractive interaction is found for all models and there is a reasonable agreement between the experimental and theoretical geometries. Moreover, the electronic structure $[Hg_3(o\text{-}C_6F_4)_3]\{Au_3(\mu\text{-}C(OEt)=NC_6H_4CH_3)_3\}_n$ (*n* = 1, 2) adducts were studied at the HF, MP2, SCS-MP2, DFT and

TABLE 6 Optimized M-C interactions. Distance R_e in pm and interaction energy $V(R_e)$ in kJ/mol

Complex	Method	M-C (R_e)	$V(R_e)$
AuC_2H_4 [133]	MP2	248.3	−24.3
	MP3	295.8	−4.4
	MP4	273.4	−7.9
	CCSD	278.2	−8.0
	CCSD(T)	268.8	−13.1
Auco [134]	MP2	197.5	−26.4
	MP4	199.8	−24.3
	CCSD(T)	205.9	−13.5
$[Hg_3(C_6F_4)_3]$\{benzene\} [135]	HF	410.6	−12.8
	MP2	338.4	−46.6
	PBE	361.4	−29.2
$\{Au_3(CH_3N = COCH_3)_3\}$\{2,4,7-trinitro-9-fluorenone\} [136]	HF	401.0	−17.8
	MP2	292.3	−105.3
	PBE	304.0	−24.9
$[Au_3(\mu\text{-}C(OEt){=}NC_6H_4CH_3)_3]_2\text{-}(C_6F_6)$ [137]	B3LYP	376.0	−44.1
	PBE	360.9	−86.1
	TPSS	368.8	−69.0
	B3LYP-D3	345.0	−108.1
	PBE-D3	334.9	−147.8
	TPSS-D3	331.4	−164.8
$[Hg_3(C_6F_4)_3]_2$-(naphthalene) [132]	HF	359.1	−29.9
	MP2	339.5	−214.4
	SCS-MP2	340.1	−122.5
	PBE	344.1	−15.7
	PBE-D3	341.6	−105.7
	TPSS	396.7	−4.3
	TPSS-D3	344.6	−98.1
	B97	402.1	−3.8
	B97-D3	374.9	−70.9

DFT-D3 levels.[132] In the $[Hg_3(o\text{-}C_6F_4)_3]\{Au_3(\mu\text{-}C(OEt){=}NC_6H_4CH_3)_3\}_n$ (n = 1, 2) complexes, the metallophilic intermolecular interaction takes place between Hg–Au. Pair-wise energies of 85.7, 39.4, 78.1, and 57.9 kJ/mol were found at the MP2, SCS-MP2, TPSS-D3, and PBE-D3 levels using the $[Hg_3(o\text{-}C_6F_4)_3]\text{-}\{Au_3(\mu\text{-}C(OEt){=}NC_6H_4CH_3)_3\}$ model (see Figure 5F). The same trend is maintained for the $[Hg_3(o\text{-}C_6F_4)_3]\{Au_3(\mu\text{-}C(OEt){=}NC_6H_4CH_3)_3\}_2$ model: 73.4, 29.3, 70.6, and 61.3 kJ mol/1 by MP2, SCS-MP2, TPSS-D3, and PBE-D3, respectively.

TABLE 7 Interaction energies between Au_{42} and *para* substituted thio-, seleno- and tellurophenols.[138,139] The energies listed correspond to the total interaction energies (ΔE_{int}(TPSS-D3) and without the dispersion contribution (ΔE_{int}(TPSS). The percentage of dispersion term is included. Interaction energies in kJ/mol

Au_{42}-XH (X = S, Se, Te)	(ΔE_{int}(TPSS-D3)			(ΔE_{int}(TPSS)			% dispersion		
	S	Se	Te	S	Se	Te	S	Se	Te
$Au_{42}\text{-}XHC_6H_4NH_2$	−160.9	−185.2	−203.9	−34.7	−27.6	−38.5	78.6	85.1	81.1
$Au_{42}\text{-}XHC_6H_4OCH_3$	−179.7	−180.9	−200.2	−34.3	−21.7	−32.2	81.0	88.0	83.9
$Au_{42}\text{-}XHC_6H_4CH_3$	−162.2	−170.1	−190.6	−28.0	−14.6	−28.0	82.8	91.4	85.3
$Au_{42}\text{-}XHC_6H_5$	−147.6	−160.5	−185.6	−25.1	−14.6	−30.1	83.1	90.8	83.8
$Au_{42}\text{-}XHC_6H_4F$	−144.2	−142.9	−168.9	−22.2	−10.0	−25.5	84.7	93.0	84.9
$Au_{42}\text{-}XHC_6H_4Cl$	−122.1	−167.2	−191.4	−22.6	−11.7	−27.6	81.6	93.0	85.6
$Au_{42}\text{-}XHC_6H_4OCOCH_3$	−147.1	−146.3	−171.8	−20.1	−6.30	−22.6	86.2	95.7	86.9
$Au_{42}\text{-}XHC_6H_4CF_3$	−145.5	−143.8	−170.1	−15.5	−2.09	−19.6	89.4	98.5	88.5
$Au_{42}\text{-}XHC_6H_4CN$	−146.7	−158.4	−181.4	−17.1	−5.85	−20.1	88.2	96.3	88.9
$Au_{42}\text{-}XHC_6H_4NO_2$	−128.3	−157.2	−182.7	−14.6	−7.11	−23.8	88.7	95.5	87.0

