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REGULAR ARTICLE

M. A. Carvajal · S. Alvarez · J. J. Novoa

The nature of the $\mathrm{Au^I} \cdots \mathrm{Au^I}$ interactions between cationic $[\mathrm{AuL_2}]^+$ complexes in the solid state

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Abstract The interaction energy of a $[\mathrm{Au\{C(NHMe)_2\}_2}]^+ \cdots [\mathrm{Au\{C(NHMe)_2\}_2}]^+$ dimer is investigated using the MP2 method and the LANL2DZ basis set when isolated or embedded in ionic an $[\mathrm{Au\{C(NHMe)_2\}_2}]_2\mathrm{anion}_2$ aggregate, a good model for the environment that these dimers feel in ionic crystals. A repulsive interaction energy is obtained when the dimer is isolated. However, it is possible to find short $\mathrm{Au^I} \cdots \mathrm{Au^I}$ separations in $[\mathrm{Au\{C(NHMe)_2\}_2}]_2\mathrm{anion}_2$ aggregates, because in these aggregates the sum of the cation $\cdots$ anion interactions overweight the sum of the cation$\cdots$ cation plus anion$\cdots$ anion interactions. This explains why short $\mathrm{Au^I} \cdots \mathrm{Au^I}$ separations are found in ionic crystals. The $\mathrm{Au^I} \cdots \mathrm{Au^I}$ interaction found in $[\mathrm{Au\{C(NHMe)_2\}_2}]_2\mathrm{anion}_2$ aggregates shows the same features observed in energetically stable dimers presenting $\mathrm{Au^I} \cdots \mathrm{Au^I}$ bonds. This makes appropriate to use the name *counterion-mediated bonds* for the $\mathrm{Au^I} \cdots \mathrm{Au^I}$ interactions found in $[\mathrm{Au\{C(NHMe)_2\}_2}]_2$ anion$_2$ aggregates and ionic crystals.

Keywords Ion$\cdots$ Ion interactions · $\mathrm{Au^I} \cdots \mathrm{Au^I}$ interactions · Density functional calculations · Counterion-mediated bonds · Supramolecular bonds

M.A. Carvajal · J.J. Novoa (✉)
Dept. Química Física,
Facultat de Química, Univ. Barcelona,
Av. Diagonal 647, 08028
Barcelona,
Spain
E-mail: juan.novoa@ub.edu

M.A. Carvajal · S. Alvarez · J.J. Novoa
CERQT, Parc Científic,
Univ. Barcelona, C. Baldiri i Reixac,
08028 Barcelona,
Spain

S. Alvarez
Dept. Química Inorgànica,
Facultat de Química,
Univ. Barcelona,
Av. Diagonal 647,
08028 Barcelona,
Spain

1 Introduction

The luminescent behavior[1] of $\mathrm{AuXY^+}$ cations (X, Y being neutral ligands) in AuXYA ionic crystals ($\mathrm{A^-}$ being a –1 charged anion) and frozen solutions has been attributed to the formation of $[\mathrm{AuXY^+}]_2$ dimers and/or $[\mathrm{AuXY^+}]_n$ aggregates presenting short $\mathrm{Au^I} \cdots \mathrm{Au^I}$ interactions [2], a class of the so called $\mathrm{d^{10}} \cdots \mathrm{d^{10}}$ interactions. The shortest $\mathrm{Au^I} \cdots \mathrm{Au^I}$ distances in these aggregates are placed within the 3.123–3.461 Å range [2]. The existence of $[\mathrm{AuXY^+}]_2$ dimers and $[\mathrm{AuXY^+}]_n$ aggregates depends on the X and Y ligands and A anion, and the most frequent packing motif found in AuXYA ionic crystals does presents neither $[\mathrm{AuXY^+}]_2$ dimers nor $[\mathrm{AuXY^+}]_n$ aggregates having short $\mathrm{Au^I} \cdots \mathrm{Au^I}$ distances between adjacent cations [1,2]. An example of a cation presenting aggregates in its salts with several anions is $[\mathrm{Au\{C(NHMe)_2\}_2}]^+$. Thus, when $\mathrm{BF_4^-}$ is used as a counteranion, the cations form stacks with inter-monomer $\mathrm{Au^I} \cdots \mathrm{Au^I}$ distances of 3.461 Å. Similar packing and $\mathrm{Au^I} \cdots \mathrm{Au^I}$ separations of less than 3.6 Å have also been obtained [2] with $\mathrm{PF_6^-}$, $\mathrm{BF_4^-}$, $\mathrm{Cl^-}$, and $\mathrm{Br^-}$.

The existence of $\mathrm{Au^I} \cdots \mathrm{Au^I}$ contacts shorter than 3.6 Å is usually considered as indicative of attractive aurophilic interactions. These interactions are a class of $d^{10} \cdots d^{10}$ interactions, and their attractive nature has been attributed to dispersion interactions. When the interacting fragments are neutral, their stability has been computed to be around 5–7 kcal/mol. [3,4]. A qualitative explanation involving the hybridization of the doubly occupied $5d_{z^2}$ orbitals and empty $6p_z$ orbitals of gold in each $[\mathrm{AuL_2}]^+$ monomer has also been proposed [5].

