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Factors Affecting Luminescence and Aurophilicity on Digold(I) Complexes and their Potential as Cation Probes

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Abstract

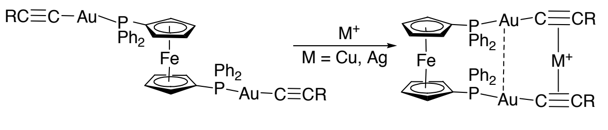
In the last few years we have analysed the factors that affect the structures and luminescence properties of Au(I) compounds, specifically in relation with the presence of aurophilic contacts and their application as cation probes. EXAFS studies have allowed us to obtain for the first time direct structural data of dissolved Au(I) compounds. An overview of the work reported to date is presented here. The optical properties of complex [Au_2Cl_2(μ-dpephos)] (dpephos = *bis*(2-diphenylphosphino) phenylether, 1) have been revisited and new results are now included. New aspects on the use of the complexes as Ag(I) probes are also discussed.

Introduction

The emissive properties of many d^{10}-metal complexes are often influenced by the presence of metal···metal (metallophilic) interactions, in particular, in the case of Au(I). In general, intense low energy emission bands are related to the presence of weak interactions (2.7-3.5 Å) between neighbouring Au atoms (aurophilicity) (1-3). The possibility of switching 'on' and 'off' the emission of Au(I) compounds by favouring or restricting Au···Au (aurophilic) contacts has interested researchers for their potential as molecular sensors or optical devices. For example, Yam *et al.* (2) have used dinuclear Au(I) complexes containing crown ether fragments or alkynyl ligands to trap an additional metal ion, concomitantly modifying the optical properties of the compounds (Scheme 1). In this context, numerous studies have focused on clarifying the relationships between the structures and the optical properties of the compounds, (1) and in some cases, no clear relation between Au···Au distances and emission properties has been found (1b). One of the difficulties is to find systems in which structural and electronic factors can be 'tuned' independently, so that the influence of each factor on the aurophilic distances and properties of the compounds can be assessed. Moreover, aurophilicity itself is difficult to assess in dissolved samples, with Au···Au association in solution normally inferred through indirect methods, such as NMR and luminescence studies (3).

Strategy

In an attempt to clarify luminescence-structure relationships in Au(I) complexes, we decided to prepare digold(I) compounds using the diphosphine ligands derived from heteroaromatic backbones (4) *bis*(2-diphenylphosphino)phenylether (dpephos), 4,6-*bis*(diphenylphosphino)dibenzofuran (dbfphos), and 9,9-dimethyl-4,5-*bis*(diphenylphosphino)xanthene (xantphos) (Chart 1) (5). It had been shown that the small variations in the backbones of these ligands affect their bite angles, but keep the electronic character relatively constant (4a). Although the bite angle relates to the chelating ability of the ligands, it may also have an effect on the metal···metal distances when bridging between two Au(I) atoms. In addition, the effect of the flexibility of the backbone on the structures of the compounds can also be analysed. Further variation of electronic and steric effects can be achieved by varying the nature of the coligands (X, Chart 1).



Scheme 1

Example of a digold compound used as cation probe by Yam et al. *(2c)*

Table 1

*Selected crystallographic data for compounds **1-5** and the free diphosphine ligands*

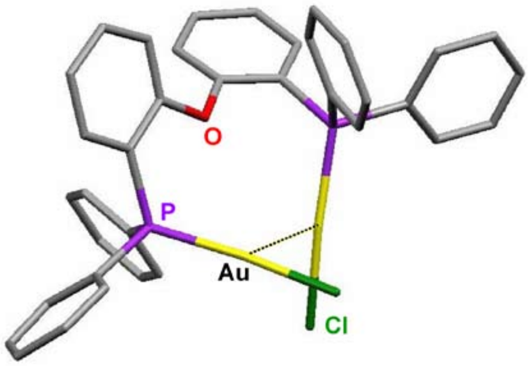
	Au···Au /Å	P – P /Å	Torsion angle Ph(O)Ph /°	Ref
dpephos	-	4.88	67	(5)
1	3.0038(6)	4.86	61	(5)
5	3.0065(15)	4.96	60	(6)
xantphos	-	4.04-4.15	0	(4a,d)
2	2.9947(4)	4.73	11	(5)
dbfphos	-	5.74	1	(4c)
3	-	5.83	1	(5)
4	3.401(1)	5.63	1	(7)

In order to obtain direct information on the solution structures of the compounds, EXAFS studies have been used to measure for the first time Au···Au distances in dissolved complexes (6). Finally, the reactivity of the digold(I) derivatives towards other d^{10}-metals has been studied (7). Some of the results of our research during the last few years are highlighted in this paper.