TABLE 8 Adsorption Energies (ΔE_{int}) in kJ/mol between MPc and Au_n (M = Fe, Co; n = 26, 58) with counterpoise correction (CP) [140]

System	Method	ΔE_{int}
FePc-Au_{26}	PBE	−16.3
	PBE-D3	−265.4
	TPSS	−0.8
	TPSS-D3	−362.8
CoPc-Au_{26}	PBE	−15.0
	PBE-D3	−257.9
	TPSS	0.4
	TPSS-D3	−355.7
FePc-Au_{58}	PBE	−28.4
	PBE-D 3	−385.8
	TPSS	0.8
	TPSS-D3	−508.7
CoPc-Au_{58}	PBE	−15.5
	PBE-D3	−369.5
	TPSS	−5.4
	TPSS-D3	−504.9

3.3 | Interaction between molecule and heavy metal

The complexes of transition metal (M) with a small ligand, for example, hydrocarbons (ethylene) and CO, deserves considerable interest because of their relevance in bond activations and other catalytic processes. In this context, we have studied the dependence on the attraction Au(0)-CO and Au(0)-Ethylene from MP2 to CCSD(T) levels[133,134] (see Figure 6A,B). In both models, oscillations in the equilibrium Au-C distance are sensible to the electron correlation potential. Au-C distances and interaction energies in these complexes are summarized in Table 6. The dispersion interaction is the principal contribution to the stability, with a low contribution from the induction term.

We have continued studying the interaction of Metal-Carbon in inorganic systems of the type $[Hg_3(o\text{-}C_6F_4)_3]_n$\{benzene\} ($n$ = 1,2) and $\{Au_3(CH_3N = COCH_3)_3\}_n$\{2,4,7-trinitro-9-fluorenone\} (n = 1,2)[135,136] (Figure 6C,D). The electronic structure and spectroscopic properties were studied at the HF, MP2 and PBE levels. Secondary π-interactions (Metal-Carbon) were found to be the main contribution to short-range stability in the complexes that have been studied. Specifically, at the MP2 and PBE levels equilibrium Hg–C distances of 338.4 and 361.4 pm; and interaction energies of 46.6 and 29.2 kJ/mol were found with n = 1, respectively. Moreover, Au-C equilibrium distances of 292.3 and 304.0 pm and interaction energies of 105.3 and 24.9 kJ/mol were found at the MP2 and PBE with n = 1, respectively, and are evidenced in Table 6. Also, a specific mention corresponds to the study of the sandwich system $[Au_3(\mu\text{-}C(OEt)=NC_6H_4CH_3)_3]_2\text{-}(C_6F_6)$[137] (see Figure 6E). The electronic structure of this complex was studied at the B3LYP, PBE and TPSS levels including the Grimme's dispersion correction (D3) (Table 6). Weak π-interactions (Au-C_6F_6) were found to be the main contribution for short-range stability in the models, but only when the dispersion (D3) correction was invoked. Here, we have been able to verify the importance of dispersion in DFT calculations.

Other Metal-π systems which have been studied by our group are referred to $[Hg(C_6F_5)_2]_2$–\{L\}, $[Hg_3(o\text{-}C_6F_4)_3]_2$\{L\} (L = naphthalene, biphenyl, fluorene) adducts[132] (see Figure 6F). These were studied at the HF, MP2, SCS-MP2, DFT, and DFT-D3 levels. The intermolecular interactions among the fragments were analyzed using the levels of theory already proposed. The van der Waals interactions between mercury and arene (Hg–arene) were found to be the main short-range stability contribution in the complexes. At the MP2, SCS-MP2, and DFT-D3 levels, equilibrium Hg–C distances are between 360 and 310 pm. The pair-wise energies were found to be between 18.0 and 6.0 kJ/mol. The results for the complex are listed in Table 6 for $[Hg_3(o\text{-}C_6F_4)_3]_2$ \{naphthalene\}, which is representative for the rest of the systems studied.