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[1] Defined in the Webster dictionary as "any emission of light not ascribable directly to incandescence, and therefore occuring at low temperatures, as in phosphorescence and fluorescence or other luminous radiation resulting from vital processes, chemical action, friction, solution, or the influence of light or of ultraviolet cathode rays, etc." In the context of the experiments quoted in reference 1, we understand that luminescense is attributed to the emision of light from a previously colorless solution when dimers or higher aggregates of the $[\mathrm{AuL_2}]^+$ cation is formed within the crystal or frozen solution.

In the case of the interactions between charged $\{[AuL_2]^+\}_2$ monomers, one has two opposing interactions: an attractive one, due to the $d^{10} \cdots d^{10}$ interactions, and a repulsive Coulombic one, due to the cationic nature of the monomers. Which of these opposing components dominates? The answer is relevant, because if the overall interaction is repulsive one cannot consider these short $Au^I \cdots Au^I$ interactions as conventional $Au^I \cdots Au^I$ intermolecular bonds (they fail to fulfill the stability criterion, a necessary condition for a chemical bond according to Pauling's definition [6]). However, these repulsive $Au^I \cdots Au^I$ interactions present many of the properties (like luminiscence) associated with energetically stable $Au^I \cdots Au^I$ interactions and taken as the signeture of a bond. Therefore, as in other similar situations, it can be convenient to call these interations *cation-mediated* $Au^I \cdots Au^I$ *bonds*, despite their repulsive nature. This is a new case of what we previously called *unconventional bonds* [7–10], due to fact that they do not satisfy the energetic requirement imposed by Pauling in its definition.

Balch et al. [1,2] proposed that the existence of $Au^I \cdots Au^I$ distances shorter than 3.6 Å in some crystals is a consequence of the attractive aurophilic interactions being stronger than the Coulombic cation–cation repulsion. However, in a previous study [11], we found that the net interaction of a $[Cu(N_2)_2]^+ \cdots [Cu(N_2)_2]^+$ dimer in a staggered conformation is repulsive by 71.4 kcal/mol (computed at the MP2/LANL2DZ level [12]) and a similar value was obtained when the Cu was substituted by the Au atom. An analysis of the interaction energy of the $[Cu(N_2)_2]^+ \cdots [Cu(N_2)_2]^+$ dimer using the IMPT perturbative method of Stone [13] indicated that its strongest component is the electrostatic one, with a value of 74.0 kcal/mol, while the dispersion component is attractive by only 3.1 kcal/mol, within the range estimated in neutral dimers [11]. Consequently, the aurophilic interaction in cations is weaker than the electrostatic repulsion by an order of magnitude. These numbers also indicated that a general description of the nature of the $Cu^I \cdots Cu^I$ interaction in dimeric aggregates must be done by looking at the electrostatic and dispersion components.

As both are $d^{10} \cdots d^{10}$ interactions, the substitution of the Cu by Au atoms is not likely to strongly modify the strength of the dispersive and Coulombic components, thus discarding the validity of the explanation proposed by Balch et al. [1, 2] However, before jumping to conclusions it seems appropriate to perform a quantitative study on the energetics of the $Au^I \cdots Au^I$ interaction in $[AuXY^+]_2$ dimers. More specifically, we will compute the interaction energy curve for the isolated dimers, searching for the presence of minima. Then, we will compute the components of the interaction as given by IMPT calculations [13]. Finally, if the net energetics of the $[AuXY^+]_2$ dimers is found to be repulsive, we have to find an alternative explanation for the presence of short distance $Au \cdots Au$ contacts within the $[AuXY^+]_2$ dimers.

We will also address in our study the luminiscent properties shown by $[AuXY^+]_2$ ionic dimers. Whenever $[AuXY^+]_n$ aggregates having short $Au \cdots Au$ distances are found in crystals, the crystals present luminescence, whereas no luminescence is seen for highly diluted solutions (the acetonitrile solution is colorless, with a λmax of 210 nm at 298 K). However, polycrystalline $[Au\{C(NHMe)_2\}_2](PF_6)$. ·0.5(acetone) presents at 300 K an emission spectrum with a λmax of 383 nm, with a significant Stokes shift (λmax in the absorption spectrum of 482 nm). Interestingly, luminescense is also observed when a colorless 6 mM solution (in acetonitrile, dimethyl sulfoxide, dimethylformamide, pyridine, or acetone) is frozen in liquid nitrogen.

