Unsupported Au(I) \cdots Cu(I) interactions: influence of nitrile ligands and aurophilicity on the structure and luminescence[†]

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The synthesis, structural characterization and the study of the photophysical properties of complexes $[AuCu(C_6F_3)_2(N\equiv C-CH_3)_2]$ 1, $[AuCu(C_6F_5)_2(N\equiv C-Ph)_2]_2$ 2, and $[AuCu(C_6F_5)_2(N\equiv C-CH=CH-Ph)_2]$ 3 have been carried out. The crystal structures of complexes 1–3 consist of dinuclear Au–Cu units built from mediated metallophilic Au(1) ··· Cu(1) interactions. In the case of complex 2 two dinuclear units interact *via* an aurophilic interaction leading to a tetranuclear Cu–Au–Au–Cu arrangement. Complex 2 is brightly luminescent in solid state at room temperature and at 77 K with a lifetime in the nanoseconds range, while complexes 1 and 3 do not display luminescence under the same conditions. The presence of the aurophilic interaction in complex 2 seems to be responsible for the blue luminescence observed. DFT and time-dependent DFT calculations agree with the experimental results and support the idea that the origin of the luminescence of these complexes arise from orbitals located in the interacting metals.

Introduction

Polynuclear complexes bearing $Au(I) \cdots Au(I)$ (aurophilic) or Au(I) · · · M (metallophilic) closed-shell interactions represent an entire interdisciplinary research area whose significance spans several interests, such as supramolecular structural analysis,1 theoretical calculations,² photophysical properties³ or potential applications.⁴ Among them, unsupported closed-shell interactions of the type Au(I) \cdots M^{4b,5} (M = Ag(I), Tl(I), Hg(II), Hg(0), etc.) are an important class of interactions since they govern the formation of many different types of structural arrangements ranging from discrete species to supramolecular assemblies. Many of these complexes bearing unsupported Au...M interactions display fascinating photoluminescent properties that can be tuned from blue to red emissions or from short-lived (fluorescent) to long-lived (phosphorescent) emitters, depending on the type and number of ligands, the heterometal, the environment around the metal centers or the intermetallic distances.^{3a} Theoretical calculations are being used to explain the nature of the metallophilic closed-shell interactions found in the solid state structures and to support and explain the photophysical properties observed experimentally.⁶ Moreover, some of these luminescent heterometallic systems can be applied as sensors for volatile organic compounds^{4a-c} or are promising candidates for their use as LEDs.4d

One of the most successful strategies for the synthesis of these type of materials is an acid-base reaction between basic gold substrates and acidic heterometal precursors. In our case, in the last few years we have developed a synthetic procedure that involves bis(perhalophenyl)aurate(I) anions. The use of these materials offers the additional advantage of the stability that perhalophenyl groups provide to the synthesized complexes. Thus, the use of $[Au(C_6X_5)_2]^-$ (X = F, Cl) Lewis basis against silver(I) or thallium(I) salts⁵ has led to broad families of compounds displaying different structural arrangements as dimers, loosely bound butterfly clusters or 1D-, 2D- and 3D-polymeric species. These special types of interactions are rather strong (around 200 kJ mol⁻¹) and they display a very strong ionic component (ca. 80%) due to the ionic nature of the metal counterparts and an additional metallophilic contribution (ca. 20%), as we have observed in several ab initio studies. Moreover, in some cases we have observed additional contributions to the unsupported interaction between metallic fragments as hydrogen bonding,^{6g} $\pi\text{--}\pi$ interactions 6a or even $C_{\textit{ipso}}\cdots M$ interactions $(C_{\textit{ipso}}$ from C₆F₅ rings of the aurate units).⁶⁶ But, although one would expect that all the coinage metals would be among the most favorable candidates for these type of materials, a view of the published literature demonstrates that gold-copper complexes are almost non-existent. Therefore, we have recently focused our attention on Cu(I) as the heterometal, and using these $[Au(C_6F_5)_2]^$ basic units we have reported the first unsupported $Au(I) \cdots Cu(I)$ interaction between aurate fragments and a [Cu(pyrimidine)],⁺ chain as a first result.⁷ Using a different strategy we have also synthesized the polymeric complex $[Au_2Cu_2(C_6F_5)_4(N \equiv C - CH_3)_2]_n$ in a transmetalation reaction between $[Au_2Ag_2(C_6F_5)]_4(N \equiv C -$ CH₃)₂]_n and CuCl.⁸ The isolation of these derivatives displaying unsupported $Au(I) \cdots Cu(I)$ interactions illustrates an easy access to a new class of Au(I)-Cu(I) compounds presenting unsupported metallophilic interactions and interesting photophysical properties.

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Scheme 1 Synthesis of complexes 1–3.

In addition, regarding properties and applications, the use of Cu(I) as the heterometal interacting with Au(I) would also open new fields of research. These fields include, for example, biological applications, as DNA spectroscopic probes through the use of N-donor ligands that are constituents of biological substrates;⁹ emitting materials for molecular light-emitting devices (MOLEDs),^{4d} or catalytic applications, since the use of weakly coordinating anions such as [AuR₂]⁻ would enhance the reactivity of Cu(I) catalytic sites.¹⁰

In order to study systematically the unsupported $Au(I) \cdots Cu(I)$ interactions we have chosen nitrile ligands for several reasons: these ligands can be easily bonded to or displaced from Cu(I) centers; changes in the alkyl or aryl substituents from the nitrile ligands keeping the rest of the molecular components unchanged may produce structural and electronic changes leading to different structural arrangements and photophysical properties. Herein we report the synthesis and structural characterization of the heterometallic complexes $[AuCu(C_6F_5)_2(N\equiv C_{-1})_2(N\equiv C_{-1}$ CH_{3}_{2}] 1, $[AuCu(C_{6}F_{5})_{2}(N \equiv C - Ph)_{2}]_{2}$ 2, and $[AuCu(C_{6}F_{5})_{2}(N \equiv C - Ph)_{2}]_{2}$ CH=CH-Ph)₂] **3** (see Scheme 1). We have analyzed the influence of acetonitrile, benzonitrile and cinnamonitrile on the structural arrangements found in the solid state and, consequently, on the photophysical properties of these complexes. We have finally interpreted the results by the use of DFT and time-dependent DFT calculations that support the experimental findings.

Results and discussion

Synthesis

The starting material $[AuCu(C_6F_5)_2(N \equiv C - CH_3)_2]$ (1) was obtained by reacting $[Au_2Ag_2(C_6F_5)_4(N \equiv C - CH_3)_2]_n$ with CuCl

through a transmetalation reaction, in a 1:2 molar ratio (1:1 with respect to silver) in acetonitrile. After filtration of the AgCl formed, complex 1 was isolated as a white solid by precipitation from the acetonitrile solution by addition of Et_2O and subsequent cooling. In this way, in the presence of an excess of acetonitrile, complex $[AuCu(C_6F_5)_2(N\equiv C-CH_3)_2]$ (1), in which a Cu(I) center is joined to two nitrile ligands, is obtained.