In recent years, we have focused our attention in the interaction of inorganic molecules on a surface of gold representing the (111) crystal plane of an electrode. The interaction of thiol and thiolate containing molecules with gold (S–Au) has gained increasing interest because of its applications in molecular electronic devices and catalysis due to the high affinity of sulfur to gold surfaces.[138] The thiol moiety is deprotonated after binding to gold, hence, we have carried out a comparative study of the S–Au bond strength between several neutral and deprotonated aromatic–sulfur systems in their anionic and radical forms with a detailed description of the nature of this interaction. We have used the DFT methodology at the TPSS and TPSS-D3 levels. The study was performed by means of computational chemistry methods, using a cluster of 42 Au atoms as a model for the Au(111) surface that allowed us to provide new chemical insights to control the S–Au interfaces interaction strength (see Figure 6G).[138] Our results revealed that the thiophenols–gold interaction is mainly dispersive where the interaction energies range between 130 and 180 kJ/mol (see Table 7). The radical and anionic thiophenolates–gold interaction increases due to a strong charge transfer character, depicting interaction energies in the range of 210 to 230 kJ/mol and 260 to 385 kJ/mol, respectively. These results suggest that for the anionic thiophenolate the binding strength can be tailored according to the electron–donor capabilities of the ligand which in turn can be finely tuned by several substituents.

The results presented above set the grounds to study the analogous compounds of selenophenol and tellurophenol-derivatives with the Au(111) surface to gain information toward potential new gold-based materials.[139] The results are shown in Table 7. The result revealed that tellurium in the anionic state provides complexes of better thermodynamic stability by 50 kJ/mol, when compared with the strongest sulfur–gold complex, also in the anionic state. Furthermore, this indicates that the anionic ligand is probably the dominant state for both selenium and tellurium as observed previously for sulfur.[139] This is a very good example of the importance of the dispersion term in the control of the weak interactions. Finally, our main findings suggest that exchanging sulfur with selenium or tellurium involves an important increase of the interaction strength, thus, making these selenophenol and tellurophenol derivatives attractive for the development of new functional materials.

Other systems studied on a cluster of gold were the metallophthalocyanines (MPc). In this concern, here we present a quantum chemical study of the formation of supramolecular complexes based on the adsorption of MPcs on gold substrates and the effect of the substrate on their electronic properties. For this purpose, we used iron- (FePc) and cobalt-phalocyanines (CoPc). To model the gold surface we used two gold clusters of different sizes, given by Au_{26} and Au_{58} accounting for gold electrode Au(111) surface[140] (see Figure 6H). Thus, both electronic and binding strength features of the adsorption process between the complexes were analyzed in detail in order to gain a deeper description of the nature of the MPc-Au(111) formation, by using DFT calculations, at the PBE and TPSS levels including the dispersive (D3). The results are shown in Table 8. Our results show that dispersion forces rule the MPc-gold interaction, with binding strengths ranging between 255 and 640 kJ/mol.

The systems described in this section, as in the previous two, allowed highlight the importance of the dispersion effect. This interaction together with others, such as bonding hydrogen and π-π, generates a substantial number of complexes with unique properties.[141,142]

4 | CONCLUSION AND OUTLOOK

The systems chemistry study here showed the importance of the noncovalent interactions in the context of supramolecular chemistry. The principal interactions mentioned in the systems chemistry were aurophillic, metallophillic, and molecule-heavy metal. Those systems have a structural orientation which is defined by certain forces that predominate in the associations among molecules. The forces that predominate in the majority of the systems studied were dispersion term. The dispersion produces geometric structures through intra- and intermolecular interactions physical-chemistry properties reflecting certain behaviors in electrical and optic. Here, we have shown the importance of the quantum theoretical modeling in the design of the supramolecular system and as can understand the experimental results.

ACKNOWLEDGMENTS

This work was financially supported by Fondo Nacional de Desarrollo Científico y Tecnológico (Fondecyt) 1020141, 1060044, 1100162, 1140503 and 1180158.