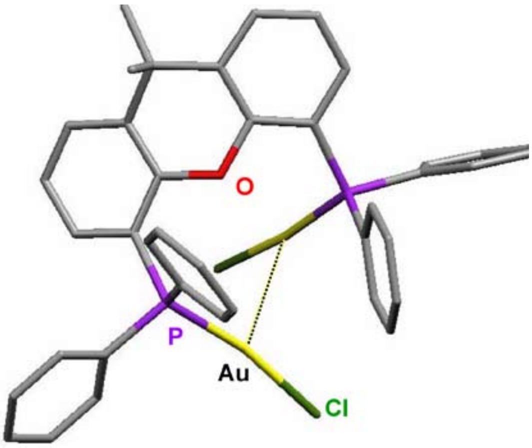
Solid-state structures

Intra vs. intermolecular weak interactions

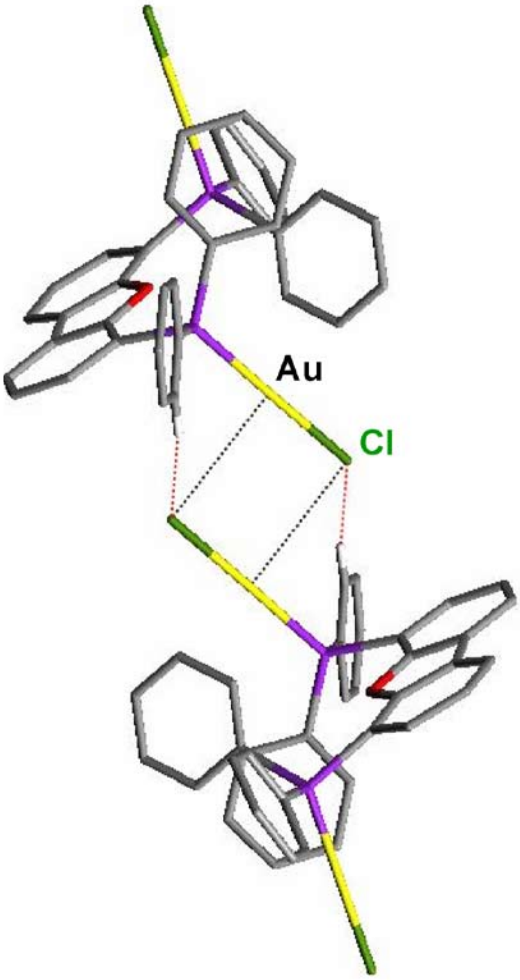
The crystal structures of the dpephos and xantphos dichloride Au(I) complexes (**1**, **2**; see Chart 1, Table 1 and Figure 1) are similar, both exhibiting Au···Au distances of *ca.* 3 Å. By contrast, the analogous compound containing dbfphos (**3**) adopts an *anti* conformation in which the metal atoms are at a long distance (7.21 Å) from each other, allowing instead the formation of intermolecular H-bonding and Au···Cl interactions (Figure 1) (5). The lack of aurophilic contact



Au···Au: 3.0038(6) Å (1)
Dpephos ligand not strained: Evidence of Au···Au contacts in concentrated solution



Au···Au: 2.9947(4) Å (2)
Xantphos ligand strained: No evidence of Au···Au contacts in solution



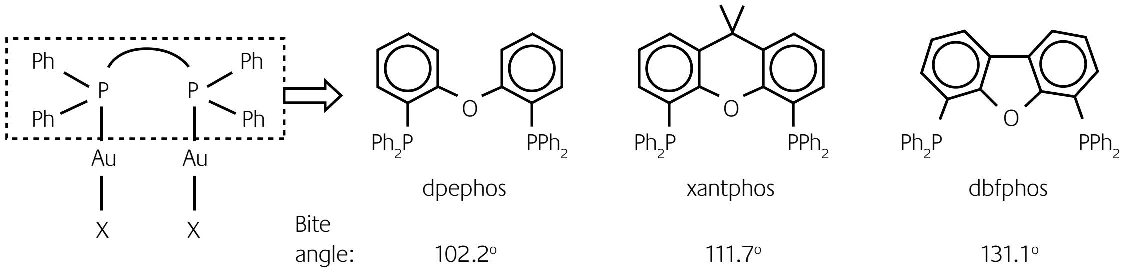
Au···Cl: 3.377 Å (3)