The reaction of complex 1 with excess or two equivalents of nitrile ligands as benzonitrile or cinnamonitrile in toluene, leads to the substitution of both acetonitrile molecules leading to complexes $[AuCu(C_6F_5)_2(N\equiv C-Ph)_2]_2$ (2) or $[AuCu(C_6F_5)_2(N\equiv C-CH=CH-Ph)_2]$ (3), respectively (Scheme 1).

The IR spectra of **2** and **3** in Nujol mulls show absorptions arising from $C_6F_{5^-}$ groups in the range 1495–1500, 949–962 and 779–784 cm⁻¹. In these complexes, the absorptions due to the organic ligands coordinated to the Cu(I) centers can be assigned. These bands appear at significantly different energies from the absorptions of the uncoordinated organic ligands. For example, complex **2** displays a band at 2260 cm⁻¹ due to the v(C=N)stretching vibration while, in the free ligand, this band appears at 2226 cm⁻¹. Complex **3** displays the corresponding v(C=N)stretching vibration at 2238 cm⁻¹ and this absorption appears at 2218 cm⁻¹ in the case of the free ligand. The IR spectra of complex **1** cannot be obtained due to the loss of acetonitrile molecules and subsequent decomposition.

The ¹H NMR spectra of complexes 1-3 in CD₃CN display the signals corresponding to the organic nitrile species (see Experimental section). The chemical shifts are similar to those of the free organic ligands as is expected due to dissociation in solution.

These complexes also display similar ¹⁹F NMR spectra in which the signals corresponding to the C_6F_5 groups bonded to Au(I) in the $[Au(C_6F_5)_2]^-$ units are observed at -114.8 (F_o), -161.6 (F_p) and -162.8 (F_m) ppm in all cases.

Complexes 1–3 behave as 1 : 1 electrolytes in 5×10^{-4} M acetonitrile solutions ($\Lambda_{M} = 112$ (1); 234 (2) and 112 (3) Ω^{-1} cm² mol⁻¹), which suggests that metallophilic interactions are not present in solution and a separation in ionic counterparts is achieved. It is also worth mentioning that the large value obtained for complex 2 (234 Ω^{-1} cm² mol⁻¹) could be, perhaps, related to an equilibrium in solution between the 1 : 1 electrolyte formed between cationic [Cu(NCPh)₂]⁺ and anionic [Au(C₆F₅)₂]⁻, and a possible 2[Cu(NCPh)₂]⁺ : {[Au(C₆F₅)₂]₂}²⁻ 2 : 1 electrolyte, through association between aurate(1) units *via* aurophilic interactions in solution, similar to those observed in the solid state structure (see below).

Crystal structures†

Crystal structures of complexes 1–3 were determined by X-ray diffraction from single crystals obtained by slow diffusion of *n*-hexane into a solution of the complex in toluene. Although the three complexes are in principle very similar and their stoichiometries correspond to the general formula $[AuCu(C_6F_5)_2(N\equiv C-R)_2]$, their crystal structures show significant differences. Thus, while complex 1 crystallizes in the *P*1 space group of the triclinic system as discrete dinuclear molecules and without solvent, complex 2 forms tetranuclear Au₂Cu₂ units through aurophilic interactions and crystallizes also without solvent, but in the centrosymmetric $P\bar{1}$ space group as 2, but as discrete dinuclear molecules and as a solvate ($[AuCu(C_6F_5)_2(N\equiv C-CH=CH-Ph)_2] \cdot 0.5PhMe$). The half a molecule of toluene in 2 is disordered over two positions with the same occupancy for both of them.

The crystal structures of 1 and 3 (Fig. 1 and 2) consists of discrete molecules $[AuCu(C_6F_5)_2(N=C-R)_2]$ in which the $[Au(C_6F_5)_2]^-$ anion and the $[Cu(N=C-R)_2]^+$ cation are held together through an unsupported $Au \cdots Cu$ contact of 2.9335(11) Å in 1 and 2.6727(4) Å in 3, both of them being considerably longer than those present in $[Au_2Cu_2(C_6F_5)_4(N=C-CH_3)_2]_n^{,8}$ (2.5741(6) and



Fig. 1 Molecular structure of complex 1 with the labelling scheme for the atom positions. Ellipsoids are drawn at the 30% level.



Fig. 2 Molecular structure of complex 3 with the labelling scheme for the atom positions. Hydrogen atoms have been omitted for clarity and ellipsoids are drawn at the 30% level.

2.5876(5) Å) where one of the pentafluorophenyl ligands of the adjacent $[Au(C_6F_5)_2]^-$ units acts as a bridge between Au and Cu, and also longer than in some clusters^{11,12} (2.589 and 2.584 Å). The higher steric demand of the alkyl substituent in complex **3** forces the molecules to pack away (shorter intermolecular Au–Cu distance of 5.641 Å), while in **1** the dinuclear units are located at a shorter, but also non interacting Au–Cu distance of 3.757 Å along the *x* crystallographic axis forming a "intermittent polymer" (see Fig. 3). In contrast, the intermolecular Au–Cu



Fig. 3 Packing in complex 1 viewed along the crystallographic y axis. Hydrogen atoms have been omitted for clarity.

distance in 3 is about 0.26 Å shorter than in 1, and the Au-Cu separation in the latter is also longer than that found in the related polymeric compound $[Cu{Au(C_6F_5)_2}(N \equiv C - Me)(\mu_2 - C_4H_4N_2)]_n^n$ (2.8216(6) Å), which also displays unsupported Au \cdots Cu interactions. The lengthening of the Au-Cu distance in the acetonitrile derivative 1 if compared to the cinnamonitrile compound 3 can be probably attributed to the higher donor capability of the N-donor ligand in 1 due to the presence of a -Me instead of a -CH=CH-Ph substituent, what makes the copper center less acidic in 1. Consequently, the attraction for the bis(aryl)aurate anion decreases and leads to a longer Au-Cu distance. In both structures the C_{ipso} atom of one of the C₆H₅ groups (C1) maintains an interaction with the copper centre of different strength with Cu-C distances of 2.919 (1) or 2.638 Å (3). Such contacts are responsible for the narrow C-Au-Cu angle in which the interacting C atom is implied (68.96° (1) or 66.36° (3)). The other one displays a value of 110.60° (1) and 114.78° (3). If the Au · · · Cu contact is considered, both 1 and 3 exhibit a distorted planar T-frame Cu(I) center formed by its additional coordination to the nitrogen atoms of two nitrile molecules (Cu-N: 1.875(15) and 1.941(14) Å in 1, and 1.866(3) and 1.871(3) Å in 3). Finally, the gold(I) atoms are linearly coordinated to two pentafluorophenyl groups with typical Au-C bond lengths (see Tables 2 and 4) showing an additional (and rather uncommon) Au...Cu contact within the dinuclear unit.