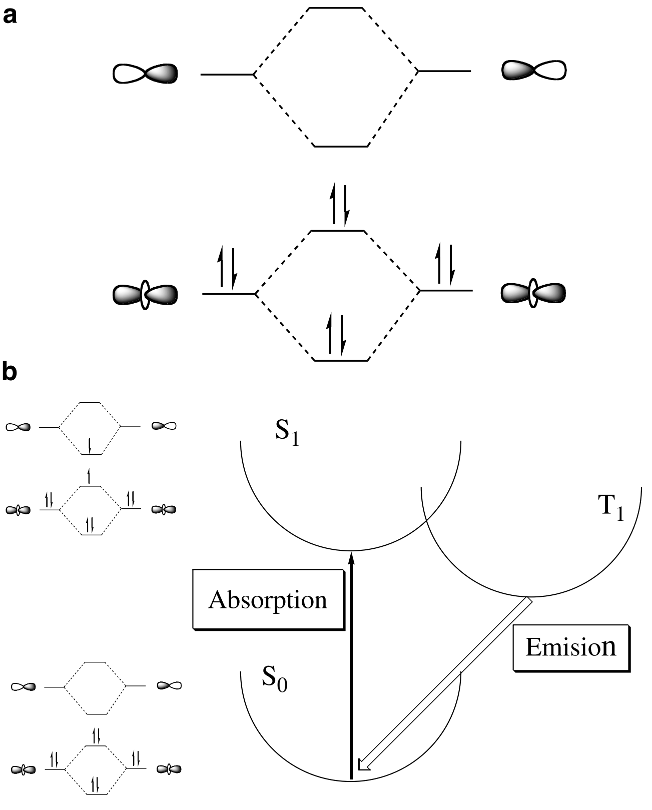

Fig. 1 Electronic structure of the $[AuXY^+]_2$ dimers

The origin of luminescence in these systems has been qualitatively associated [14–18] with, excitations from the HOMO to the LUMO of the dimer (Fig. 1). These orbitals usually correspond to the antibonding combination of the filled Au $5d_{z^2}$ orbitals and to the bonding combination of the empty Au $6p_z$ orbitals of the two monomers, respectively (Fig. 1). Notice that such splitting of the dimer orbitals is obtained whenever the HOMO and LUMO orbitals of the interacting fragments overlap, and that this overlap only depends on the distance and orientation of the interacting fragments. Therefore, luminiscence should also be found when the interaction within the dimers is repulsive but interactions with other nearby systems overcome such repulsion and induce a short distance between the components of the dimers. We have previously seen that cationic dimers can become energetically stable when anions are placed in the vicinity of the dimer in the right position forming neutral cation$_n$anion$_m$ aggregates. Extrapolating such idea to our case, we could

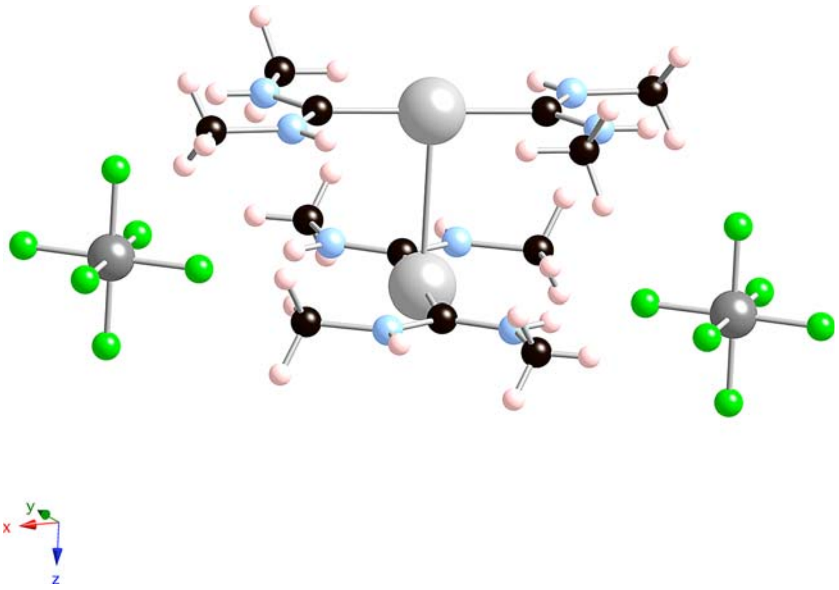

Fig. 2 Geometry of the $[Au\{C(NHMe)_2\}_2]^+ \cdots [Au\{C(NHMe)_2\}_2]^+$ dimer, extracted from the $[Au\{C(NHMe)_2\}_2]PF_6 \cdot 0.5$(acetone) crystal. The closest PF_6^- anions are also shown

obtain energetically stable $[AuXY^+]_2[anion^-]_2$ aggregates where the $[AuXY^+]_2$ dimers are placed at a geometry where $Au^I \cdots Au^I$ distances of the order of those found in energetically stable dimers. In this situation, it would be possible to find luminiscence in the $[AuXY^+]_2[anion^-]_2$ aggregates. Fig. 2, shows a $[AuXY^+]_2[anion^-]_2$ aggregate for the $[Au\{C(NHMe)_2\}_2]^+$ cation and the is PF_6^- anion. We will show that such aggregate is energetically stable and presents an electronic spectra with the same characteristics as obtained in energetically stable dimers showing short $Au^I \cdots Au^I$ distances. Thus, as we will show below, the presence of luminescence does not necessarily imply that the interaction between the two monomers is attractive, although certainly energetically stable dimers present such a property.

2 Methodology

The calculation of the $[Au\{C(NHMe)_2\}_2]^+ \cdots [Au\{C(NHMe)_2\}_2]^+$ interaction energy was done using the second− order Möller–Plesset perturbative method (MP2) implemented in the Gaussian-98 suite of programs. [19] We employed two types of bases set: (1) *Basis I*, where the Au atoms is described using the LANL2DZ basis set [12] (where the inner electrons are described by pseudopotentials and the outer electrons with a DZ basis set), while all other atoms are described using the D95V basis set [20]; (2) *Basis II*, where for the Au we use the LANL2DZ basis set complemented by a set of f functions, [21] while all other atoms are described by the 6–311G(d,p) basis set. [22] Unless otherwise stated, the calculations were done using Basis I, and Basis II was only used in a few cases, with the aim of testing the effect of including the *f* functions on values obtained using Basis I.

