
Luminescence in Gold-Heterometal Complexes*

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Received: 18 December 2000

There are four types of gold-heteroatom complexes which display luminescence: dinuclear complexes, tri- and tetranuclear complexes, polymeric chains, and clusters. The present state of knowledge on the preparation and properties of each of these types is summarized here.

Following the first report of a luminescent gold(I) complex ($[\text{AuClPPH}_3]$) in 1970 by Dory *et al* (1), the study of luminescent gold(I) complexes has developed very rapidly during the last three decades. It has been shown that the luminescence has its origin in the nature of the ligands, in the geometry around the metal centre or in the presence of metal-metal interactions. These studies have led to a definition of the conditions needed for a gold complex to show luminescence (2, 3).

The most recent studies have been concerned with the synthesis of heterometallic systems with short metal-metal interactions and the determination of their optical properties. These complexes, are undoubtedly interesting from a theoretical viewpoint and include a new class of photoluminescent materials in which the emission results mainly from the interactions among the different metal centres.

The nature of the emissive properties of some of these complexes makes them suitable for use in selective sensors for organic or inorganic materials; and for others it is possible to obtain information about their electronic structure, which is responsible for example, for their conducting characteristics. In short, the understanding of the photophysics and photochemistry of this type of substance could permit the design of complexes with appropriate metals and ligands chosen for individual applications. Consequently, areas such as microelectronics and medicine could benefit from the growing research in

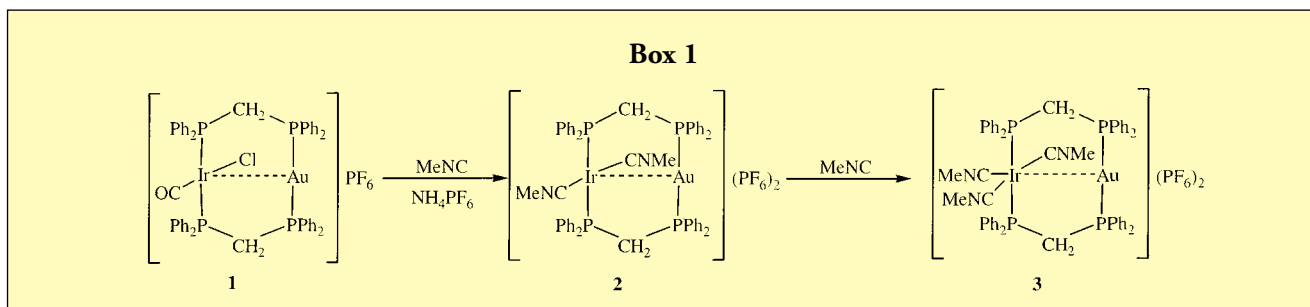
this field, where the needs for optoelectronic materials for a range of applications is increasing every day.

In this paper we review luminescent complexes containing gold-heterometal interactions. It is divided into four parts: dinuclear complexes, tri- and tetranuclear derivatives, polymeric chains, and clusters.

DINUCLEAR COMPLEXES

The first study of a luminescent heterodinuclear complex $[\text{AuIrCl}(\text{CO})(\text{dppm})_2](\text{PF}_6)$ (1) (dppm = bis(diphenylphosphino)methane), which incorporates one d^{10} ion (Au(I)) and a d^8 ion (Ir(I)) was reported by Balch *et al* in 1990 (4). The metal-metal separation in this complex is 2.986(1) Å and the absorption spectrum has a band at 440 nm ($\epsilon = 18600 \text{ M}^{-1}\text{cm}^{-1}$) and a weaker band at 518 nm ($\epsilon = 800 \text{ M}^{-1}\text{cm}^{-1}$) that are assigned to a $d\sigma^* \rightarrow p\sigma$ transition and the spin-forbidden counterpart of this transition, respectively. The emission spectrum recorded at -78°C consists of two bands: a strong one at 498 nm, assigned to fluorescence, and a weak one at 570 nm, assigned to phosphorescence. If the temperature is lowered to -196°C these bands move to 484 and 582 nm, changing their relative intensity, a result which is explained by the authors as a temperature-dependent quenching of the phosphorescence.

