First EXAFS studies on aurophilic interactions in solution†

Héctor de la Riva, Aranzazu Pintado-Alba, Mark Nieuwenhuyzen, Christopher Hardacre* and M. Cristina Lagunas*

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EXAFS has been used to directly show the existence of Au···Au interactions in dissolved Au(I) complexes for the first time; the information has been used to understand the optical properties of these materials.

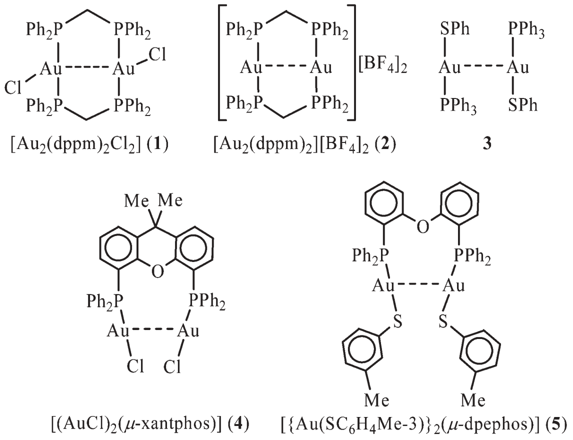
Whereas the use of X-ray absorption spectroscopy to obtain structural information of molecular species in the solid state and in solution is well established, studies regarding secondary interactions such as solvent–solute interactions or metal···metal (metallophilic) contacts, are more scarce.[1,2] However, structural information of secondary interactions in solution is essential to gain insight into the properties and reactivities of the compounds, as well as to determine the importance of the various competing interactions in the absence of crystal packing forces. In this work, aurophilic contacts, *i.e.* Au···Au interactions of *ca.* 3 Å common in Au(I) complexes,[3] are evaluated in solution by using extended X-ray absorption fine structure (EXAFS) spectroscopy.

The influence of aurophilicity on the structure and properties of Au(I) complexes has often been highlighted, and its implications in photochemistry, crystal engineering, or medicine studied by many groups.[3,4] While crystallographic data on Au···Au distances are abundant, there is no direct structural evidence of their presence in solution; however, there is evidence that such contacts exist from optical[4] and NMR studies.[4e–f] EXAFS has been previously used to study aurophilicity in the solid state,[5] and to examine other metal···metal (*e.g.*, Pt···Pt) contacts in solution.[2]

In order to assess aurophilicity in dissolved Au(I) compounds, Au L_{III} EXAFS spectra‡ have been collected in the solid state and in solution for three types of complexes (Chart 1), which demonstrate 'fully-supported' (**1**,**2**),[6–8] 'unsupported' (**3**)[9,10] and 'semi-supported' (**4**,**5**)[11] aurophilic interactions. As well as Au···Au distances, the EXAFS also shows important information in Au···anion and Au···solvent interactions for compounds **1** and **2** in the solid state and on dissolution. The X-ray crystal structures and optical properties of complexes **1–3** are known.[4e,6–10] Of significant interest is the influence of diphosphine flexibility and bite angle on the properties of Au(I) complexes. For example, we have recently reported the structure and optical behaviour of complex **4**,[11] which shows an aurophilic interaction of 2.995 Å and intense solid-state luminescence at 620 nm. Such emission is lost in dichloromethane solution, presumably due to the loss of the aurophilic interaction. This paper examines the structural effect of dissolving the complexes **1–5** in chloroform or acetonitrile. In addition, the synthesis and crystal structure of complex **5** are reported (Fig. 1).§

k^3-Weighted EXAFS spectra and *pseudo*-radial distribution functions are shown in Fig. 2 (see also ESI†). The data obtained from the models for the EXAFS spectra have been compared with the crystallographic data of the compounds (Table 1).

In complexes **1** and **2**, the Au–P and Au···Au distances determined by EXAFS for the solids and the solutions agree well with those found in their crystal structures. As expected, given the rigidity provided by two chelating ligands, no significant change in aurophilic distance was observed upon dissolution. However, a Au···Cl distance of 3.17 Å was found for **1** in the solid state but not in the solution phase structure. It should be noted that, despite the similarity between the Au···Au distance in solution (3.08 Å)



$[Au_2(dppm)_2Cl_2]$ (**1**) $[Au_2(dppm)_2][BF_4]_2$ (**2**) **3**

$[(AuCl)_2(\mu\text{-xantphos})]$ (**4**) $[\{Au(SC_6H_4Me\text{-}3)\}_2(\mu\text{-dpephos})]$ (**5**)

Chart 1

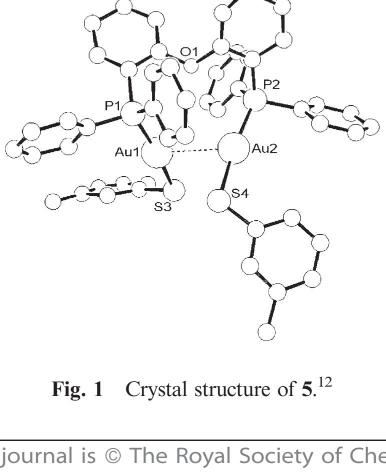


Fig. 1 Crystal structure of **5**.[12]