In these calculations the two monomers were always oriented in the same staggered conformation ($\tau = 90°$) found in the $[Au\{C(NHMe)_2\}_2](PF_6)$. ·0.5(acetone) crystal,[1] without further reoptimization of the geometry. When appropriate, the interaction energy was corrected for the possible basis set superposition error (BSSE) using the full counterpoise method. [23–25]

The components of the interaction energy can be quantitatively determined using the perturbative IMPT method of Stone, [13] in which the interaction energy (E_{int}) is obtained as the sum of five components:

$$E_{int} = E_{er} + E_{el} + E_p + E_{ct} + E_{disp} \tag{1}$$

E_{er} is the exchange-repulsion component which presents a net repulsive character dominated by the Pauli repulsion that two electrons feel when forced to be in the same region of the space despite the attractive nature of its exchange part. E_{el} is the electrostatic component associated with the electrostatic interaction of two fragments having their isolated electronic distribution. E_p and E_{ct} are the polarization and charge-transfer components, respectively. The first is associated with, the polarization of the electronic distribution of the fragments when in the presence of other fragments and their electronic distributions are allowed to relax, and the second with the electronic charge transfer from one fragment to the other. Finally, E_{disp} is the dispersion component, a nonclassical term whose origin is due to the correlated motions of the electrons in their orbitals (the closest classical image is the interaction between the instantaneous dipole moments generated in the fragments by the motion of their electrons).

All IMPT calculations [2,6] were done using an all-electron gaussian basis set, because our current IMPT implementation does not work with pseudopotentials. The all-electron basis set was selected in such a way that it is smaller than 255

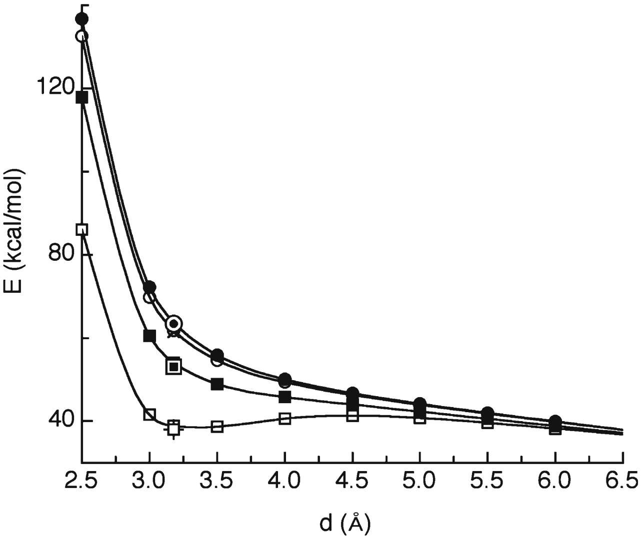

Fig. 3 Interaction energy curve (E) of the $[Au\{C(NHMe)_2\}_2]^+ \cdots [Au\{C(NHMe)_2\}_2]^+$ dimer as a function of the $Au \cdots Au$ distance (d) computed using the HF *(circles)* and MP2 *(squares)* levels. *Unfilled simbols* correspond to non-BSSE corrected values, while *filled symbols* correspond to BSSE-corrected values. The values obtained with the SDD basis set are shown with the symbols ⊗ (HF) and ⊞ (MP2)

functions (the maximum size in the implementation available to us) and reproduces the shape of the interaction energy curve of the dimer computed at the MP2/LANL2DZ level. The all electron basis set for Au is a contracted [6s, 4p, 3d, 1f] basis, [27] supplemented by two p polarization functions (exponents: 0.034 and 0.108) and a set of s and p diffuse functions (exponents: 0.00598 and 0.00279). For the remaining atoms, we used the 3–21G basis set, [28] substituting the methyl groups by hydrogen atoms, because the size of this basis for the full $[Au\{C(NHMe)_2\}_2]^+ \cdots [Au\{C(NHMe)_2\}_2]^+$ dimer exceeds the 255 functions allowed by our program.

Finally, we have computed the electronic spectra of the $[Au\{C(NHMe)_2\}_2]^+$ monomer and the $([Au\{C(NHMe)_2\}_2]^+)_2 (PF_6^-)_2$ aggregate, looking for the shifts usually taken as a manifestation of a bond (by comparing the previous spectra to that of the isolated monomer). All these computations were done using the time-dependent DFT (TDDFT) formalism [29–31] implemented in Gaussian-03, [32] which had been previously shown to provide reasonable results for the electronic transitions. In these TDDFT computations we used the PBE0 functional [33] and the LANL2DZ basis set.[12]