* Dedicated to Professor R Usón on the occasion of his 75th birthday



Treatment of this complex with methyl isocyanide and ammonium hexafluorophosphate (see Box 1) produces the dinuclear derivatives $[\text{AuIr}(\text{CNCH}_3)_2(\text{dppm})_2](\text{PF}_6)_2$ (**2**) and $[\text{AuIr}(\text{CNMe})_3(\text{dppm})_2](\text{PF}_6)_2$ (**3**) (5). In the case of the former, as for the precursor complex (**1**), two absorption bands appear in the spectrum: a strong band at 492 nm ($\epsilon = 5100 \text{ M}^{-1}\text{cm}^{-1}$), which is assigned to the $\sigma^*(d_z^2 d_z^2) \rightarrow (\sigma p_z p_z)$ transition (z axis along the metal-metal bond), and the counterpart of this transition at 608 nm ($\epsilon = 90 \text{ M}^{-1}\text{cm}^{-1}$). The emission bands are at 540 nm and 668 nm and are assigned as being due to fluorescence and phosphorescence, respectively, on the basis of measurements of their lifetimes. By contrast, the tris(methylisocyanide) complex does not have the 492 nm absorption band in its spectrum and instead has two bands at 332 nm ($\epsilon = 6700 \text{ M}^{-1}\text{cm}^{-1}$) and 298 nm ($\epsilon = 11000 \text{ M}^{-1}\text{cm}^{-1}$), with a phosphorescent emission at 580 nm. This result can be explained on the basis of the molecular orbital diagram shown in Figure 1. This diagram for complex (**2**) shows the filled d_z^2 and empty p_z orbitals for iridium and gold (z axis along the Au-Ir interaction). Addition of an axial methylisocyanide ligand fills the empty p_z orbital, now involved in the new Ir-C bond and subsequently raises the filled d_z^2 orbital; thus, the $\sigma(d_z^2 d_z^2) \rightarrow \sigma(p_z p_z)$

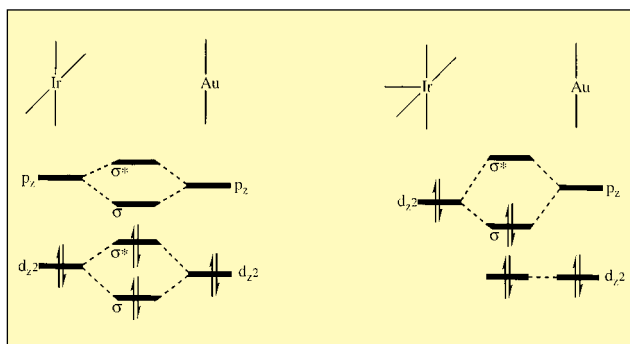


Figure 1 Qualitative molecular orbital diagrams for the gold-iridium complexes $[\text{AuIr}(\text{CNCH}_3)_2(\text{dppm})_2](\text{PF}_6)_2$, **2** and $[\text{AuIr}(\text{CNMe})_3(\text{dppm})_2](\text{PF}_6)_2$, **3**

transition assigned previously to the band at 492 nm is lost. Moreover, the character of the bond goes from a symmetrical interaction to a donor(iridium- d_z^2)-acceptor(gold- p_z) one, in accordance with the gold-iridium distances found experimentally (2.944(1) Å for **2**; 2.817(1) Å for **3**).

In addition, the ligands can play a significant role in the optical properties of binuclear complexes. In the complex $[\text{AuPt}(\text{CN})_2(\text{dppm})_2]\text{ClO}_4$ (**4**) (6) an intense absorption band at 320 nm is associated with the metal-metal interaction. As before, this band is also assigned to a $d\sigma^* \rightarrow p\sigma$ transition, which is dipole-allowed, and in the emission spectrum the dominant feature is an intense band at 570 nm, whose long excited state lifetime suggests that the emission should come from a spin-triplet excited state $^3[\text{Au-Pt}]$ and is, thus, assigned as phosphorescence. This state has turned out to be an excellent reductant with a rich photochemistry. Nevertheless, molecular orbital calculations carried out on this complex (**7**) indicate that the transition responsible for the luminescence ($d\sigma^* \rightarrow p\sigma$) has a substantial contribution from the P-Pt(CN)₂-P moiety and it is not only metal localized. Therefore, it could be more appropriate to describe it as a metal perturbed $\text{Pt}(5d_z^2) \rightarrow (6p_z, \pi^*)$ charge transfer transition.