ORCID

Fernando Mendizabal https://orcid.org/0000-0002-6912-8630

REFERENCES

[1] S. Arroca, B. Barak, *Computational Complexity. A Modern Approach*, Cambridge University Press, Cambridge **2009**.
[2] C. E. Maldonado, Ciencias de la Complejidad y Desarrollo Tecnológico, Revista Ignis, No. 4, **2009**.
[3] K. Mainzer, *Thinking in Complexity*, Ed. 3, Spinger-Verlang, New York **1997**.
[4] G. M. Whitesides, R. F. Ismagliov, *Science* **1999**, *284*, 89.
[5] R. F. Ludlow, S. Otto, *Chem. Soc. Rev.* **2008**, *37*, 101.
[6] E. Mattia, S. Otto, *Nat. Nanotechnol.* **2015**, *10*, 111.
[7] B. Grzybowski, S. Otto, D. Philp, *Chem. Commun.* **2014**, *50*, 14924.
[8] O. Miljanic, *Chem.* **2017**, *2*, 502.
[9] J.-M. Lehn, *Rep. Prog. Phys.* **2004**, *64*, 249.
[10] A. Otero de la Roza, G. DiLabio, *Non-covaleny Interactions in Quantum Chemistry and Physics*, Elsevier, Amsterdam, Netherlands **2017**.
[11] A. S. Mahadevi, G. N. Sastry, *Chem. Rev.* **2016**, *116*, 2775.
[12] J. Rezac, P. Hobza, *Chem. Rev.* **2016**, *116*, 5038.
[13] A. J. Stone, *The Theory of Intermolecular Forces*, Clarendon Press, Oxford **1996**.
[14] A. J. Misquita, *Intermolecular Interactions, Handbook of Computational Chemistry* (Ed: J. Leszcynski), Anna Kaczmarek-Kedziera, Tomasz Puzyn, Manthos G. Papadopoulos, Heribert Reis, Manoj K. Shukla (Co-Editors), Springer International Publishing, Switzerland **2017**, 295–235.
[15] M. Waller, S. Grimme, in *Handbook of Computational Chemistry* (Eds: J. Leszcynski et al.), Springer International Publishing, Switzerland **2017**, 593.
[16] D. Braga, F. Grepioni, *Acc. Chem. Res.* **2000**, *33*, 601.
[17] J.-M. Lehn, J. L. Atwood, J. E. D. Davies, D. D. MacNicol, G. Vögtle, *Comprehensive Supramolecular Chemistry*, Pergamon, Oxford **1996**.
[18] G. R. Desiraju, *J. Chem. Sci.* **2010**, *122*, 667.
[19] I. K. Mati, S. L. Cockroft, *Chem. Soc. Rev.* **2010**, *39*, 4195.
[20] P. Pyykkö, *Chem. Soc. Rev.* **2008**, *37*, 1967.

[21] L. C. Gilday, S. W. Robinson, T. A. Barendt, M. J. Langton, B. R. Mullaney, P. D. Beer, *Chem. Rev.* **2015**, *115*, 7118.

[22] K. M.-C. Wong, V. K-M. Au, V. W.-W. Yam, *Comprehensive Inorganic Chemistry II*, 2nd ed. (Eds: J. Reedijk, K. Poeppelmeier, K.), Elsevier, Oxford, UK **2013**, 59.

[23] V. W-W. Yam, V. K-M. Au, S. Y-L. Leung, *Chem. Rev.* **2015**, *115*, 7589.

[24] M-C. Tang, A. K-W. Chan, M-Y. Chan, V. W-W. Yam, *Top. Curr. Chem (Z)* **2016**, *46*, 374.

[25] J. M. López-de-Luzuriaga, M. Monge, M. E. Olmos. *Dalton Trans.* **2017**, *46*, 2046.

[26] P. Pyykkö, *Chem. Rev.* **1997**, *97*, 597.

[27] K. E. Riley, M. Pitonak, P. Jurecka, P. Hobza, *Chem. Rev.* **2010**, *110*, 5023.

[28] M. P. Waller, H. Kruse, C. Mück-Lichtenfeld, S. Grimme, *Chem. Soc. Rev.* **2012**, *41*, 3119.

[29] A. Tkatchenko, D. Alfe, K. S. Kim, *J. Chem. Theory Comput.* **2012**, *8*, 4317.

[30] S. Grimme, A. Hansen, J. G. Brandenburg, C. Bannwarth, *Chem. Rev.* **2016**, *116*, 5105.

[31] C. Hättig, F. Weigend, *J. Chem. Phys.* **2000**, *113*, 5154.

[32] O. Christiansen, H. Koch, P. Jørgensen, *Chem. Phys. Lett.* **1995**, *243*, 409.

[33] R. Send, D. Sundholm, *Phys. Chem. Chem. Phys.* **2007**, *9*, 2862.

[34] N. O. C. Winter, C. Hättig, *Chem. Phys.* **2012**, *401*, 217.

[35] S. Grimme, *J. Comput. Chem.* **2006**, *27*, 1787.

[36] M. Casida, *Recent Advances in Density Functional Methods (I)*, (Ed. D. Chong), World Scientific, New York, USA **1995**.