3 Results and discussion

3.1 The nature of the interaction in isolated $[Au\{C(NHMe)_2\}_2]^+ \cdots [Au\{C(NHMe)_2\}_2]^+$ dimers

We started our study by computing the interaction energy curve of the $[Au\{C(NHMe)_2\}_2]^+ \cdots [Au\{C(NHMe)_2\}_2]^+$ dimer as a function of the $Au \cdots Au$ distance using Basis I. We remind the reader that the geometry of the dimer was taken from the crystal structure of $[Au\{C(NHMe)_2\}_2](PF_6) \cdot 0.5$(acetone) and the orientation and geometry of the monomers was kept fixed while the $Au \cdots Au$ distance was changed. The HF and MP2 interaction energy curves for this staggered ($\tau = 90°$) conformation (see Fig. 3) are repulsive at all distances (notice the positive sign of the interaction energy). The MP2 curve presents a very shallow minimum around 3.2 Å that disappears when the BSSE is corrected. The use of Basis II does not change the previous conclusions. However, as it is well known that the counterpoise method tends to overcorrect the BSSE when small basis sets are used,[23–25] we further tested the unphysical origin of the minimum of the uncorrected MP2/LANL2DZ curve by recomputing the MP2 interaction energy in the 3.2 Å region using an even better quality basis set (the SDD basis set).[34] Figure 3 shows that the MP2/SDD BSSE-corrected interaction energy curve almost matches the MP2/LANL2DZ BSSE-corrected curve. Consequently, no minimum is found for the BSSE-corrected HF and MP2 curves, and we can safely conclude the repulsive nature of the interaction energy between two isolated $[Au\{C(NHMe)_2\}_2]^+$ cations placed in an staggered conformation. This fact allow us to discard the existence of a bond between the two isolated $[Au\{C(NHMe)_2\}_2]^+$ monomers, according to Pauling's definition of a chemical bond, similar to what we previously found for the $\{[CuL_2]^+\}_2$ dimers[11].

To further characterize the nature of the $[Au\{C(NHMe)_2\}_2]^+ \cdots [Au\{C(NHMe)_2\}_2]^+$ interaction energy, we have evaluated the weight of the different components of the interaction energy, as given by an IMPT calculation. Such calculation was done for the $[Au\{C(NHMe)_2\}_2]^+ \cdots [Au\{C(NHMe)_2\}_2]^+$ dimer at its crystal geometry, where the $Au \cdots Au$ distance is 3.188 Å (the CH_3 groups were substituted by hydrogens, see above). The values obtained for the energetic component are: $E_{er} = 25.4$, $E_{el} = 41.8$, $E_p = -2.5$, $E_{ct} = -1.0$, and $E_{disp} = -12.2$ kcal/mol (negative values are associated to attractive interaction energy components). The sum of these components gives a total interaction energy of 51.5 kcal/mol, very close to the MP2 BSSE-corrected value computed for the same model system with the all electron basis set (58.7 kcal/mol). The similarity of the two values confirms the proper behaviour of the perturbative series in our IMPT calculation. It is also worth pointing here that the MP2 BSSE-corrected interaction energy computed for the full $[Au\{C(NHMe)_2\}_2]^+ \cdots [Au\{C(NHMe)_2\}_2]^+$ dimer placed at an $Au \cdots Au$ distance of 3.188 Å is 54.8 kcal/mol.

The IMPT calculation indicates that the main reason behind the repulsive nature of the $[Au\{C(NHMe)_2\}_2]^+ \cdots [Au\{C(NHMe)_2\}_2]^+$ interaction energy is the very strong repulsion due to the electrostatic component, which dominates over the sum of all other components. The repulsive exchange-repulsion component has a value within the range found generally for systems placed at this distance. The remaining three components are all energetically attractive, the most important of them being the dispersion component. If we associate all the dispersion component with the aurophilic interaction, then we can conclude that in the $([Au\{C(NHMe)_2\}_2]^+)_2$ dimer the Coulombic repulsion associated with the cationic nature of the dimer dominates over the aurophilic interaction. However, it is worth noting that previous studies on dicoordinated $\mathrm{Au^I}$ dimers have shown that not all dispersion is due to the Au···Au dispersion (an important part of the total dispersion was identified as originating from the metal-ligand and ligand-ligand interactions) [35].

The net repulsive nature of the interaction energy of the $[\mathrm{Au\{C(NHMe)_2\}_2}]^+\cdots[\mathrm{Au\{C(NHMe)_2\}_2}]^+$ dimer raises two interesting questions: (1) If the interaction is repulsive, why does the dimer present a short Au···Au distance? (2) Why does it present luminescence? We will address the two points in the following subsections.

3.2 $[\mathrm{Au\{C(NHMe)_2\}_2}]^+\cdots[\mathrm{Au\{C(NHMe)_2\}_2}]^+$ interactions in the solid state