In the complex $[\text{AuPt}(\text{PhC}\equiv\text{C})_2(\text{dppm})_2]$ (**5**) (8), where the ligands bonded to platinum are phenylacetylide, although the same transition is proposed, the calculations suggest a significant contribution from the empty π^* orbitals of the phenylacetylide in the lowest electronic excited state of the dinuclear complex. Moreover, the emission centred at about 500 nm has a vibrational structure with a spacing of 2106 cm^{-1} , corresponding to the stretching $\nu(\text{C}\equiv\text{C})$ mode.

The same authors have also studied the optical properties of the gold-rhodium complex $[\text{AuRh}(\text{CN}^t\text{Bu})_2(\text{dppm})_2](\text{ClO}_4)_2$ (**6**) (9). In this complex, which is similar to the heterobimetallic complexes $[\text{AuPt}(\text{CN})_2(\text{dppm})_2]\text{ClO}_4$ (**4**) and $[\text{AuPt}(\text{PhC}\equiv\text{C})_2(\text{dppm})_2]$ (**5**), the antibonding

interaction between the dz^2 orbitals of rhodium and gold give rise to $d\sigma^*$, while the bonding interaction of the p_z orbitals leads to $p\sigma$. Thus, the two emission bands centred at 500 nm and 610 nm are derived from the $^1(d\sigma^*p\sigma)$ and $^3(d\sigma^*p\sigma)$ states, respectively. Nevertheless, the analysis of the excitation spectrum reveals that the transition $^1(d\sigma^* \rightarrow p\sigma)$ shows that this could be mainly derived from the $Rb \rightarrow \pi^*$ (isocyanide, phosphine) transition.