The crystal structure of **2** (Fig. 4) consists of a tetranuclear compound formed by two $[Au(C_6F_5)_2]^-$ and two $[Cu(N \equiv C - Ph)_2]^+$ units joined together through unsupported $Au \cdots Cu$ and $Au \cdots Au$ contacts, leading to an unusual Cu-Au-Au-Cu arrangement (opposite to Coulomb's rule) where repulsive instead of attractive forces could be expected. An analogous situation was previously described by us for the Au-Tl complex $\{[Tl(bipy)]_2[Au(C_6F_5)_2]_2\}_n^{6e}$, where a Tl-Au-Au-Tl disposition of metals is found, although it may be influenced by the presence of bridging bipy ligands.



Fig. 4 Molecular structure of complex 2 with the labelling scheme for the atom positions. Hydrogen atoms have been omitted for clarity and ellipsoids are drawn at the 30% level.

Surprisingly, a Au···Au interaction (of 3.0011(5) Å) also appears in **2** and it is considerably shorter than in the Au–Tl polymeric compound (3.4092(3) Å) despite the apparent absence of leading forces. The Au ··· Cu contacts, with Au-Cu separations of 2.6163(12) and 2.6092(12) Å, are stronger than in the polymeric $[Cu{Au(C_6F_5)_2}(N \equiv C - Me)(\mu_2 - C_4H_4N_2)]_n^7$ (2.8216(6) Å) and also stronger than in complexes 1 (2.9335(11) Å) and 3 (2.6727(4) Å). The presence of phenyl substituents in the nitrile ligands, with a higher withdrawing capability than the substituents in 1 or 3, makes the copper even more acidic than in complex 3 and, hence, leads to shorter Au...Cu lengths. The slightly shorter Au-Cu distances present in the acetonitrile derivative $[Au_2Cu_2(C_6F_5)_4(N \equiv C - CH_3)_2]_n$, (2.5741(6)) and (2.5876(5)) Å) could seem to be contradictory; nevertheless, an additional factor has to be taken into account in this last case: the presence of pentafluorophenyl bridging ligands between Au and Cu, which get the metal centers even closer. As in the structures of 1 and 3 one of the carbon atoms bonded to gold in each $[Au(C_6F_5)_2]^$ fragment maintains an interaction with a copper centre, displaying Cu-C distances of 2.723 and 2.706 Å, intermediate between those observed in 1 and 3. The corresponding C-Au-Cu angles are again narrow (70.0 and 69.4°) if compared to the other two C-Au-Cu angles (107.1 and 108.3°). Again, the copper centers show a nearly planar environment (see Table 3) by coordination to the nitrogen atoms of two benzonitrile ligands and considering the Au ··· Cu contact. The Cu-N bond lengths, ranging form 1.869(8) to and 1.877(8) Å, are all equal and similar to those commented above for 1 and 3. Finally, if the metal-metal interactions are taken into account, the environment of the gold(I) atoms could be described as distorted square-planar, although with significant deviations from linearity in the Cu–Au–Au angles (165.68(3) and $153.02(3)^{\circ}$), which is more pronounced in Au2, and with both planes forming an angle of about 48°.

Photophysical properties

The absorption spectra of complexes **1–3** in acetonitrile solutions $(4.5 \times 10^{-6} \text{ M})$ are shown in Fig. 5. Complex **1** displays absorption bands between 200 ($\varepsilon = 5.7 \times 10^4$) and 260 nm ($\varepsilon = 8.2 \times 10^3 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$). Complex **2** displays a similar profile with bands between 200 ($\varepsilon = 13.4 \times 10^4$), 260 ($\varepsilon = 1.9 \times 10^4$), and a less intense band at 270 nm ($\varepsilon = 7.1 \times 10^3 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$) showing a band edge at lower energy than that of complex **1**. Finally, complex **3** shows an absorption spectrum with bands also placed between 200 ($\varepsilon = 15.3 \times 10^4$) and 250 ($\varepsilon = 4.9 \times 10^4$), and a low energy band



Fig. 5 Absorption spectra of **1** (blue), **2** (green) and **3** (red) in 4.5×10^{-6} M CH₃CN at room temperature. Inset: absorption spectra of free benzonitrile and cinnamonitrile ligands in 4.5×10^{-6} M CH₃CN solutions).

at 270 nm ($\varepsilon = 9.8 \times 10^4 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$) showing also a lower energy band edge if compared to those of complexes 1 or 2.

These profiles are very similar to the one observed for the gold(I) precursor complex NBu₄[Au(C_6F_5)₂] (which displays bands between 200 and 264 nm with similar intensities) and that were assigned to π - π * transitions in the pentafluorophenyl rings.^{5a,6d,7} Nevertheless, the bands at 270 nm observed for compounds 2 and 3, respectively, are not found in the precursor $NBu_4[Au(C_6F_5)_2]$, (see Fig. 5). In this sense, the $d^{10} \rightarrow d^9 s^1$ transitions of the free Cu⁺ ion are at much lower energies: 21 390 cm⁻¹ (467 nm) and 26260 cm⁻¹ (381 nm) for the spin forbidden and allowed transitions, respectively.13 Previous work of Che and co-workers14 showed that the transition $[3d\sigma^* \rightarrow 4p\sigma]$ in a dinuclear copper complex occurs at a similar energy, 276 nm ($\varepsilon = 10.8 \times$ 10³ mol⁻¹ dm³ cm⁻¹). Nevertheless, the formation of dinuclear copper species in solution is highly unlikely to be responsible for this behaviour. Similarly, absorptions arising from remaining Au-Cu interactions in solution are also unlikely since the three complexes behave as 1:1 electrolytes when conductivity measurements are carried out (see Experimental section).

Therefore, these absorptions seem not to have their origins in the copper center. Instead, they could be assigned to intraligand (nitrile) transitions influenced by the metal centers. Taking into account that the absorptions due to the nitrile group (C=N) appear below 190 nm we propose that these absorptions in solution are due to π - π * transitions between orbitals in the phenyl groups of the nitrile substituents. In fact, the absorption spectra of these ligands (benzonitrile and cinnamonitrile) in acetonitrile display bands at 270 and 272 nm, respectively (see inset in Fig. 5).

From the three complexes, only in the case of complex $[AuCu(C_6F_5)_2(N=C-Ph)_2]_2$ (2) is luminescence in the solid state observed (Fig. 7). It emits at 442 nm (exc. 392 nm) at room temperature and also emits at a similar energy (exc. 371 nm) at liquid nitrogen temperature (77 K) (Fig. 6). This curious non-dependence on the temperature, which is termed as *luminescence rigidochromism* in other luminescent gold–heteropolynuclear systems,^{6e,15} has its origin in an effect that relates the emission features with the environmental rigidity in charge transfer states formed in transitions from a fluid to a rigid solvent.¹⁶ Different to that in solution, in the solid state this phenomenon is not fully understood, since in transitions mostly metal-based one would expect a shortening

392

1.0

0.9

0.8

0.7

0.6

0.5

0.4

0.3

0.2

0.1

0.0

-0.1

Intensity (a.u.)