To understand the reasons behind the existence of short $\mathrm{Au^I}\cdots\mathrm{Au^I}$ contacts between the two monomers in the $[\mathrm{Au\{C(NHMe)_2\}_2}]^+$ salts, we have to use models that also incorporate anions, thus including all important forces present in the crystal (cation–cation, anion–anion, and cation–anion). The smallest aggregate that contains the $[\mathrm{Au\{C(NHMe)_2\}_2}]^+\cdots[\mathrm{Au\{C(NHMe)_2\}_2}]^+$ dimeric unit, its counterions, and preserves the electroneutrality is the $[\mathrm{Au\{C(NHMe)_2\}_2}]_2[\mathrm{PF_6}]_2$ aggregate depicted in Fig. 2, which was extracted from the $[\mathrm{Au\{C(NHMe)_2\}_2}]\mathrm{PF_6}\cdot 0.5$ (acetone) crystal [1,2]. This crystal can be viewed as a propagation of the $[\mathrm{Au\{C(NHMe)_2\}_2}]_2[\mathrm{PF_6}]_2$ aggregate by applying the appropriate symmetry operations. Therefore, it is a good model to understand the interactions in $[\mathrm{Au\{C(NHMe)_2\}_2}]\mathrm{PF_6}\cdot 0.5$(acetone). At the MP2/Basis I level, the values of the previous three classes of ionic interactions are (all in kcal/mol, in parenthesis the BSSE-corrected values, repulsive values are positive): cation–cation = 38.9 (54.8); anion–anion = 30.1 (30.1); and four different cation–anion = −60.6, −65.0, −65.1, −65.9 (−57.6, −62.0, −62.0, −62.9). Therefore, the net MP2 attractive cation–anion interaction energy of the tetramer is −256.6 kcal/mol (BSSE-corrected value −244.5 kcal/mol), which is bigger than the sum of the cation –cation and anion–anion repulsion components (69.0 kcal/mol; BSSE-corrected value 84.9 kcal/mol). The net stabilization of the tetramer (non-BSSE corrected value: −187.6 kcal/mol, BSSE corrected value: −129.6 kcal/mol) is in the range found for other ionic crystals studied previously [6,14–18] A similar stabilization is found by substracting the energy of the tetramer from the energy of the isolated fragments (−174.3; BSSE-corrected value −146.9 kcal/mol). The difference between the interaction computed is due to the polarization of the dimers, accounted only in one of the two energetic differences. When the results are computed at the MP2/Basis II level (that is, using a basis set that includes f functions on gold) the results are almost identical: the cation– cation interaction is 30.0 kcal/mol (BSSE-corrected : 48.3 kcal/mol), the anion– anion interaction is 30.1 kcal/mol (BSSE-corrected : 30.1 kcal/mol, and the cation– anion interactions are −63.3, −67.0, −67.0, and −63.4 (BSSE-corrected: −58.8, −63.3, −63.3, and −58.8). Relative to the isolated fragments, the aggregate is stable by 191.4 kcal/mol (BSSE-corrected: −155.5 kcal/mol). Therefore, we have a very small basis set truncation effect in our BSSE-corrected interaction energies.

Despite the fact that the dimer is stabilized by the cation –anion interactions, as shown in Fig. 4, the distribution of electronic density presents a funnel connecting the two Au atoms, a feature indicative of the presence of a (−3,1) bond critical point [36,37] in between these two atoms. The same funnel is found in an isolated $[\mathrm{Au\{C(NHMe)_2\}_2}]^+\cdots[\mathrm{Au\{C(NHMe)_2\}_2}]^+$ dimer placed at the geometry found in the $(\mathrm{cation})_2(\mathrm{anion})_2$ aggregate (Fig. 4, top), thus suggesting that the presence of a (−3,1) bond critical point [24] is not always associated with attractive interactions (that is, it is a necessary but not sufficient condition for the existence of a bond, defined according to Pauling's conventional view, as the energetic stability criterion is not satisfied).

3.3 The origin of luminescence in the $[\mathrm{Au\{C(NHMe)_2\}_2}]\mathrm{X}$ salts

We turn now our attention to the luminescence of the $[\mathrm{Au\{C(NHMe)_2\}_2}]^+\cdots[\mathrm{Au\{C(NHMe)_2\}_2}]^+$ dimers. Luminescence[1] is usually taken as a signal of an attractive interaction, and indeed it can be given a straightforward orbital interpretation for the case of dimers of neutral [AuXL] complexes. In that case, the $[\mathrm{AuXL}]_2$ minimum is found for a Au···Au distance of around 3.2 Å. At such distance the orbitals of the two monomers overlap and give rise to bonding and antibonding combinations (the process is graphically shown for pure Au $5d_{z^2}$ and $6p_z$ orbitals in Fig. 1, here taken as representative of the HOMO and LUMO in a simplified way). As a consequence, the HOMO–LUMO gap decreases in the dimer relative to that of the monomer and the energy range of the HOMO–LUMO transitions shifts from UV towards the visible (i.e., to smaller energies and larger wavelengths).

As shown above, the net interaction energy between two cationic monomers $[\mathrm{Au\{C(NHMe)_2\}_2}]^+$ is repulsive. However, the ionic $[\mathrm{Au\{C(NHMe)_2\}_2}]_2(\mathrm{PF_6})_2$ aggregate is energetically stable due to the presence of the attractive cation–anion interactions, thus forcing the two $[\mathrm{Au\{C(NHMe)_2\}_2}]^+$ monomers to be at a distance similar to those found in stable [AuXL]···[AuXL] dimers of neutral complexes. Therefore, the orbitals of the monomers overlap as in the energetically stable neutral dimers, giving raise to a similar orbital interaction scheme (Fig. 1). Consequently, the energy gap separating the singlet ground state from the singlet and triplet excited states decreases upon ionic aggregation, and luminescent properties similar to those found in energetically stable dimers should be expected.