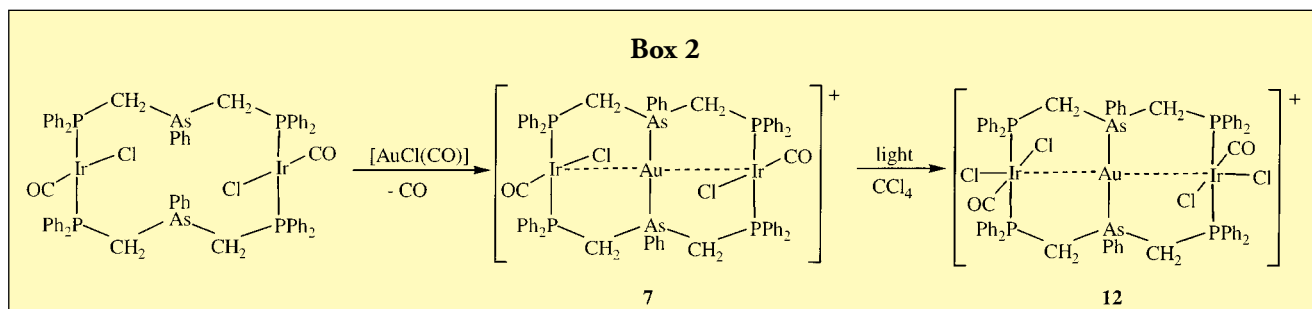
TRI- AND TETRANUCLEAR COMPLEXES

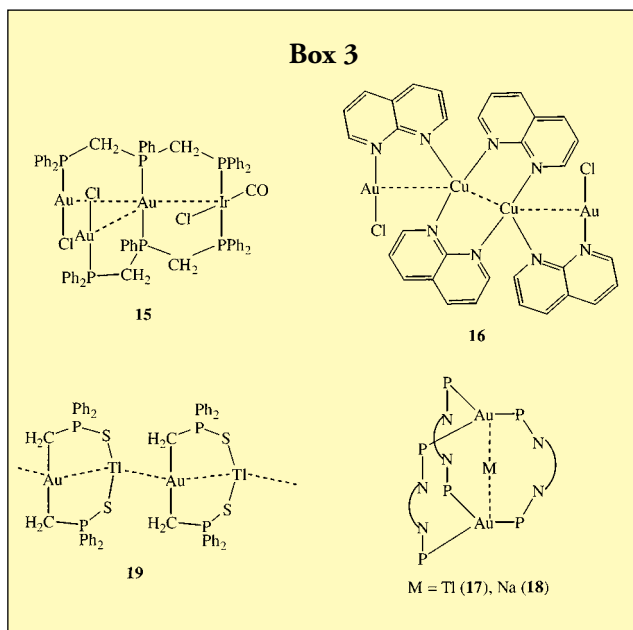
Heterotrinnuclear complexes can readily be obtained using binuclear metallomacrocycles as precursors (Box 2). For example, the incorporation of a gold centre into a diiridium macrocycle leads to the trinuclear complexes $[\text{AuIr}_2\text{X}_2(\text{CO})_2(\text{dpma})_2]\text{BPh}_4$ (**10**) ($\text{X} = \text{Cl}$, **7**; Br , **8**; I , **9**) ($\text{dpma} = \text{bis}(\text{diphenylphosphinomethyl})\text{phenylarsine}$). In contrast, the corresponding $d^{10}-d^8-d^{10}$ complex $[\text{Au}_2\text{IrCl}(\text{CO})(\text{dpma})_2]^{2+}$ (**10**) (**11**) is obtained in a surprising reaction starting from the iridium compound $[\text{Ir}(\text{CO})(\text{dpma})_2](\text{PF}_6)$ (**11**) by reaction with the gold (I) precursor $[\text{AuCl}(\text{SMe}_2)]$. The synthesis of both d^8-d^{10} and $d^{10}-d^8-d^{10}$ systems allows an interesting comparison. Both systems show similar absorption bands at 508 nm ($\epsilon = 32000 \text{ M}^{-1}\text{cm}^{-1}$) and 498 nm ($\epsilon = 31400 \text{ M}^{-1}\text{cm}^{-1}$), respectively, and in both of them the transition involves a combination of the filled d_z^2 and empty p_z orbitals, with the z axis being oriented along the metals in the same way as for the dinuclear complexes described previously. Regarding the emission spectra, the former shows bands at 606 (Cl), 614 (Br) or 624 (I) nm and the latter two bands: a high energy emission at 560 nm and a low energy emission at 680 nm. On cooling to -196°C , the intensity of the low energy band increases relative to that of the higher energy band. This fact supports the assignment of these bands to fluorescence and phosphorescence respectively. Finally, complex

$[\text{AuIr}_2\text{Cl}_2(\text{CO})_2(\text{dpma})_2]^+$ (**7**) is able to react with carbon tetrachloride under UV light, yielding the oxidized product $[\text{AuIr}_2\text{Cl}_4(\text{CO})_2(\text{dpma})_2]^+$ (**12**) (see Box 2).