442



500

λ (nm)

600

400



Fig. 7 Theoretical model systems $[AuCu(C_6F_5)_2(N\equiv C-CH_3)_2]$ (1a), $[AuCu(C_6F_5)_2(N\equiv C-Ph)_2]_2$ (2a) and $[AuCu(C_6F_5)_2(N\equiv C-CH=CH-Ph)_2]$ (3a) (hydrogen atoms are omitted for clarity).

of the metal–metal distances when the temperature is lowered, which would lead to a reduction of the HOMO–LUMO band gap and, consequently, a red shift of the emission energy. In this case, this *rigidochromism* could be related to the short distances in the Cu(I)–Au(I)–Cu(I) metal arrangement where further contraction provoked by decreasing temperature is unlikely.

As in the other heterometallic complexes reported, the complex behaves as non-luminescent in fluid solutions, recovering the property when the solvent is evaporated. This result is interpreted in terms of a rupture of the metal–metal interactions provoked by the solvent and their recovery when the solvent is evaporated, suggesting that the absence of these interactions give rise to the loss of the luminescence. Taking into account that the three complexes display gold–copper interactions; that all three have copper in a similar coordination environment and bonded to the same type of ligands; that the number of ligands around copper is relatively low and an attack by basic solvents is possible; and that only in the case of complex **2** luminescence is observed, it is likely that the main difference, *i.e.* the gold–gold interactions that appear in **2**, are of capital importance for its luminescent behavior.

The lifetime measurements, determined by the phasemodulation technique in the solid state at room temperature displays two components within the nanosecond time scale [τ_1 = 65 ns, $\tau_2 = 17$ ns; $\chi^2 = 8.6$], indicating that the emission probably originates from an excited state of singlet parentage and, consequently, is tentatively assigned as fluorescence. Similarly, the Stokes-shift between excitation and emission peaks is only 2886 cm⁻¹, which is indicative of a small distortion of the excited state if compared to the ground state and, therefore, supporting the assignation of fluorescence for this transition. Interestingly, the lifetime of the previously reported $[Cu{Au(C_6F_5)_2}](N \equiv C -$ Me) $(\mu_2$ -C₄H₄N₂)]_n,⁷ which shows a polymeric copper-pyrimidine structure with $[Au(C_6F_5)_2]^-$ units interacting with each copper center, is much longer (10.3 µs) and assigned as phosphorescence. In that complex, the luminescent behaviour was assigned to arise from a MMLCT (metal(gold)-metal(copper)-to-ligand-chargetransfer) state. The observed quenching of the luminescence in basic solvents by formation of a five-coordinate copper complex that stabilizes the excited state and destabilizes the ground state supports this assignation.¹⁷ This quench was observed even in glassy (EtOH: MeOH: CH₂Cl₂ 8:2:1) solutions at 77 K. In this case, a glassy solution of complex 2 shows an emission at 420 nm, suggesting that the formation of the five-coordinate copper complex is not produced and, consequently, the quench is not observed, or, if it is formed, the luminescence is not arising only

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from the gold–copper interactions. In fact, theoretical TD-DFT calculations agree with this assignation (see theoretical studies part).

Therefore, taking into account the previous comments, what we propose is that the luminescence in this complex arises from a transition between orbitals mostly metal-based and for which the higher contribution is from orbitals of the interacting gold(I) centers, although a π - π * transition in the perhalophenyl groups cannot be excluded. In this sense, previous luminescence studies on a heteronuclear gold-silver complex with pentafluorophenyl groups showed that in acetone solutions, where the metalmetal interactions are not present, luminescence appeared at a slightly higher energy (405 nm) by excitation at 332 nm that arose from pentafluorophenyl localized π - π * excited states.^{5a} In contrast to our case, the precursor complex NBu₄[Au(C₆F₅)₂] is not luminescent in solid state, which reinforces the interacting gold(I) centers as the main contributors to the orbitals responsible for this behaviour in the solid state.

Theoretical results

In view of the results reported in the photophysical studies section, single point DFT calculations on model systems $[AuCu(C_6F_5)_2(N \equiv C - CH_3)_2]$ (1a), $[AuCu(C_6F_5)_2(N \equiv C - CH_3)_2]$ Ph_{2}_{2} (2a) and $[AuCu(C_{6}F_{5})_{2}(N \equiv C - CH = CH - Ph)_{2}]$ (3a) and time-dependent DFT calculations on model $[AuCu(C_6F_5)_2(N \equiv C Ph_{2}_{2}$ (2a) have been carried out. These theoretical models represent the solid state structures of compounds 1-3 since all the metallophilic interactions responsible for the observed dinuclear (complexes 1 and 3) or tetranuclear (complex 2) arrangements are considered in the model systems. All models have been built up from the X-ray diffraction results (Fig. 7). In order to check that the use of these model systems is qualitatively correct we have optimized a simplified model system $[AuCu(C_6F_5)_2(N\equiv CH)_2]$ at DFT B3LYP level of theory and using a C_s symmetry in order to keep the computational costs feasible. The optimized geometry reproduces fairly well the structures found in the solid state showing a Au–Cu interaction of 2.60 Å and one Cu–C_{inee} interaction of 2.24 Å. The C_s symmetry prevents the nitrile ligands adopting a similar relative disposition as found in the X-ray analyses of the complexes, but other structural parameters such as distances and angles are comparable (see ESI for details[†]).

We first studied the electronic structures of models **1a–3a** obtained through single-point DFT calculations. With these results we can build up qualitative molecular orbital diagrams for each model system and the shape of the frontier orbitals can be checked. Thus, we can check the contribution of each part of the molecule to the frontier orbitals. These DFT calculations can be used to explain how the structural differences among complexes **1–3** affect the electronic structures by the qualitative molecular orbital diagrams for each model system.

Model system [AuCu(C₆F₅)₂(N=C-CH₃)₂] **1a** shows a large HOMO-LUMO gap of 4.464 eV. The HOMO orbital for model **1a** is located at the [Au(C₆F₅)₂]⁻ fragment, meanwhile the LUMO orbital is mainly placed at the Cu(I) and Au(I) centers with some contribution from the nitrile and pentafluorophenyl groups. In the case of model [AuCu(C₆F₅)₂(N=C-CH=CH-Ph)₂] **3a** the HOMO-LUMO gap is intermediate (3.285 eV) with the HOMO



Fig. 8 Frontier molecular orbitals and HOMO-LUMO gaps for model systems 1a, 3a and 2a (left to right).

orbital placed at the $[Au(C_6F_5)_2]^-$ fragment and the LUMO orbital placed at the cinnamonitrile ligand. Model $[AuCu(C_6F_5)_2(N=C-Ph)_2]_2$ (**2a**) displays the shortest HOMO–LUMO gap (3.03 eV) and interesting differences regarding the shape of the frontier orbitals are observed. Thus, the main difference arises from the HOMO shape that in the case of model **2a** is centred on the interacting Cu ··· Au ··· Cu metals with a higher contribution from the gold centers and showing a $nd_z^2\sigma^*$ character.