[37] R. Bauernschmitt, R. Ahlrichs, *Chem. Phys. Lett.* **1996**, *256*, 454.

[38] C. Møller, M. S. Plesse, *Phys. Rev.* **1934**, *46*, 618.

[39] K. Raghavachari, J. B. Anderson, *J. Phys. Chem.* **1996**, *100*, 12960.

[40] R. Ahlrichs, M. Bär, M. Häser, H. Horn, C. Kölmel. *Chem. Phys. Lett.* **1989**, *162*, 165.

[41] M. J. Frisch, G. Trucks, H. Schlegel, G. Scuseria, M. Robb, J. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, *Gaussian009*, Pittsburgh, PA **2003**.

[42] S. Grimme, *J. Comp. Chem.* **2003**, *24*, 1529.

[43] M. P. Johansson, D. Sundholm, J. Vaara, *Angew. Chem. Int. Ed. Engl.* **2004**, *43*, 2678.

[44] S. Grimme, S. Ehrlich, H. Krieg, *J. Chem. Phys.* **2010**, *132*, 154104.

[45] W. Hujo, S. Grimme, *J. Chem. Theor. Comput.* **2011**, *7*, 3866.

[46] S. F. Boys, F. Bernardi, *Mol. Phys.* **1970**, *19*, 553.

[47] P. Habza, R. Zahradnik, *Chem. Rev.* **1988**, *88*, 871.

[48] G. Chalasinski, M. M. Szczesniak, *Chem. Rev.* **2000**, *100*, 4227.

[49] R. J. Bartlett, *Modern Electronic Structure Theory Part.1* (Ed. D.R. Yarkony), World Scientific, Singapore **1995**.

[50] R. J. Bartlett, *Recent Advances in Computacional Chemistry*, Vol. 3, Word Scientific, Singapore, **1997**.

[51] P. Pyykkö, N. Runeberg, F. Mendizabal, *Chem. Eur. J.* **1997**, *3*, 1451.

[52] F. Mendizabal, S. Miranda-Rojas, L. Barrientos, *Comp. Theor. Chem.* **2015**, *1057*, 74.

[53] S. Grimme, *J. Chem. Phys.* **2003**, *118*, 9095.

[54] M. Gernkamp, S. Grimme, *Chem. Phys. Letters* **2004**, *392*, 229.

[55] P. Pyykkö, X.-G. Xiong, J. Li, *Faraday Discuss.* **2011**, *152*, 169.

[56] S. -G. Wang, W. H. E. Schwarz, *J. Am. Chem. Soc.* **2004**, *126*, 1266.

[57] R.-F. Liu, C. A. Franzese, R Malek, P. S. Zuschowski, J. G. Angyan, M. M. Szczesniak, G. Chalasinski, *J. Chem. Theory Comp.* **2007**, *7*, 2399.

[58] A. Austin, G. A. Petersson, M. J. Frisch, F. J. Dobek, G. Scalmani, K. Thossell, *J. Chem. Theory Comput.* **2012**, *8*, 4989.

[59] A. Otero-de-la-Roza, J. D. Mallory, E. R. Johnson, *J. Chem. Phys.* **2014**, *140*, 18A504.

[60] Y. Zhao, N. E. Schultz, D. G. Truhlar, *J. Chem. Theory Comput.* **2006**, *2*, 364.

[61] Y. Zhao, D. G. Truhlar, *Theor. Chem. Acc.* **2008**, *120*, 215.

[62] O. Lehtonen, D. Sundholm, R. Send, M. P. Johansson, *J. Chem. Phys.* **2009**, *131*, 024301.

[63] A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648.

[64] T. Yanai, D. P. Tew, N. C. Handy, *Chem. Phys. Lett.* **2004**, *393*, 51.

[65] J. Heyd, J. E. Peralta, G. E. Scuseria, R. L. Martin, *J. Chem. Phys.* **2005**, *123*, 174101.

[66] P. Pyykkö, *Angew. Chem. Int. Ed.* **2004**, *43*, 4412.

[67] D. Andrae, M. Häusserman, H. Dolg, H. Stoll, H. Preuss, *Theor. Chim. Acta* **1990**, *77*, 123.

[68] A. Bergner, M. Dolg, W. Küchle, H. Stoll, H. Preuss, *Mol. Phys.* **1993**, *80*, 1431.

[69] PPs are found in University of Stuttgart, Institute for Theoretical Chemistry Pfaffenwaldring 55, D-70569 Stuttgart, Germany. Stuttgart/Cologne energy-consistent (ab initio) pseudopotentials suitable for wavefunction-based and density functional calculations: http://www.tc.uni-koeln.de/PP/index.en.html

[70] T. Dunning, P. Hay, *Modern Theoretical Chemistry*, Vol. 3, (Ed. H. Schaefer), Plenum Press, New York, USA **1997**, 1.