Related polynuclear complexes can be prepared starting from the mononuclear iridium complex $[\text{Ir}(\text{CO})(\text{dpmp})](\text{PF}_6)$ (**13**) ($\text{dpmp} = \text{bis}(\text{diphenylphosphinomethyl})\text{phenylphosphine}$) (**12**). Its reaction with KCN and $[\text{AuCl}(\text{SMe}_2)]$ leads to the trinuclear complex $[\text{Au}_2\text{Ir}(\text{CN})_2(\text{dpmp})_2](\text{PF}_6)$ (**14**). Reaction with three equivalents of the same gold(I) precursor gives rise to the tetranuclear $[\text{Ir}(\text{CO})\text{ClAu}(\text{AuCl})_2(\text{dpmp})_2](\text{PF}_6)$ (**15**) (Box 3). In this complex the coordination of the central gold atom is unusual, since it is in close contact with the other two gold atoms with the iridium centre giving rise to a $d^8-d^{10}(d^{10})-d^{10}$ system. Its absorption spectrum shows an intense absorption at 454 nm ($\epsilon = 9500 \text{ M}^{-1}\text{cm}^{-1}$) assigned to a $\sigma^*(d_z^2, d_z^2, d_z^2) \rightarrow \sigma(p_z p_z p_z)$ transition which is delocalized along the nearly linear Au-Au-Ir unit. The emission spectrum shows two bands at 568 and 660 nm, the intensities of which are temperature dependent. As for complex (**14**) the absorption spectrum consists of one band at 578 nm ($\epsilon = 15800 \text{ M}^{-1}\text{cm}^{-1}$). Likewise, as for the other trinuclear complexes, the emission spectrum shows two bands at 612 and 782 nm, which are temperature dependent. The observed shift of the bands in both compounds to lower energies, compared to the analogous binuclear complex (**1**), can be attributed to the involvement of three metal ions within the chromophore, and this leads to an increase of the energy of the σ^* orbital and a stabilization of the σ orbital; thus the gap between them is reduced.

In case of the tetranuclear complex $[\text{AuCu}(\text{PPh}_3)(\mu\text{-C}_7\text{H}_5\text{N}_2)_2]_2$ (**16**) (**13**) (Box 3), two different metal-metal interactions appear: gold-copper of $3.0104(6) \text{ \AA}$ and copper-copper of $2.941(1) \text{ \AA}$. The product has emission bands at 440 nm in solution and at 550 nm in the solid state. From molecular orbital calculations, these bands can be assigned to a





transition from the π^* orbital of the 7-azaindolate ligand to the d_z^2 orbital of Cu(I), but the ligand emission is nevertheless strongly affected by Au(I). The difference in the emission properties in the solid state and in solution arises from the fact that while the $\text{Au}^1 \cdots \text{Cu}^1$ interaction may exist in the solid state, it may not exist in solution because of the non rigid structure of the complex.

The structures of trinuclear complexes in which the metals are in close contact are described by Catalano *et al* (14). The compounds of general formula $[\text{Au}_2\text{M}(\text{PPh}_2\text{phen})_3](\text{PF}_6)_2$ ($\text{M} = \text{Tl}$, **17**; Na , **18**) ($\text{PPh}_2\text{phen} = 2,9$ -bis(diphenylphosphino)-1,10-phenanthroline) are based on trigonal Au(I) centres, encapsulating Tl(I) or Na ions (see Box 3). The bands that appear in the electronic absorption spectra of both complexes are assigned to intraligand transitions. In the case of the gold-thallium complex, however, there are two bands at 390 and 600 nm. The low energy emission is assigned to a metal-centred phosphorescence process, based on its large Stoke's shift, long lifetime (10 μs), and the independence of solvent, whereas the high energy band is likely to arise from a fluorescence process. The nature of the intense emission can be attributed to the strong Au-Tl interaction of about 2.91 Å. The corresponding sodium species, which shows an emission at 580 nm, is considerably less emissive in the fluid state, perhaps due to the presence of a dissociative equilibrium, which is favoured by the loosely-held Na^+ ion.

POLYMERIC CHAINS

The first report of an extended linear chain that exhibits luminescence was published by Fackler *et al* in 1988 (15). It described the gold-thallium complex $[\text{AuTl}(\text{MTP})_2]$ (**19**) ($\text{MTP} = \text{Ph}_2\text{P}(\text{CH}_2)\text{S}$) that forms a one dimensional polymer in the solid state with short relativistic Tl-Au bonds of about 3 Å (Box 3). Following this, the reaction between the same gold(I) precursor, $\text{PPN}[\text{Au}(\text{MTP})_2]$, and $\text{Pb}(\text{NO}_3)_2$ in a 2:1 molar ratio, was reported to yield a luminescent gold-lead extended linear chain product. The chain is formed by the interaction between the gold centres of the $[\text{Au}_2\text{Pb}(\text{MTP})_4]$ (**20**) units (16).