As we have mentioned in the experimental photophysical results, complex $[AuCu(C_6F_5)_2(N\equiv C-Ph)_2]_2$ is the only one that displays photoluminescent properties upon excitation with UV light. This trend would also be supported with the theoretical results. Thus, when no aurophilic interactions are present (complexes 1 and 3) a large HOMO-LUMO gap is observed in which charge transfer absorptions arising from $[Au(C_6F_5)_2]^{-1}$ fragments to the metals (complex 1) or to the nitrile ligands (complex 3) may occur, but at rather high energy. Nevertheless, when an aurophilic interaction is present (complex 2) the HOMO-LUMO gap is reduced due to the destabilization of the HOMO orbital and the stabilization of the LUMO orbital. These trends arise from the combination of the nd_{z}^{2} or the ns/np atomic orbitals of the metals that leads to the corresponding more stable sigma-bonding orbital and less-stable sigma-antibonding orbital (see Fig. 9). Therefore, it is likely that this shortening in the HOMO-LUMO gap would lead to a more energetically available excited state responsible for luminescent emissions in the visible range.

In a second step we have also carried out time-dependent DFT calculations on model system **2a**. These calculations permit us to reproduce the absorption spectrum of this complex by the computation of the first few spin-allowed singlet excitations. A careful analysis of the oscillator strengths and the shape of the orbitals involved in each excitation relays important information about the photophysical properties of this complex. Thus, the obtained theoretical excitation profile can be compared with the experimental excitation spectra in solid state where the



Fig. 9 Qualitative formation of $nd_z^2\sigma$ antibonding and ns/np bonding orbitals through Cu ··· Au ··· Cu interactions (the *z*-axis is placed along the metal–metal interaction direction).

metallophilic Cu–Au–Au–Cu arrangement is kept. Fig. 10 displays the first few singlet excitations (red bars) that are compared with the excitation profile (blue line) (see Table 5).



Fig. 10 Comparison between theoretical first few singlet excitations (red bars A–I) with the experimental excitation profile in solid state (black line).

Although excitations A–C appear at lower energy and could not be related to the experimental excitation spectrum, the theoretical singlet excitations D–I agree well with the experimental excitation energy. Therefore, the orbitals involved in these singlet transitions may be related to the fluorescent behaviour observed for complex **2**, especially those excitations with larger oscillator strengths, G and H.

The most intense high energy transitions G and H arise from the HOMO orbital located at the $Cu \cdots Au \cdots Au \cdots Cu$ interacting metal centers (mainly at the gold atoms) and arrive to LUMO + 4 and LUMO + 6 orbitals that are placed at the nitrile ligands and the metals, respectively. These two singlet excitations would be responsible for the observed high energy fluorescent emission for complex **2**, that would arise from a mixed metal-centered (MC) and metal-to-ligand-charge-transfer (MLCT) transition in agreement with the results described in the photophysical studies section (Fig. 11). Obviously, the rupture of the gold–gold interactions would increase the HOMO–LUMO gap and would change the shape of the occupied frontier orbitals, preventing that transition.



Fig. 11 Most intense theoretical singlet excitations in the high energy region.

This is in agreement with the absence of visible luminescence in complexes 1 and 3 or even in 2 in solution, where the gold–gold interactions are loss.

Experimental

Instrumentation

Infrared spectra were recorded in the 4000–200 cm⁻¹ range on a Perkin-Elmer FT-IR Spectrum 1000 spectrophotometer, using Nujol mulls between polyethylene sheets. Conductivities were measured in *ca*. 5×10^{-4} M acetonitrile solutions with a Jenway 4510 conductimeter. C, H, N analyses were carried out with a C.E. Instrument EA-1110 CHNS-O microanalyser. Mass spectra were recorded on a HP-5989B Mass Spectrometer API-Electrospray with interface 59987A. ¹H and ¹⁹F NMR spectra were recorded on a Bruker ARX 300 in CD₃CN. Chemical shifts are quoted relative to SiMe₄ (¹H external) and CFCl₃ (¹⁹F, external). Absorption spectra in solution were registered on a Hewlett Packard 8453 Diode Array UV-visible spectrophotometer. Excitation and emission spectra as well as lifetime measurements were recorded with a Jobin-Yvon Horiba Fluorolog 3-22 Tau-3 spectrofluorimeter.

Crystallography

The crystals were mounted in an inert oil on glass fibers and transferred to the cold gas stream of a Nonius Kappa CCD diffractometer equipped with an Oxford Instruments lowtemperature attachment. Data were collected by monochromated Mo K α radiation ($\lambda = 0.71073$ Å). Scan type ω and ϕ . Absorption corrections: numerical (based on multiple scans). The structures were solved by direct methods and refined on F^2 using the program SHELXL-97.¹⁸ If the crystal structure of complex 1 is refined in the $P\bar{1}$ space group (even with disorder) a second copper center is symmetry generated resulting in a 1-D polymer built *via* Au···Cu interactions, but with a sequence ···Au···Cu···Cu···Cu···Cu···Au··· and with distances shorter than 1 Å between the Cu atoms. Thus, it had to be refined in the *P*1 space group. All non-hydrogen atoms were

Table 1 Data collection and structure refinement details for 1–3

Compound	1	2	3.0.5toluene
Chemical formula	$C_{16}H_6AuCuF_{10}N_2$	$C_{52}H_{20}Au_2Cu_2F_{20}N_4$	$C_{30}H_{14}AuCuF_{10}N_2 \cdot 0.5C_7H_8$
Crystal habit	Orange prism	Colorless prism	Colorless prism
Crystal size/mm	$0.25 \times 0.2 \times 0.18$	$0.18 \times 0.16 \times 0.12$	$0.4 \times 0.3 \times 0.1$
Crystal system	Triclinic	Triclinic	Triclinic
Space group	<i>P</i> 1	$P\overline{1}$	$P\overline{1}$
a/Å	6.6903(1)	13.423(1)	8.1519(1)
b/Å	7.6776(2)	13.459(1)	14.5421(2)
c/Å	8.7851(2)	16.492(2)	14.9953(2)
$\alpha /^{\circ}$	84.411(2)	101.794(6)	62.108(1)
$\beta/^{\circ}$	88.645(2)	98.641(7)	78.587(1)
$\gamma/^{\circ}$	79.218(1)	119.560(6)	77.368(1)
U/Å ³	441.170(17)	2424.13(4)	1523.65(3)
Ζ	1	2	2
$Dc/g \text{ cm}^{-3}$	2.547	2.194	1.960
M	6761.73	1601.73	899.01
F(000)	314	1512	862
T/°C	-100	-100	-100
$2\theta_{\rm max}/^{\circ}$	72	54	60
μ (Mo K α)/mm ⁻¹	9.616	7.019	5.596
No. of reflections measured	10 897	39910	30 949
No. of unique reflections	4070	10 180	7817
$R_{ m int}$	0.0419	0.0584	0.069
$R^{a}(I > 2\sigma(I))$	0.0389	0.0464	0.0280
wR^b (F^2 , all refl.)	0.0920	0.1292	0.0638
No. of parameters	268	721	525
No. of restraints	96	288	164
S^c	1.050	1.150	1.024
Max. $\Delta \rho / e \dot{A}^{-3}$	2.252	3.312	0.975