[71] J.-M. Lehn, *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 89.

[72] F. Biedermann, H.-J. Schneider *Chem. Rev.* **2016**, *116*, 5216.

[73] S.-L. Zheng, C. L. Nygren, M. Messerschmidt, P. Coppens, *Chem. Commun.* **2006**, *35*, 3711.

[74] R.-L White-Morris, M. M. Olmstead, A. L. Balch, *Inorg. Chem.* **2003**, *42*, 6741.

[75] M. Böge and J. Heck, *Chem. Eur. J.* **2016**, *22*, 6787.

[76] W. Lu, K. T. Chan, S.-X. Wu, Y. Chena, C.-M. Che, *Chem. Sci.* **2012**, *3*, 752.

[77] B. Wong, H.-L. Wong, Y.-C. Wong, M.-Y. Chan, V. W.i-W. Yam, *Angew. Chem. Int. Ed.* **2016**, *55*, 1.

[78] R. Echeverría, J. M. López-de-Luzuriaga, M. Monge, S. Moreno, M. E. Olmos, *Inorg. Chem.* **2016**, *55*, 10523.

[79] E. J. Fernández, A. Laguna, J. M. López-de- Luzuriaga, M. Monge, M. Nema, M. E. Olmos, J. Pérez, C. Silvestru, *Chem. Commun.* **2007**, *36*, 571.

[80] K. M.-C. Wong, V. W.-W. Yam. *Acc. Chem. Res.* **2011**, *44*, 424.

[81] C.-K. Li, X.-X. Lu, K. M. Wong, C.-L. Chan, N. Zhu, V. W.-W. Yam, *Inorg. Chem.* **2004**, *43*, 7421.