Figure 1

*Crystal structures of dichloride compounds **1-3** (5)*

Chart 1

Diphosphine ligands used (bite angles obtained from reference 4a) and examples of digold(I) complexes prepared



X = Cl [diphosphine = dpephos (**1**), xantphos (**2**), dbfphos (**3**)] (5)
CC(C_6H_5) [diphosphine = dbfphos (**4**)] (7)
S(C_6H_4Me-3) [diphosphine = dpephos (**5**)] (6)

in **3** could be attributed to both the rigidity and large bite angle of dbfphos. However, the structure of the alkynyl derivative [{Au(CCPh)}$_2$(μ-dbfphos)] (7) (**4**, Figure 3) shows that dbfphos can indeed accommodate an Au···Au fragment, although the interaction is relatively weak (*ca.* 3.4 Å). Such weak interaction has also been found in another dbfphos derivative: [{Au(SC_6H_4Cl-4)}$_2$(μ-dbfphos)] (8). Since both the aryl-alkynyl and aryl-sulfide ligands are more sterically demanding than chloride, the lack of aurophilicity in **3** is most likely determined by the intermolecular Au···Cl and CH···Cl interactions which, as a whole, have a greater influence on the overall structure of the complex than a relatively long aurophilic contact.

The crystal structure of the dpephos thiolate complex **5** contains an intra-molecular Au···Au contact of 3.0065(15) Å (6), which is similar in length to that in **1** (Table 1) despite the softer donor character of the thiolate ligand compared to chloride. This contrasts with prediction from theoretical studies that the aurophilic interaction energy increases with the softness of the ligand (9). Whereas some experimental evidence exists in support of this (10), it has also been shown that softer donors do not always lead to shorter Au···Au distances (11).

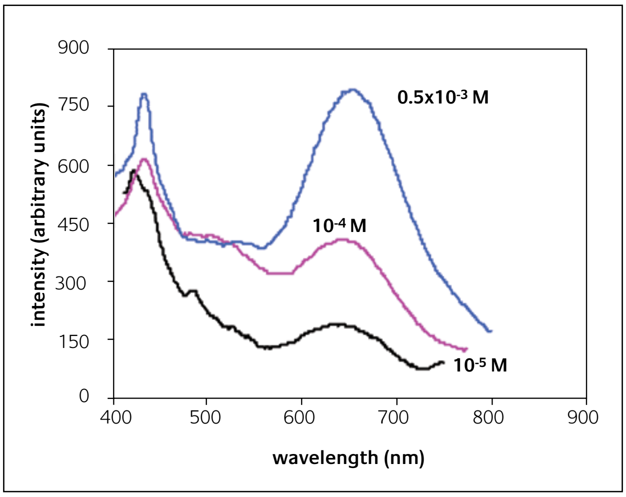
The aurophilic interaction in complex **1** or **2** forces the Au coordination environments to deviate from linearity, with P-Au-Cl angles of 170.57(9)° and 174.26(9)° for **1**, or 168.47(7)° and 173.07(6)° for **2**. Moreover, the two P-Au-Cl fragments in each compound are almost perpendicular to each other, with values of *ca.* 81° and 91° for the Cl-Au-Au-Cl torsion angle in **1** and **2**, respectively. Analogous features are observed in the crystal structure of [(AuCl)$_2${μ-(3,3'''-dihexyl-3',3''-bis(diphenylphosphino)-2,5':2',2'':5'',2'''-quaterthiophene)}] [Au···Au: 3.0879(7) Å, P-Au-Cl: 174.28(10)°, Cl-Au-Au-Cl: *ca.* 86°] (12). However, dinuclear Au-chloride complexes with more flexible and/or shorter bridging-diphosphine ligands often show both smaller torsion angles and larger P-Au-Cl angles (13). For example, [(AuCl)$_2${μ-bis(diphenylphosphino) methane}] [Au···Au: 3.351(2) Å] (13a) and [(AuCl)$_2${μ-(1,1,-bis (diphenylphosphino)bicyclopropyl)}] [Au···Au: 3.085(1) Å] (13a) have P-Au-Cl angles of *ca.* 175° and Cl-Au-Au-Cl torsion angles of *ca.* 72° and 56°, respectively. Diphosphine derivatives analogous to **3** (i.e., with an *anti* disposition of the AuCl fragments) are also known (14), but these often aggregate in chains (14a,d-j) or dimers (14a-c) through inter-molecular Au···Au contacts. Head-to-tail dimers bonded through Au···Cl contacts have been identified in the monophosphine complex [AuCl{P(C_4H_3O)$_3$}]$_2$ (15). The Au-P and Au-Cl distances in **1**-**3** range between 2.22-2.23 Å and 2.28-2.31 Å, respectively, and are not significantly different from those in analogous complexes (13-15). The Au coordination environments and torsion angles in **4** and **5** are similar to those found in **1** and **2** [**4**: P-Au-C = 166.4(2)°, 171.1(2)°, C-Au-Au-C = *ca.* 93°; **5**: P-Au-S = 172.8(2)°, 172.9(2)°, S-Au-Au-S = *ca.* 81°]. The P-Au-S/C angles are also generally smaller than those found in analogous complexes, whereas the torsion angles are larger (16).