The gold-thallium complex (**19**) has one band in its absorption spectrum at 320 nm ($\epsilon = 2900 \text{ M}^{-1}\text{cm}^{-1}$). In the emission spectrum the band that appears at 602 nm (77 K) in the solid state is displaced to 536 nm when the measurement is carried out in frozen solution. This energy difference could be caused by the aggregation of $[\text{AuTl}(\text{MTP})_2]$ units in the solid state to a greater extent than in solution.

In the case of the gold-lead compound, the emission spectrum shows a strong dependence on both the temperature and the state of the sample. Thus, the emission band that appears in THF solution at 555 nm (298 K) is shifted to 480 nm in frozen solution or appears at 752 nm in the solid state. The interesting blue shift of the emission band with the decrease of temperature is described as *luminescence rigidochromism*. On the other hand, the shift to low energy in the solid state emission may be related to the polymeric structure of the complex in the solid state.

Fenske-Hall molecular orbital calculations indicate that the ground state metal-metal interactions in these compounds are the result of the mixing of the empty $6s$ and $6p_z$ orbitals of gold(I) with the filled $6s$ and the empty $6p_z$ orbitals of thallium (I) and lead (II) (see Figure 2).

By reacting a mixture of triphenylphosphine oxide, thallium nitrate and lithium bis(pentafluorophenyl) aurate(I) another gold-thallium complex of formula $[\text{AuTl}(\text{C}_6\text{F}_5)_2(\text{OPPh}_3)_2]$ (**21**) is obtained (17). This complex is the first example of an extended unsupported gold-thallium linear chain. The complex shows luminescence in the solid state at 293 K (494 nm) and at 77K (494 and 530 nm), but is not emissive in solution. This suggests that the emission arises from interactions between the metals. These interactions and, thus, their emissive properties are recovered by evaporation of the solvents, but only when these solvents do not contain halogen. The result is different when the solid is dissolved in halocarbons, because even though the emission is also

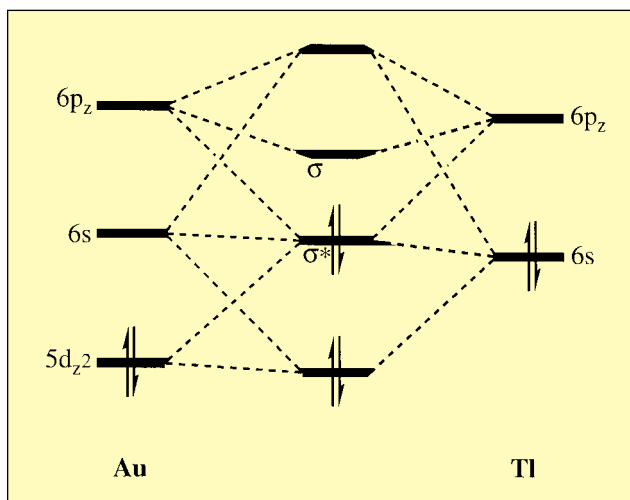


Figure 2 Qualitative molecular orbital diagrams for gold(I)-thallium(I) complexes with metal-metal interactions

quenched the evaporation of the solvent does not give the original product but an uncharacterized solid. If the dissolution in halocarbons is carried out in the dark, then the evaporation of the solvent does give rise to the original solid. This surprising result seems to indicate that the excited state reached by UV irradiation is able to react with halocarbons *via* an electron transfer reaction (Figure 3).

The use of the $[\text{Au}(\text{C}_6\text{F}_5)_2]^-$ moiety as a Lewis base also gives rise to the synthesis of structurally different heterometallic extended linear chain compounds. Very recently, a compound of formula $[\text{Au}_2\text{Ag}_2(\text{C}_6\text{F}_5)_4(\text{OCMe}_2)_2]$ (**22**) has permitted the observation of an oligomerization process in solution that leads to emission of radiation (18). This is important because in spite of the fact that metal-metal