We have tested the validity of these ideas by comparing the energy of the electronic transitions of the monomer with those found in the $(\mathrm{cation})_2(\mathrm{anion})_2$ aggregate (see Fig. 5, where only the cationic part of the aggregate is shown because the orbitals of the anions do not mix with those of the cations). Both electronic transitions were computed using the TD-DFT formalism. It is clearly seen in Fig. 5 that

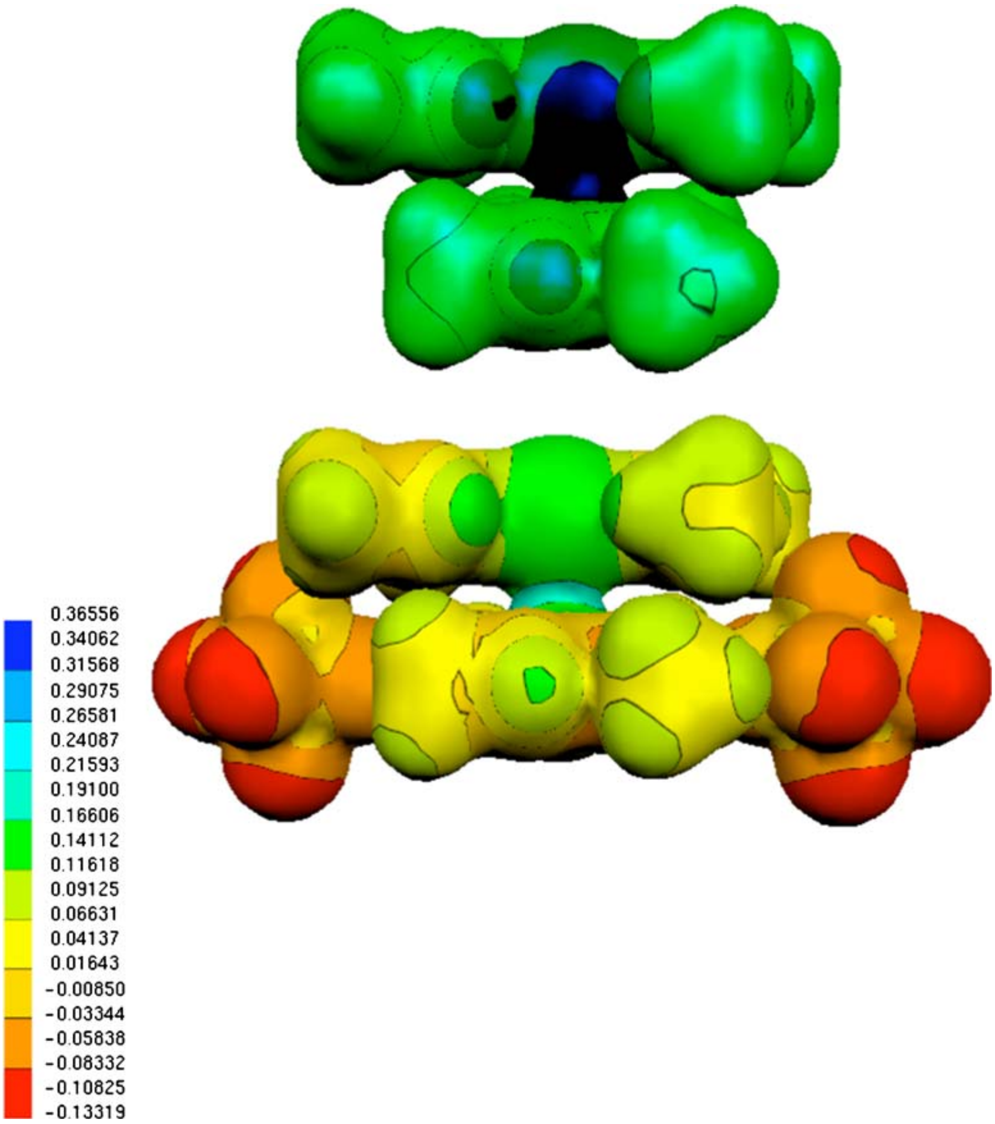

Fig. 4 Electronic density of the $[Au\{C(NHMe)_2\}_2]^+ \cdots [Au\{C(NHMe)_2\}_2]^+$ dimer (the isodensity surface of 0.1 a.u. has been plotted) on top of which the molecular electrostatic energy has been projected (*color scale* shown in the figure). Top plot: isolated dimer at the geometry of Figure 2; *lower plot*: dimer in a $[Au\{C(NHMe)_2\}_2]^+ \cdots [Au\{C(NHMe)_2\}_2]^+ \cdots (PF_6^-)_2$ tetramer at the geometry of the Fig. 2

the lowest energy transition in the $(cation)_2(anion)_2$ aggregate is shifted to larger wavelengths (smaller energies). Such a transition corresponds to a monoexcitation from the HOMO to the LUMO of the $(cation)_2(anion)_2$ aggregate, corresponding to a charge transfer transition from the Au d_{z^2} orbital to a π^* orbital of the $\{C(NHMe)_2\}$ ligands (Figure 6), without participation of the counteranions. Notice that in this system the LUMO is not metal-centered, as in the general case illustrated in Fig. 1 (there is only a small participation of the p_z orbitals of the metal). However, the HOMO-LUMO gap in the aggregate is smaller than that for the monomers, a fact that generates a red shift in the absorption and emission electronic spectra. We have looked at all the orbitals from the LUMO up to the LUMO+13 and none has the shape expected for a combination of monomeric Au p_z orbitals. We have computed the lowest energy singlet–triplet transition, despite the fact that its computed oscillation strength is not appropriately computed with the present programs (it is predicted to be zero in all cases). Such transition is found at 349 nm, indicating that the lowest energy triplet is placed 36 nm below the first excited singlet. Therefore, a shift is also found in the emission spectra, which is in good agreement with the predictions of our model.