Phosphine flexibility and bite angle

In order to gain some information about how 'comfortable' the diphosphine ligands are when bridging between two Au(I) fragments at close proximity, a comparison between the structures of the free ligands (4,5) and those of compounds **1**-**5** (5-7) has been made. Two parameters that relate to the strain of the diphosphines in the complexes are the distances between the P atoms and the torsion angles between the phenyl rings of the heteroaromatic backbone. These, together with the Au···Au distances (where appropriate) have been included in Table 1. Despite their different bite angles, both the dpephos and xantphos ligands allow similar aurophilic contacts, but the xantphos ligand in complex **2** is more strained than dpephos in **1**; *i.e.*, the distance between the P atoms of the xantphos significantly increases upon coordination and the xanthene backbone is twisted along the central ring. The dpephos, by contrast, does not need to change significantly its conformation to accommodate two Au(I) fragments in **1** or **5**. As expected, the rigid planar dibenzofuran backbone of the dbfphos does not distort on coordination. The distance between the P atoms only varies slightly from the free ligand to complexes **3** and **4**

Figure 2

*Concentration-dependent spectra of complex **1** in dichloromethane at 77 K*



(without and with aurophilic contact, respectively). Therefore, dbfphos is not significantly strained in either conformation, allowing other factors (*i.e.,* competition between *intra*- and *inter*-molecular contacts) to influence the overall structure of the complex.

Luminescence and aurophilicity: Solid-state emission of 1-3

The luminescence of dinuclear Au(I) complexes is generally considered to originate from metal-centered (MC) transitions modified by the aurophilic interaction (e.g., $d\sigma^*/d\delta^* \rightarrow p\sigma/s\sigma$ transitions, where $d\sigma^*$ or $d\delta^*$ is generated by overlap of Au $5d_{z2}$ or $5d_{x2\text{-}y2}$ orbitals, respectively) or metal-to-ligand charge transfer (MLCT). The latter can also be modified by the aurophilic contact, which gives rise to metal-metal-to-ligand charge transfer (MMLCT) states (e.g., $d\sigma^*/d\delta^* \rightarrow \pi^*$). (1-3) In addition, Patterson, Fackler et *al.* (17) have shown that the formation of excited-state Au-Au bonded species in solution is responsible for the tunable luminescence behaviour of $K[Au(CN)_2]$. Interestingly, this is dependent of concentration, temperature, solvent and excitation wavelength and reflects the presence in solution of oligomers of various lengths and geometries ($([Au(CN)_2^-]_n$; $n \geq 2$).

Regarding luminescence from the phosphine ligands, it has been established that the lowest energy absorption for aryl phosphines is associated with a $l \rightarrow a_\pi$ (or $n \rightarrow \pi^*$) transition involving the promotion of an electron from the lone pair orbital (l) on phosphorus to an empty antibonding orbital of π origin on a phenyl ring. The $l \rightarrow a_\pi$ transition becomes a $\sigma \rightarrow a_\pi$ transition on coordination, and emission bands arising from the latter are often labelled as intra-ligand charge transfer (ILCT) transitions (18). Finally, arylphosphine complexes can also show emission from intraligand (IL) states involving $\pi \rightarrow \pi^*$ transitions in the aryl substituents.