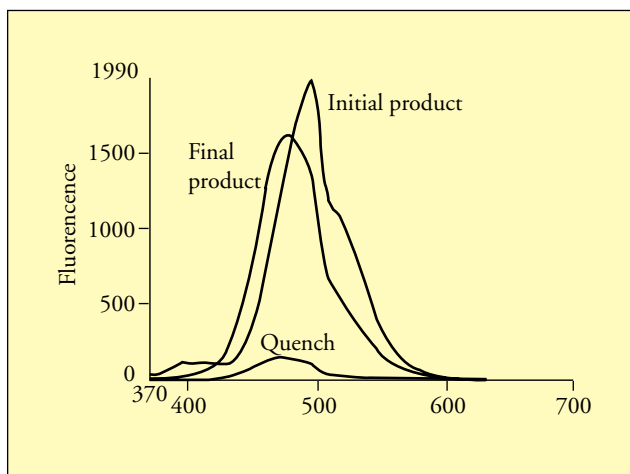


Figure 3 Emission spectra of $[\text{AuTl}(\text{C}_6\text{F}_5)_2(\text{OPPh}_3)_2]$, **21**, before and after treatment with dichloromethane

interactions are common in the solid state their presence in solution is usually controversial. For example, indications of these oligomerization processes have been observed in solutions at high concentrations (19 - 22) or by comparison of a frozen solution (77K) with solid state in the complex $[\text{AuTl}(\text{MTP})_2]$ (**19**) (15, 16), but conclusive evidence has not yet been obtained.

Complex (**22**) is emissive in the solid state (546 nm) and in solution, but it is very interesting that changes in the concentration of the sample give rise to changes in the emission wavelengths and, therefore, a deviation from Lambert-Beer's law. The representation of the emission wavelengths versus the inverse of concentration is a simple linear fit, in which the extrapolation to infinite concentration (zero on the x axis) clearly matches (547.04 nm) the solid state emission (Figure 4). This fact indicates a clear correlation between the aggregation process through gold-gold contacts in solution and the emissive behaviour in solid state.

DFT (Density Functional Theory) calculations were also carried out to assign the molecular orbitals involved in the transitions that lead to luminescence, with the conclusion that metal centred $(d\sigma^*)^1(p\sigma)^1$ or $(d\delta^*)^1(p\sigma)^1$ excited states are responsible for the luminescence in the solid state, while in dilute solutions the luminescence arises from $\pi\pi^*$ excited states in the pentafluorophenyl ligands or from π - $MMCT$ transitions (see Figure 5).

On the other hand, the use of the trinuclear carbenate $[\text{AuC}(\text{O}-\text{R})=\text{NR}'_3]$ ($\text{R} = \text{Et}$; $\text{R}' = \text{C}_6\text{H}_4\text{CH}_3$, **23**) or pirazolate $[\text{Au}(\mu\text{-C}^2, \text{N}^3\text{-Rim})_3]$ ($\text{Rim} = \text{benzylimidazolate}$, **24**; methylimidazolate , **25**) ring complexes in reactions with silver(I) or thallium(I) salts

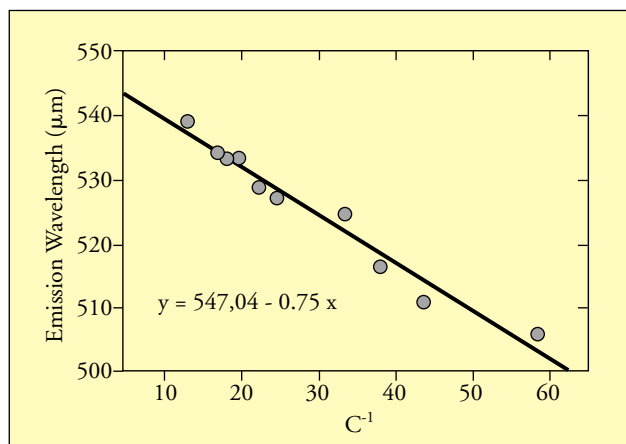


Figure 4 Representation of the emission wavelengths versus the inverse of concentration for complex $[\text{Au}_2\text{Ag}_2(\text{C}_6\text{F}_5)_4(\text{OCMe}_2)_2]$, **22**