[82] O. Piovesana, P. F. Zanazzi. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 561.
[83] B. Chiari, O. Piovesana, T. Tarantelli, P. F. Zanazzi. *Inorg. Chem.* **1985**, *24*, 366.
[84] J. F. Parker, K. A. Kacprzak, O. Lopez-Acevedo, H. Haäkkinen, R. W. Murray, *J. Phys. Chem. C* **2010**, *114*, 8276.
[85] J. Akola, K. A. Kacprzak, O. Lopez-Acevedo, M. Walter, H. Grönbeck, H. Häkkinen, *Phys. Chem. C* **2010**, *114*, 15986.
[86] O. Bumbu, C. Ceamanos, O. Crespo, M. C. Gimeno, A. Laguna, C. Silvestru, M. D. Villacampa, *Inorg. Chem.* **2007**, *46*, 11457.
[87] C.-L. Margaret Yeung, V. W.-W. Yam, *Chem. Soc. Rev.* **2015**, *44*, 4192.
[88] V. W.-W. Yam, K. M.-C. Wong, *Chem. Commun.* **2011**, *47*, 11579.
[89] N. Runeberg, M. Schütz, H.-J. Werner, *J. Chem. Phys.* **1999**, *110*, 7210.
[90] F. Mendizabal, P. Pyykkö, *Phys. Chem. Chem. Phys.* **2004**, *4*, 900.
[91] J. Muñiz, C. Wang, P. Pyykkö, *Chem. Eur. J.* **2011**, *17*, 368.
[92] L. E. Sansores, R. Salcedo, A. Martinez, N. Mireles, *Theochem* **2006**, *763*, 7.
[93] J. Muñiz, L. E. Sansores, P. Pyykkö, A. Martinez, R. Salcedo, *J. Mol. Model.* **2009**, *15*, 1165.
[94] J. Muñiz, L. E. Sansores, A. Rojano, A. Martinez, R. Salcedo, *Theochem* **2009**, *901*,232.
[95] R-F. Liu, C. A. Franzese, R. Malek, P. S. Zuchowski, J. G. Angyan, M. M. Szczesniak, G. Chalasinski, *J. Chem. Theory Comput*. **2011**, *7*, 2399.
[96] M. Andrejic, R. A. Mat, *Phys. Chem. Chem. Phys.* **2013**, *15*, 18115.
[97] E. J. Fernández, P. G. Jones, A. Laguna, J. M. López-de-Luzuriaga, F. Mendizabal, M. Monge, M. E. Olmos, M. Pérez, *Chem. Eur. J.* **2003**, *9*, 456.
[98] E. J. Fernández, J. M. López-de-Luzuriaga, M. Monge, Montiel, M. E. Olmos, J. Pérez, A. Laguna, F. Mendizabal, A. A. Mohamed, J. P. Fackler, *Inorg. Chem.* **2004**, *43*, 3573.
[99] R. Donamaría, M. C. Gimeno, V. Lippolis, J. M. López-de-Luzuriaga, M. monge, M. E. Olmos, *Inorg. Chem.* **2016**, *55*, 11299.
[100] D. J. Liptropt, P. P. Power. *Nature Rev. Chem.* **2017**, 1, 10.1038/s41570-016-0004.
[101] H. Schmidbaur, *Gold-Progress in Chemistry, Biochemistry and Technology*, John Wiley & Sons, New York **1999**.
[102] M. C. Gimeno, A. Laguna, *Comprenhensive Coordinanation Chemistry 1*, Vol. 6 (Eds.: C. McCleverty, T.J. Meyer), Elsevier, Amsterdam **2004**, 911.
[103] H. Schmidbaur, A. Schier, *Chem. Soc. Rev.* **2008**, *37*, 1931.
[104] A. Laguna (Ed), *Modern Supramolecular Gold Chemistry*. Wiley-VCH, Weinheim **2008**.
[105] X. Liu, J. Zhang, X. Guo, S. Wu, S. Wang, *Nanotechnology* **2010**, *21*, 095501.
[106] H. Schmidbaur, A. Schier, *Chem. Soc. Rev.* **2012**, *41*, 370.
[107] J. P. Fackler, *Inorg. Chim. Acta* **2015**, *424*, 83.
[108] G. Tárkányi, P. Király, G. Pálinkás, A. Deák, *Magn. Reson. Chem.* **2007**, *45*, 917.
[109] A. Deák, T. Megyes, G. Tárkányi, P. Király, L. Biczók, G. Pálinkás, P.J. Stang, *J. Am. Chem. Soc.* **2006**, *128*, 12668.
[110] W. J. Hunks, M. C. Jennings, R. J. Puddephatt, *Inorg. Chem.* **2002**, *41*, 4590.
[111] A. Codina, E. J. Fernandez, P. G. Jones, A. Laguna, M. J. Lopez-de-Luzuriaga, M. Monge, M. E. Olmos, J. Perez, M. A. Rodrıguez, *J. Am. Chem. Soc.* **2002**, *124*, 6781.
[112] F. Mendizabal, P. Pyykkö, N. Runeberg, *Chem. Phys. Lett.* **2003**, *370*, 733.
[113] I.-P. Zhang, Y.-B. Wang, X.-C. Huang, Y.-Y. Lin, X.-M. Chen, *Chem. Eur. J.* **2005**, *11*, 552.
[114] F. Mendizabal, D. Reyes, C. Olea-Azar, *Int. J. Quantum Chem.* **2006**, *106*, 906.
[115] L. Magnko, M. Schweizer, G. Rauhut, M. Schütz, H. Stoll, H.-J. Werner, *Phys. Chem. Chem. Phys.* **2002**, *4*, 1006.
[116] A. Fernando, K. L. D. Weerawardene, N. V. Karimova, C. M. Aikens, *Chem. Rev.* **2015**, *115*, 6112.
[117] J. R. Reimers, M. J. Ford, S. M. Marcuccio, J. Ulstrup, N. S. Hush, *Nat. Rev. Chem.* **2017**, 1, 10.1038/s41570-0017.
[118] C. Lensch, P. G. Jones, G. M. Sheldrick, Z. Naturforsch. B **1982**, *37*, 944.
[119] S. Riedel, P. Pyykkö, R. A. Mata, H.-J. Werner, *Chem. Phys. Lett.* **2005**, *405*, 148.
[120] M. M. Alam, E. Fromager, *Chem. Phys. Lett.* **2012**, *554*, 37.
[121] S. Canales, O. Crespo, M.C. Gimeno, P.G. Jones, A. Laguna, F. Mendizabal, *Organometallics* **2000**, *19*, 4985.
[122] S. Canales, O. Crespo, M. C. Gimeno, P. Jones, A. Laguna, F. Mendizabal, *Organometallics* **2001**, *20*, 4812.
[123] F. Mendizabal, G. Zapata-Torres, C. Olea-Azar, *Chem. Phys. Lett.* **2003**, *382*, 92.
[124] F. Mendizabal, P. Pyykkö, *Phys. Chem. Chem. Phys.* **2004**, *6*, 900.
[125] F. Mendizabal, C. Olea-Azar, *Int. J. Quantum Chem.* **2005**, *103*, 34.
[126] F. Mendizabal, C. Olea-Azar, R. Briones, *Theochem* **2006**, *764*, 193.
[127] F. Mendizabal, B. Agulera, C. Olea-Azar, *Chem. Phys. Lett.* **2007**, *447*, 345.
[128] F. Mendizábal, G. Zapata-Torres, C. Olea-Azar, *Chem. Phys. Lett.* **2005**, *412*, 477.
[129] R. Mera, F. Mendizabal, *Chem. Phys. Lett.* **2009**, *479*, 156.
[130] F. Mendizabal, *Int. J. Quantum Chem.* **2008**, *108*, 1164.
[131] M. Rodríguez-Castillo, M. Monge, J. M. López-de-Luzuriaga, M. E. Olmos, A. Laguna, F. Mendizabal, *Comput. Theor. Chem.* **2011**, *965*, 163.
[132] F. Mendizabal, S. Miranda-Rojas, L. Barrientos, *Phys. Chem. Chem. Phys.* **2015**, *17*, 26417.
[133] F. Mendizabal, *Int. J. Quantum Chem.* **1999**, *73*, 317.
[134] F. Mendizabal, *Organometallics* **2001**, *20*, 261.
[135] F. Mendizabal, D. Burgos, C. Olea-Azar, *Chem. Phys. Lett.* **2008**, *463*, 272.
[136] F. Mendizabal, *Int. J. Quantum Chem.* **2010**, *110*, 1279.
[137] F. Mendizabal, R. Salazar, *J. Mol. Model.* **2013**, *19*, 1973.
[138] S. Miranda-Rojas, A. Muñoz-Castro, R. Arratia-Pérez, F. Mendizabal, *Phys. Chem. Chem. Phys.* **2013**, *15*, 20363.
[139] S. Miranda-Rojas, R. Salazar-Molina, J. Kästner, R. Arratia-Pérez, F. Mendizabal, *RSC Adv.* **2016**, *6*, 4458.
[140] S. Miranda-Rojas, P. Sierra-Rosales, A. Muñoz-Castro, R. Arratia-Pérez, J. H. Zagal, F. Mendizabal, *Phys. Chem. Chem. Phys.* **2016**, *18*, 29516.
[141] J. Philipp, P. R. Schreiner, *Angew. Chem. Int. Ed.* **2015**, *54*, 12274.
[142] J. Hermann, R. A. DiStasio, A. Tkatchenko, *Chem. Rev.* **2017**, *117*, 4714.