The chloride derivatives **1-3** provide a good model system to study the effect of aurophilicity on luminescence. Our research (5) showed that their emission in the solid state was clearly affected by the Au···Au interaction.

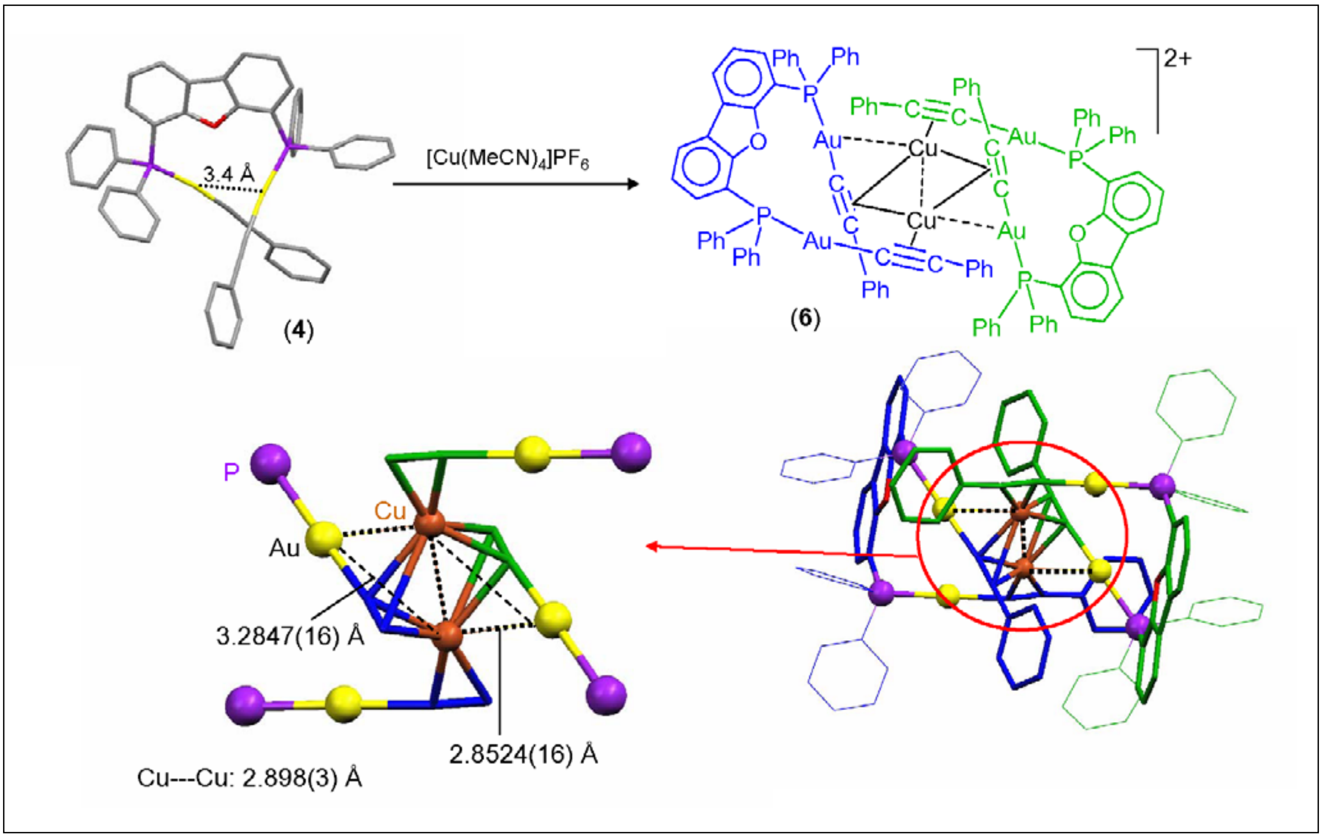


Figure 3

*Reaction of **4** with Cu(I) to give **6**. Crystal structures of **4** and **6** (7)*

Thus, whereas complex **3** shows a structured band at 420-500 nm (*r.t.* or 77 K), assigned to IL $\pi \rightarrow \pi^*$ transitions, compounds **1** and **2** exhibit an intense emission at 620 nm (*r.t.*), with a small shoulder at *ca*. 450 nm. The low energy (LE) band at 620 nm is associated to the aurophilic contact and is assigned to a MC or MMLCT transition, while the high energy (HE) emission is considered to have an ILCT ($\sigma \rightarrow a_\pi$) origin.