produces luminescent sandwich-type compounds having stacked structures (23, 24). Thus, the resultant ($\text{Au}_3\text{MAu}_3, \dots$) ($\text{M} = \text{Ag}, \text{Tl}$) pattern of metal atoms also shows short aurophilic interactions between Au_3MAu_3 molecular units. These complexes display a strong visible luminescence under UV excitation, which is sensitive to temperature, (*luminescence thermochromism*) as well as to the metal ion interacting with the six gold atoms. The bands present in the emission spectra are due to phosphorescence, and this is consistent with their extended-chain structures. Moreover, the bands are likely to be associated with excited states that are delocalized along the crystallographic axis of the chain. Thus, when the temperature is decreased, the metal-metal distances are reduced, resulting in a lower band gap energy. Consequently, a red shift of the luminescence is observed when the materials are cooled.

CLUSTERS

In spite of the great number of gold-heterometal clusters synthesized, as far as we are aware only in a few of them have had their optical properties determined. For instance, the complexes $[\text{AuPt}_2\text{X}_3(\text{dppm})_2]$ ($\text{X} = \text{Cl}$, **26**; Br , **27**) (25) show intense red luminescence (674 nm, $\text{X} = \text{Cl}$; 660 nm, $\text{X} = \text{Br}$) in frozen solutions, but no emission at room temperature, where perhaps the gold atom is not in contact with the platinum centres. Molecular orbital calculations performed on $\text{Pt}_2(\text{PH}_3)_4\text{Cl}_2$ and on the AuCl adduct indicates that adding the third metal centre produces a significant modification of the HOMO and LUMO orbitals giving rise to a stabilization of the LUMO (originally Pt-Pt $d\sigma^*$) and HOMO (originally Pt-Pt $d\sigma$). Thus,

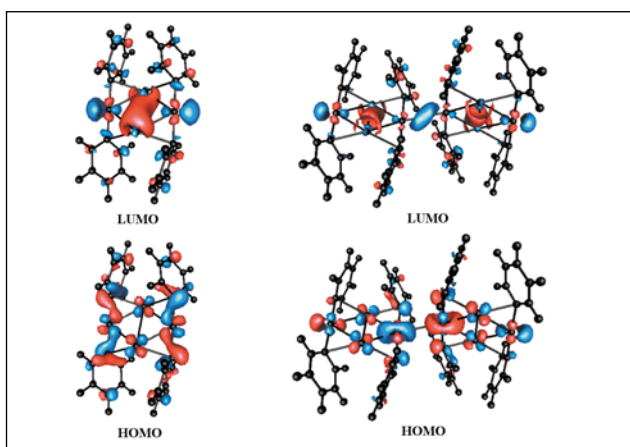


Figure 5 HOMO and LUMO molecular orbitals for the $[\text{AuAg}(\text{C}_6\text{H}_5)_2]_2$ and $[\text{AuAg}(\text{C}_6\text{H}_5)_2]_4$ model systems

both orbitals acquire the character of the added metal.

The complex $[\text{Au}_2\text{Pt}_2(\text{dmb})_2(\text{PPh}_3)_4](\text{PF}_6)_2$ (**28**) ($\text{dmb} = 1,8\text{-diisocyno-}p\text{-menthane}$) (26) has a metal-metal bond that is encapsulated inside an organometallic fragment. This cluster is luminescent and its emission band, placed at 875 nm (shoulder at 920 nm) at 12 K, is the lowest energy band ever reported for a tetranuclear compound. This is assigned to phosphorescence, based on the large Stokes shift and lifetime measurements. In this case the molecular orbital calculations show that the HOMO is largely localized within the platinum metals and the LUMO, within the CNR system; nevertheless, the asymmetry of the band with a relative intensity, which remains constant with the temperature, cannot exclude a $\text{PtAu} \rightarrow \pi^*(\text{CNR})$ charge transfer.

ACKNOWLEDGEMENT

The support of the Spanish DGES (PB97-1010-C02-02) is gratefully acknowledged.

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