 ${}^{a} R: (F) = \sum ||F_{\circ}| - |F_{c}|| / \sum |F_{\circ}| . {}^{b} wR: (F^{2}) = [\sum \{w(F_{\circ}^{2} - F_{c}^{2})^{2}\} / \sum \{w(F_{\circ}^{2})^{2}\}]^{0.5}; w^{-1} = \sigma^{2}(F_{\circ}^{2}) + (aP)^{2} + bP, where P = [F_{\circ}^{2} + 2F_{c}^{2}] / 3 and a and b are constants adjusted by the program. {}^{c} S = [\sum \{w(F_{\circ}^{2} - F_{c}^{2})^{2}\} / (n-p)]^{0.5}, where n is the number of data and p the number of parameters$

Table 2	Selected bon	d lengths [Å]	and angles [°]	for complex 1
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Au-C(11)	2.028(14)	Cu–N(2)	1.875(15)
Au-C(1)	2.064(12)	Cu-N(1)	1.941(14)
Au–Cu	2.9335(11)		
C(11)-Au-C(1)	179.4(5)	N(2)-Cu-N(1)	149.8(8)
C(11)–Au–Cu	110.7(3)	N(2)–Cu–Au	95.9(5)
C(1)–Au–Cu	69.0(3)	N(1)–Cu–Au	114.1(4)

 Table 4
 Selected bond lengths [Å] and angles [°] for complex 3

Au–C(11)	2.031(3)	Cu-N(1)	1.866(3)
Au-C(1)	2.053(3)	Cu-N(2)	1.871(3)
Au–Cu	2.6727(4)		
C(11)-Au- $C(1)$	176.12(13)	N(1)-Cu-N(2)	155.88(12)
C(11)-Au-Cu	114.78(8)	N(1)–Cu–Au	108.73(9)
C(1)–Au–Cu	66.36(9)	N(2)–Cu–Au	94.10(9)

Table 3 Selected bond lengths [Å] and angles [°] for complex 2 $\,$

Au(1)–C(1)	2.052(9)	Cu(1)–N(1)	1.869(8)
Au(1)-C(11)	2.066(9)	Cu(1)-N(2)	1.870(8)
Au(2)-C(31)	2.062(10)	Cu(2)-N(3)	1.870(8)
Au(2)–C(21)	2.079(9)	Cu(2)-N(4)	1.877(8)
Au(1)-Cu(1)	2.6163(12)	Au(1)-Au(2)	3.0011(5)
Au(2)–Cu(2)	2.6092(12)		
C(1)-Au-C(11)	175.5(3)	N(3)-Cu(2)-N(4)	155.3(3)
C(31)–Au(2)–C(21)	176.5(3)	N(1)-Cu(1)-Au(1)	107.2(2)
Cu(1)- $Au(1)$ - $Au(2)$	165.68(3)	N(2)-Cu(1)-Au(1)	96.5(2)
Cu(2)- $Au(2)$ - $Au(1)$	153.02(3)	N(3)-Cu(2)-Au(2)	96.5(2)
N(1)-Cu-N(2)	152.9(4)	N(4)-Cu(2)-Au(2)	104.8(2)

anisotropically refined with the only exception of C14 (otherwise non-positive definite), and hydrogen atoms were included using a riding model. Further details on the data collection and refinement methods can be found in Table 1. Selected bond lengths and angles are shown in Tables 2–4 and crystal structures of **1–3** can be seen in Fig. 1–4. CCDC 708198–708200 contains the supplementary crystallographic data for this paper.†

Excitation	$\lambda_{\rm calc}/{\rm nm}$	Oscil. str. (s) ^a	Contributions ^b
A	482.3	0.0681	$318a \rightarrow 319a$ (96)
В	470	0.11	$318a \rightarrow 320a$ (95)
С	432.3	0.0218	$318a \rightarrow 322a$ (97)
D	377.4	0.0107	$315a \rightarrow 320a$ (90)
Е	354.3	0.0208	$313a \rightarrow 320a$ (50)
			$312a \rightarrow 319a(17)$
F	353.4	0.0263	$312a \rightarrow 319a$ (53)
			$312a \rightarrow 320a$ (16)
G	337.6	0.0507	$318a \rightarrow 323a$ (88)
H	335.4	0.297	$318a \rightarrow 325a$ (78)
Ι	333.6	0.0152	$312a \rightarrow 320a$ (42)
			$312a \rightarrow 321a$ (25)

 a Value is $|{\rm coeff}|^2 \times 100.$ b Oscillator strength shows the mixed representation of both velocity and length representations.

DFT and TD-DFT calculations

The molecular structures used in the theoretical studies on $[AuCu(C_6F_5)_2(N\equiv C-CH_3)_2]$ (1a), $[AuCu(C_6F_5)_2(N\equiv C-Ph)_2]_2$ (2a) and $[AuCu(C_6F_5)_2(N\equiv C-CH=CH-Ph)_2]$ (3a) were taken from the X-ray diffraction data for complexes 1–3, respectively. Keeping all distances, angles and dihedral angles frozen, single-point DFT calculations were performed on the models. In them, the single-point ground-state calculations and the subsequent calculations of the electronic excitation spectra, the B3-LYP functional¹⁹ as implemented in TURBOMOLE²⁰ was used. The excitation energies were obtained at the density functional level by using the time-dependent perturbation theory approach (TD-DFT),²¹⁻²⁵ which is a DFT generalization of the Hartree–Fock linear response (HF-LR) or random-phase approximation (RPA) method.²⁶

In all calculations, the Karlsruhe split-valence quality basis sets²⁷ augmented with polarization functions²⁸ were used (SVP). The Stuttgart effective core potentials in TURBOMOLE were used for Au and Cu.²⁹ Calculations were performed without any assumption of symmetry for **1a–3a**.