It is interesting to note that complex **2** showed thermochromic behaviour, with the relative intensities of the two emissions inverted at 77 K, indicative of a thermally activated energy transfer from the HE to the LE excited state (5). Complex **1** also shows a similar behaviour, but this was not previously described. In fact, subsequent work has shown a very complex optical behaviour for **1**, with a small number of samples showing 'anomalous' luminescence. The solid-state emission spectra of these 'anomalous' samples showed both at *r.t.* and 77 K one band centered at *ca*. 437 nm with a shoulder at *ca*. 482 nm, with the LE emission band at 620 nm absent. Despite extensive studies, the nature of the 'anomalous' samples could not be clarified. No significant differences were found in the ^{1}H and ^{31}P{^{1}H}-NMR spectra, CHN elemental analyses or XRPD patterns of 'normal' and 'anomalous' samples. The data were recorded for samples recrystallised from a variety of solvent mixtures, and before and after exhaustive drying, but conclusive reproducible results were not obtained. This suggests that the quenching of the emission at 620 nm is due to the presence of traces of one or more impurities, undetectable by the characterisation techniques used. Catalano et al. (19) reported the unusual luminescence behaviour of complexes [Au_2(μ-dpim)$_2$]X_2 (dpim = 2-diphenylphosphino-1-methylimidazole; X = BF_4, ClO_4), for which two different crystalline forms were identified. The formation of each form was independent of the crystallisation solvents or the anion. Both forms had identical crystal structures but exhibited different emission properties. The authors suggest that an undetectable impurity (most likely Cl anions from the precursor) was responsible for this behaviour. An analogous explanation can be proposed for the anomalous emission of complex **1**. In addition, the presence of small amounts of Au-nanoparticles or a small percentage of solvent of crystallization may also play a role. Whilst this behaviour fustrates a full understanding of the system, it highlights the sensitivity of these compounds to low levels of other species.

Aurophilicity in solution: luminescence and EXAFS studies

Neither **1** nor **2** emitted in solution at *r.t.*, but their luminescence could be recorded in dichloromethane at 77 K. (5) In these conditions complex **2** only showed one band at 430 nm suggesting that the aurophilic contacts were lost in solution. However, complex **1** still exhibited two bands at 431 and 654 nm. The presence of Au···Au interactions in solution could also be inferred from the ^{13}C-NMR spectrum of **1**, which showed inequivalent Ph groups for the diphosphine ligand (5). This can be due, but not necessarily, to a rigid structure in which Au···Au contacts are present. To clarify the solution behaviour of **1**, further investigations have been carried out, including variable-concentration luminescence studies, ESI-MS and low-temperature ^{31}P NMR spectroscopy. Results, however, are still inconclusive (see below).

The emission spectra of **1** have been measured at concentrations between 10^{-3} and 10^{-5} M in dichloromethane at 77 K. As the concentration increases the intensity of the LE band increases relative to that of the HE emission (Figure 2). Accordingly, aurophilic contacts in **1** seem to be more favoured in concentrated solutions, but the reason for this is currently not clear. Whereas concentration-dependent emission spectra have been reported for Au(I) complexes, these generally apply to compounds containing inter-molecular aurophilic contacts (3), which would be clearly less favoured in very dilute conditions. It is possible that the intra-molecular contact of **1** is lost in solution, but that aggregates or chains form at high concentrations through inter-molecular interactions. To obtain further evidence of the solution structure of **1**, ESI-MS and variable-temperature ^{31}P NMR spectra were recorded. The latter were obtained for samples at two different concentrations (10^{-3} and 10^{-4} M in $CDCl_3$) with similar results: the singlet (22.4 ppm) present at *r.t.* broadens as the temperature is lowered. This is consistent with a dynamic process in solution, but does not clarify its nature. In the mass spectrum (ESI$^+$) of **1**, peaks for [M-Cl]$^+$ and [2M-Cl]$^+$ fragments can be identified (20). While this shows that it is possible to form dimeric species at the conditions of the experiment, such species do not necessarily exist in the solutions used for luminescence/NMR measurements. It has to be noted that under the MS conditions, the compound readily looses one Cl- ligand, and this may favour aggregation. Finally, solvent quenching of the LE emission also needs to be taken into account as a plausible explanation for the concentration-dependent luminescence of **1**.