AUTHOR BIOGRAPHIES

Lorena Barrientos was born in Santiago, Chile in 1980. She studied Education in Chemistry at the Universidad Metropolitana de Ciencias de la Educación, where she graduated with distinction from the first of her class. During 2004, she worked on inorganic complexes for dye-sensitized solar cells at Universidad de Chile. In 2009, she obtained Doctor of Chemistry degree from the Universidad de Chile, working on metal nanoparticles onto supramolecular complexes and metal nanostructures (nanowires, nanofibers, thin films). At present, she is Assistant Professor of the Department of Inorganic Chemistry at Pontificia Universidad Católica de Chile. She is interested in the development of supramolecular architectures, nanotechnologies, and nanofabrication. She has obtained the doctoral (2005) and postdoctoral (2009) fellowships from the National Commission for Scientific and Technological Research (CONICYT).

Sebastian Miranda-rojas obtained his Pharmaceutical Chemist and PhD (2012) in Chemistry from University of Chile. This was followed by Postdoctoral Research at Pontificia Universidad Católica de Santiago, Chile, where he worked with professor Alejandro Toro-Labbe (2012-2014). He is an Assistant Professor at the University Andres Bello, Faculty of Science from 2015. His research interests are in developing theoretical modeling of electronic properties, Dynamic and mechanic Molecular, catalysis in protein, and weak van der Waals interactions.

Fernando Mendizabal was born in Santiago, Chile in 1967. He obtained his BS (1990) and PhD (1996) in Chemistry from University of Chile. This was followed by Postdoctoral Research at University of Helsinki, Finland, where he worked with professor Pekka Pyykkö (1996-1997). He is a Professor at the University of Chile, Faculty of Science. His research focuses on weak van der Waals interactions in molecules and extended solids of heavy metals (gold, mercury, thallium, etc.), inorganic physicochemistry, theoretical and computational chemistry. All these lines are inserted in the area of Supramolecular Chemistry of the complex systems. He has given more than 18 invited talks plus 50 seminars and colloquia, published more than 90 articles in academic journal, and two book chapters.

How to cite this article: Barrientos L, Miranda-Rojas S, Mendizabal F. Noncovalent interactions in inorganic supramolecular chemistry based in heavy metals. Quantum chemistry point of view. *Int J Quantum Chem*. 2019;119:e25675. https://doi.org/10.1002/qua.25675