Synthesis

Preparation of [AuCu(C₆F₅)₂(N≡C-Me)₂] (1). To an acetonitrile solution (20 ml) of [Au₂Ag₂(C₆F₅)₄(N≡C-Me)₂]_n⁸ (96 mg, 0.070 mmol) was added CuCl (14 mg, 0.141 mmol) and a precipitate is observed (AgCl). The mixture was stirred for 2 h and the solid was eliminated by filtration. The solvent of the solution was evaporated to *ca*. 5 ml and addition of Et₂O (20 ml) at low temperature led to precipitation of complex **1** as a white solid. Yield: 70%. $\Lambda_{\rm M} = 112 \,\Omega^{-1} \,{\rm cm}^2 \,{\rm mol}^{-1}$. Elemental analysis (%) calcd. for **1** (C₁₆H₆AuCuF₁₀N₂): C 28.40, H 0.89, N 4.14; found: C 28.28, H 0.78, N 4.33; ¹⁹F (298 K, CD₃CN) $\delta = -162.84 \,({\rm m}, 2F, F_m)$, $-161.64 (t, 1F, F_p, J_{F_0-F_p} = 19.4 \,{\rm Hz}), -114.80 \,({\rm m}, 2F, F_o) \,{\rm ppm}; {}^{1}{\rm H}$ (298 K, CD₃CN) $\delta = 1.95 \,({\rm s}, 3{\rm H}, {\rm CH}_3) \,{\rm ppm}; \,{\rm MS:} m/z$ (%) 531.3 [Au(C₆F₅)₂]⁻, 1125.4 [Au₂Cu(C₆F₅)₄]⁻ (ES-).

[AuCu(C₆F₅)₂(N≡C-Ph)₂]₂ (2). To a toluene solution (15 ml) of [AuCu(C₆F₅)₂(N≡C-Me)₂] (1) (95 mg, 0.140 mmol) was added N≡C-Ph (60 µl, exc.) and after 30 min of stirring the solvent was evaporated to *ca*. 5 ml. Addition of *n*-hexane gave rise to a white solid. Yield: 50%. $\Lambda_{\rm M} = 234 \,\Omega^{-1} \,{\rm cm}^2 \,{\rm mol}^{-1}$. Elemental analysis (%) calcd. for **2** (C₅₂H₂₀Au₂Cu₂F₂₀N₄): C 38.99, H 1.26, N 3.50; found: C 38.99, H 1.40, N 3.41; ¹⁹F (298 K, CD₃CN) δ = −162.86 (m, 2F, F_m), −161.67 (t, 1F, F_p, J_{Fo-Fp} = 19.4 Hz), −114.81 (m, 2F, F_o) ppm; ¹H (298 K, CD₃CN) δ = 7.30 (m, 2H, H₃, H₅), 7.44 (m, 1H, H₄), 7.48 (m, 2H, H₂, H₆) ppm; MS: *m/z* (%) 530.6 [Au(C₆F₅)₂]⁻, 1124.6 [Au₂Cu(C₆F₅)₄]⁻ (ES-).

[AuCu(C₆F₅)₂(N≡C-CH=CH-Ph)₂] (3). To a solution of [AuCu(C₆F₅)₂(N≡C-Me)₂] (1) (90 mg, 0.133 mmol) in 15 ml of toluene was added N≡C-CH=CH-Ph (80 µl, exc.). The mixture was stirred for 30 min and the solvent was evaporated to *ca*. 5 ml. Addition of *n*-hexane (15 ml) led to precipitation of complex **3** as a white solid. Yield: 60%. $\Lambda_{\rm M} = 112 \ \Omega^{-1} \ {\rm cm}^2 \ {\rm mol}^{-1}$. Elemental analysis (%) calcd. for **3** (C₃₀H₁₄AuCuF₁₀N₂): C 42.25, H 1.65, N 3.28; found: C 42.57, H 1.81, N 3.80; ¹⁹F (298 K, CD₃CN) δ = -162.86 (m, 2F, F_m), -161.67 (t, 1F, F_p, J_{F0-Fp} = 19.4 Hz), -114.80 (m, 2F, F_o) ppm; ¹H (298 K, CD₃CN) δ = 5.86 (m, 1H, CH-CN), 7.21–7.30 (m, 1H, CH–Ph), 7.26 (m, 5H, Ph) ppm; MS: m/z (%) 530.5 [Au(C₆F₅)₂]⁻, 1124.5 [Au₂Cu(C₆F₅)₄]⁻ (ES–).

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References

- 1 Modern Supramolecular Gold Chemistry, ed. A. Laguna, Wiley-VCH, Weinheim, 2008.
- 2 (a) P. Pyykkö, Chem. Rev., 1997, 97, 597; (b) P. Pyykkö, Angew. Chem., Int. Ed., 2004, 43, 4412; (c) P. Pyykkö, Inorg. Chim. Acta, 2005, 358, 4113; (d) P. Pyykkö, Chem. Soc. Rev., 2008, 37, 1967.
- 3 (a) E. J. Fernández, A. Laguna and J. M. López-de-Luzuriaga, *Dalton Trans.*, 2007, 1969; (b) J. M. Forward, J. P. Fackler, Jr., Z. Assefa, in *Optoelectronic Properties of Inorganic Compounds*, ed. D. M. Roundhill and J. P. Fackler, Jr., Plenum, New York, 1999, pp. 195–226.
- 4 (a) E. J. Fernández, A. Laguna, J. M. López-de-Luzuriaga and M. Monge, Spanish Patent P200001391, 2003; (b) E. J. Fernández, J. M. López-de-Luzuriaga, M. Monge, M. E. Olmos, J. Pérez, A. Laguna, A. A. Mohamed and J. P. Fackler, Jr., J. Am. Chem. Soc., 2003, 125, 2022; (c) E. J. Fernández, J. M. López-de-Luzuriaga, M. Monge, M. E. Olmos, R. C. Puelles, A. Laguna, A. A. Mohamed and J. P. Fackler, Jr., Inorg. Chem., 2008, 47, 8069; (d) H. V. R. Dias, H. V. K. Diyabalanage, M. G. Eldabaja, O. Elbjeiranni, M. A. Rawashdeh-Omary and M. A. Omary, J. Am. Chem. Soc., 2005, 127, 7489.
- 5 (a) E. J. Fernández, M. C. Gimeno, A. Laguna, J. M. López-de-Luzuriaga, M. Monge, P. Pyykkö and D. Sundholm, J. Am. Chem. Soc., 2000, 122, 7287; (b) E. J. Fernández, A. Laguna, J. M. López-de-Luzuriaga, M. Monge, M. Montiel, M. E. Olmos, R. C. Puelles and J. C. Sáenz, Dalton Trans., 2005, 1162; (c) E. J. Fernández, P. G. Jones, A. Laguna, J. M. López-de-Luzuriaga, M. Monge, M. E. Olmos and R. C. Puelles, Organometallics, 2007, 26, 5931; (d) E. J. Fernández, A. Laguna, J. M. López-de-Luzuriaga, M. Monge, M. E. Olmos and J. Pérez, J. Am. Chem. Soc., 2002, 124, 5942; (e) V. J. Catalano, B. L. Bennett and H. M. Kar, J. Am. Chem. Soc., 1999, 121, 10235; (f) A. Burini, J. P. Fackler, Jr., R. Galassi, B. R. Pietroni and R. J. Staples, Chem. Commun., 1998, 95; (g) A. Burini, R. Bravi, J. P. Fackler, Jr., R. Galassi, T. A. Grant, M. A. Omary, B. R. Pietroni and R. J. Staples, Inorg. Chem., 2000, 39, 3158; (h) A. Burini, A. J. P. Fackler, Jr., R. Galassi, T. A. Grant, M. A. Omary, M. A. Rawashdeh-Omary, B. R. Pietroni and R. J. Staples, J. Am. Chem. Soc., 2000, 122, 11264; (i) V. J. Catalano, M. A. Malwitz and B. C. Noll, Chem. Commun., 2001, 581.
- 6 (a) E. J. Fernández, A. Laguna, J. M. López-de-Luzuriaga, M. Monge, P. Pyykkö and N. Runeberg, Eur. J. Inorg. Chem., 2002, 750; (b) E. J. Fernández, A. Laguna, J. M. López de Luzuriaga, M. Monge, M. E. Olmos and R. C. Puelles, J. Phys. Chem. B, 2005, 109, 20652; (c) E. J. Fernández, J. M. López-de-Luzuriaga, M. Monge, M. Montiel, M. E. Olmos, J. Pérez, A. Laguna, F. Mendizabal, A. A. Mohamed and J. P. Fackler, Jr., Inorg. Chem., 2004, 43, 3573; (d) E. J. Fernández, A. Laguna, J. M. López de Luzuriaga, F. Mendizabal, M. Monge, M. E. Olmos and J. Pérez, Chem.-Eur. J., 2003, 9, 456; (e) E. J. Fernández, P. G. Jones, A. Laguna, J. M. López-de-Luzuriaga, M. Monge, M. E. Olmos and J. Pérez, Inorg. Chem., 2002, 41, 1056; (f) E. J. Fernández, A. Laguna, J. M. López-de-Luzuriaga, M. Monge, M. E. Olmos and M. Montiel, Inorg. Chem., 2007, 46, 2953; (g) E. J. Fernández, A. Laguna, J. M. López-de-Luzuriaga, M. Monge, M. Nema, M. E. Olmos, J. Pérez and C. Silvestru, Chem. Commun., 2007, 571; (h) M. A. Carvajal, S. Alvarez and J. J. Novoa, Chem.-Eur. J., 2004, 10, 2117; (i) M. A. Carvajal, J. J. Novoa and S. Alvarez, Theor. Chem. Acc., 2006, 116, 472; (j) S.-L. Zheng, C. L. Nygren, M. Messerschmidt and P. Coppens, Chem. Commun., 2006, 3711; (k) S.-L. Zheng, A. Volkov, C. L. Nygren and P. Coppens, Chem.-Eur. J., 2007, 13, 8583.
- 7 E. J. Fernández, A. Laguna, J. M. López-de-Luzuriaga, M. Monge, M. Montiel and M. E. Olmos, *Inorg. Chem.*, 2005, **44**, 1163.
- 8 E. J. Fernández, A. Laguna, J. M. López-de-Luzuriaga, M. Monge, M. Montiel, M. E. Olmos and M. Rodríguez-Castillo, *Organometallics*, 2006, 26, 3639.