We have recently reported the first EXAFS data on aurophilic as well as Au···solvent/anion contacts for dissolved Au(I) complexes (6). Compounds **2** and **5** were included in this study, but data of good enough quality could not be obtained in the case of complex **1**, thus preventing a direct correlation between EXAFS and luminescence data. The structures modelled from the solid-state EXAFS data of **2** and **5** agreed well with the crystal structures of the compounds, including the Au···Au distances. EXAFS data obtained from *ca*. 3 x 10^{-2} M dichloromethane solutions of **2** and **5** showed that the Au···Au contact could be modelled with confidence only in the case of the dpephos complex **5**. This compound has an analogous crystal structure to **1** but luminesence studies have given inconsistent results (possibly due to the presence of small amounts of impurities, as discussed for **1** above), and again correlation of solution EXAFS and luminescence data has not been possible. Further work in this and other thiolate derivatives is currently underway and will be presented in a future paper.

Although it has not been possible to fully confirm the solution structures of the compounds, some evidence for the presence of Au···Au contacts has been obtained for dissolved **1** (luminescence, NMR) and **5** (EXAFS) but not **2**. Given the higher flexibility of the dpephos compared to the xantphos ligand, this is somewhat counterintuitive. However, as dicussed above, the more rigid xantphos ligand must undergo significant distortion upon coordination and such strain may favour the loss of the intra-molecular aurophilic contact on dissolution (Figure 1). Alternatively, the intra-molecular contact in the solid-state structures of the dpephos derivatives **1** and **5** may be replaced by inter-molecular interactions in solution.

Gold(I) complexes as cation probes: Luminescent clusters

As mentioned above, alkynyl compounds have been proposed as cation probes (2) (Scheme 1). However, since the structures of the final products in these systems are unknown, it is difficult to establish the relation between variable Au···Au distances and the observed changes in luminescence. We have reacted several dialkynyl derivatives with Ag(I) and Cu(I) and found that complicated structural changes take place. For example, the reaction between **4** and $[Cu(CH_3CN)_4]PF_6$ resulted in compound **6** (7), which crystallised as a dimer with an unusual Au_4Cu_2 core held through π-alkynyl-Cu coordination and metallophilic interactions (Figure 3) and showed an intense solid-state emission at 530 mm, significantly red-shifted from that of the parent compound (508 nm). In subsequent work, it has been shown that **4** also reacts with $AgPF_6$ to form a product in which Ag(I) coordinates to the π(C≡C) bond. The emission spectra of the Ag(I) derivative also consists of a broad band (547 nm), but at lower energy than that of the Cu(I) complex. Although the structural changes are more complicated than initially anticipated, the dialkynyl complex **4** acts as a cation probe, with different changes in the optical response when exposed to Ag(I) and Cu(I). Further work involving other metals as well as the more flexible dpephos precursors is currently underway.

Conclusions

A systematic approach using diphosphines of various bite angles and flexibilities and a range of techniques both in the solid and solution states, has improved our understanding on the factors that influence the structures and properties of Au(I) complexes. Whereas the aurophilic interaction is strong enough to force a strained solid-state conformation in the xantphos derivative **2**, there is no evidence that this is maintained in solution. The solid-state structures of the dpephos derivatives **1** and **5**, with similar Au···Au contacts of *ca.* 3 Å, but a less strained ligand conformation, seem to be kept in concentrated solution. However, it is also possible that aggregation through inter-molecular Au···Au interactions occurs in solution. The more rigid dbfphos, with a larger bite angle, only allows a very weak aurophilic contact, in competition with other intermolecular interactions. Characteristic low energy emission is found for the complexes with Au···Au interactions. The alkynyl digold(I) complex **4** can act as a cation probe, with different optical responses to Ag(I) and Cu(I). The structural changes involved in these processes are, however, highly complex, with the formation of an unusual cluster in the case of Cu(I).

Acknowledgements

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