It is interesting to note here that similar bonding phenomena have also been reported previously between charged fragments that repel each other when isolated [6,11], but which are forced to be at short distances by cation–anion interactions with species external to the dimer. Due to the

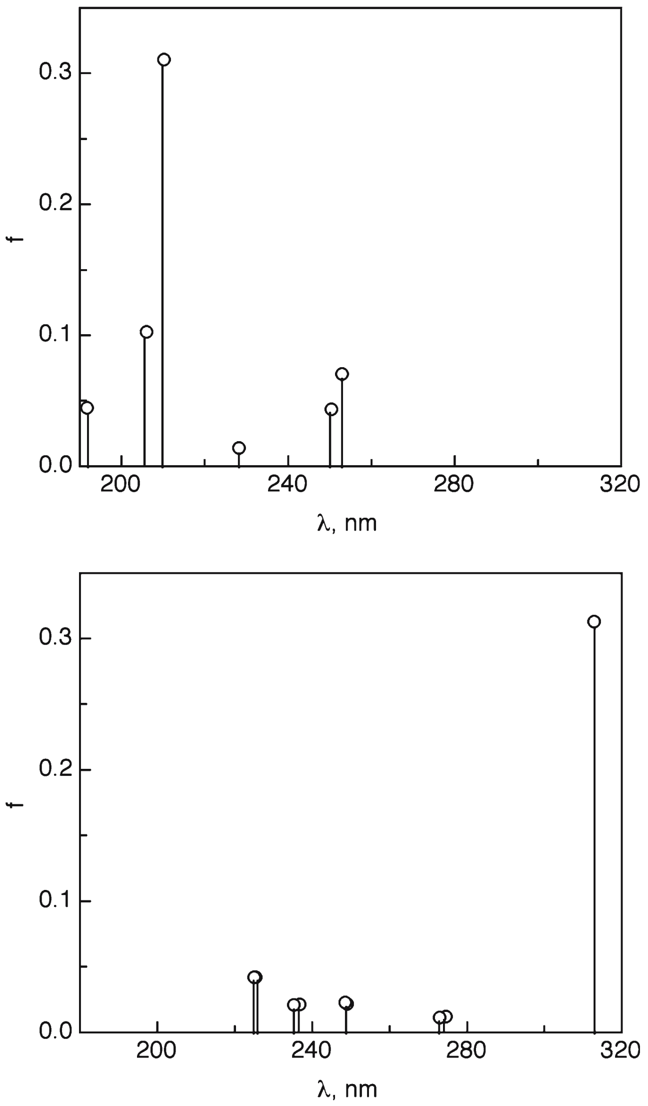

Fig. 5 Electronic spectra computed for the $[Au\{C(NHMe)_2\}_2]^+$ monomer (above) and the $(cation)_2(anion)_2$ aggregate (below) computed using the TD-DFT method

bonding properties that the $AuXY^+ \cdots AuXY^+$ dimers present in $(AuXY^+)_2(anion)_2$ aggregates, and the fact that they are a consequence of the cation$\cdots$anion interaction, we propose to name the $AuXY^+ \cdots AuXY^+$ interaction a *charged-mediated bond*, thus stressing the bonding properties over the repulsive nature of the $AuXY^+ \cdots AuXY^+$ isolated interaction.

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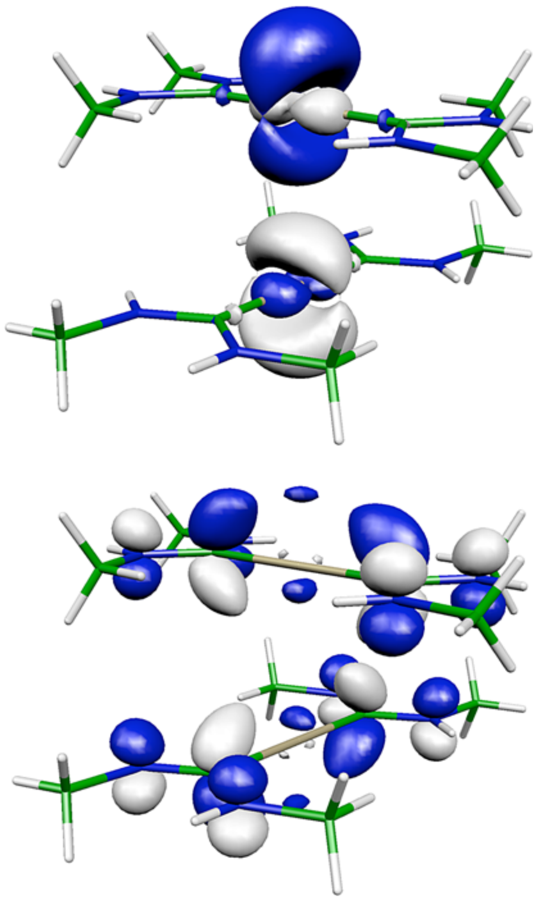

Fig. 6 Shape of the HOMO (above) and LUMO orbitals (below) of the $[Au\{C(NHMe)_2\}_2]^+ \cdots [Au\{C(NHMe)_2\}_2]^+$ dimer of the $cation_2anion_2$ aggregate computed using the HF method

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