- 9 (a) P. C. Ford, E. Cariati and J. Bourassa, *Chem. Rev.*, 1999, 99, 3625;
 (b) D. R. McMillin and K. M. McNett, *Chem. Rev.*, 1998, 98, 1201.
- 10 Y. Zhang, W. Sun, A. M. Santos and F. E. Kühn, *Catal. Lett.*, 2005, 101, 35.
- 11 V. G. Albano, C. Castellari, C. Femoni, M. C. Iapalucci, G. Longoni, M. Monari and S. Zacchini, J. Cluster Sci., 2001, 12, 75.
- 12 H.-J. Haupt, O. Seewald, U. Florke, V. Buss and T. Weyhermuller, J. Chem. Soc., Dalton Trans., 2001, 3329.
- 13 C. E. Moore, Natl. Stand. Ref. Data Ser. (US, Natl. Bur. Stand). NSRDS-NBS, 1971, 35, 51.
- 14 Z. Mao, M. Y. Chao, Z. Hui, C. M. Che, W. F. Fu, K. K. Cheung and N. Zhu, *Chem.-Eur. J.*, 2003, 9, 2885.
- 15 (a) S. Wang, G. Garzón, C. King, J. C. Wang and J. P. Fackler, Jr., *Inorg. Chem.*, 1989, **28**, 4623; (b) M. Wrighton and D. L. Morse, *J. Am. Chem. Soc.*, 1974, **96**, 998.
- 16 M. K. Itokazu, A. S. Polo and N. Y. Murakami Iha, J. Photochem. Photobiol., A, 2003, 160, 27.
- 17 (a) S. Sakaki, H. Mizutani and Y. Kase, *Inorg. Chem.*, 1992, 31, 4575;
 (b) M. K. Eggleston, D. R. McMillin, K. S. Koenig and J. A. Pallenberg, *Inorg. Chem.*, 1997, 36, 172; (c) R. M. Everly, R. Ziesel, J. Suffert and D. R. McMillin, *Inorg. Chem.*, 1991, 30, 559; (d) K. Shinozaki and Y. Kaizu, *Bull. Chem. Soc. Jpn.*, 1994, 67, 2435.

- 18 G. M. Sheldrick, SHELXL-97, Program for refinement of crystal structures, University of Göttingen, Germany, 1997.
- 19 (a) A. D. Becke, J. Chem. Phys., 1992, 96, 215; (b) A. D. Becke, J. Chem. Phys., 1993, 98, 5648; (c) C. Lee, W. Yang and R. G. Parr, Phys. Rev. Lett., 1998, B37, 785.
- 20 R. Ahlrichs, M. Bär, M. Häser, H. Horn and C. Kölmel, *Chem. Phys. Lett.*, 1989, **162**, 165.
- 21 R. Bauernschmitt and R. Ahlrichs, Chem. Phys. Lett., 1996, 256, 454.
- 22 R. Bauernschmitt and R. Ahlrichs, J. Chem. Phys., 1996, 104, 9047.
- 23 R. Bauernschmitt, M. Häser, O. Treutler and R. Ahlrichs, *Chem. Phys. Lett.*, 1997, 264, 573 and references therein.
- 24 E. K. U. Gross and W. Kohn, Adv. Quantum Chem., 1990, 21, 255.
- 25 M. E. Casida, in *Recent advances in density functional methods*, ed. D. P. Chong, World Scientific, Singapore, 1995, vol. 1.
- 26 J. Olsen and P. Jørgensen, in *Modern electronic structure theory*, ed. D. R. Yarkony, World Scientific, London, 1995, vol. 2.
- 27 A. Schäfer, H. Horn and R. Ahlrichs, J. Chem. Phys., 1992, 97, 2571.
- 28 T. H. Dunning, Jr., J. Chem. Phys., 1994, 100, 5829.
- 29 D. Andrae, U. Haeussermann, M. Dolg, H. Stoll and H. Preuss, *Theor. Chim. Acta*, 1990, 77, 123.