School of Chemistry, The Queen's University of Belfast, Belfast, UK BT9 5AG. E-mail: c.hardacre@qub.ac.uk; c.lagunas@qub.ac.uk; Fax: +44 (0)2890 974687; Tel: +44 (0)2890 974436

† Electronic supplementary information (ESI) available: XRPD studies for complex **1**; EXAFS data and *pseudo*-radial distribution functions for **1–5**; CIF file for **5**; experimental details on the preparation of **1–5**. See http://dx.doi.org/10.1039/b508863a

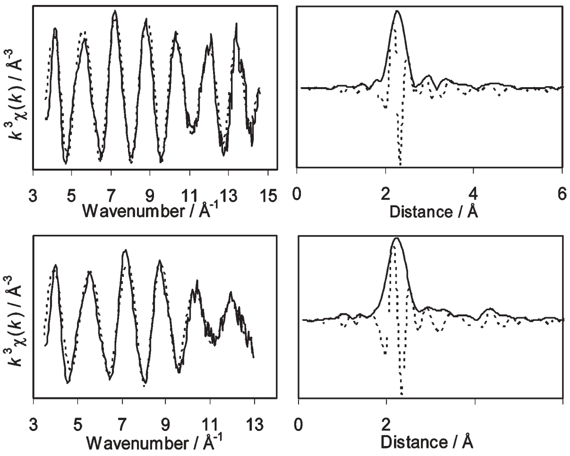


Fig. 2 EXAFS (experimental: solid line; fitted: dotted line) and *pseudo*-radial distribution functions (imaginary part shown in dotted line) for complex **2** in the solid state (above) and dissolved in acetonitrile (below).

Table 1 Selected parameters from the fitted EXAFS spectra of **1–5** in the solid state and dissolved in chloroform (**1**, **3**, **4**, **5**) or acetonitrile (**2**): distances between Au and neighbouring atoms (r), Debye–Waller factors (σ) and fit factors (R).[a] Single crystal X-ray crystallographic data is included for comparison, denoted as crystal in the table

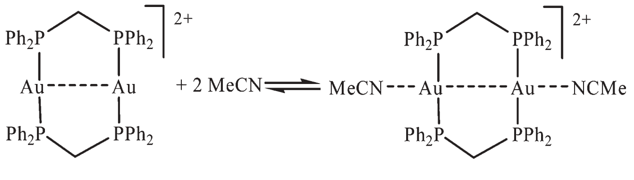
	r/Å (σ/Å^{-2})			R(%)
1	Au–P	Au···Cl	Au···Au	
Solid	2.34 (0.007)	3.17 (0.013)	2.93 (0.010)	20.7
Solution	2.31 (0.010)	—	3.08 (0.021)	23.0
Crystal[6]	2.315[b]	2.951[c] or 2.771[d]	2.994	
2	Au–P	Au···F/N	Au···Au	
Solid	2.32 (0.007)	3.36 (0.008) (F)	2.90 (0.016)	24.9
Solution	2.32 (0.011)	2.88 (0.007) (N)	2.97 (0.030)	28.6
Crystal[7]	2.311	3.28 (F)	2.931	
3	Au–P	Au–S	Au···Au	
Solid	2.30 (0.006)	2.35 (0.021)	3.08 (0.019)	21.9
Solution	2.26 (0.011)	2.30 (0.002)	—	38.0
Crystal[9]	2.271	2.31	3.145	
4	Au–P	Au–Cl	Au···Au	
Solid	2.29 (0.006)	2.32 (0.026)	2.99 (0.026)	19.8
Solution	2.21 (0.003)	2.31 (0.001)	—	38.9
Crystal[11]	2.238[b]	2.304[b]	2.9947(4)	
5	Au–P	Au–S	Au···Au	
Solid	2.26 (0.002)	2.36 (0.006)	3.01 (0.031)	20.0
Solution	2.30 (0.003)	2.34 (0.023)	2.89 (0.011)	34.9
Crystal	2.277[b]	2.315[b]	3.006	

[a] The number of atoms in each shell is 1, except for the P shell in **1** and **2**, where the coordination number is 2; [b] Average value; [c] Acetonitrile-containing crystal;[6b] [d] Acetone-containing crystal.[6a]

and the Au···Cl distance in the solid (3.17 Å), a coordinating chlorine atom could not be fitted to the solution phase EXAFS of **1** instead of or in addition to the gold coordination shell. Crystallographic data for **1** indicate that the Au···Cl distance depends on the nature of the solvent co-crystallised with the compound. Thus, two crystal structures have been reported for complex **1**: one containing acetone [Au···Cl: 2.771(4) Å],[6a] and one with acetonitrile [Au···Cl: 2.951(1) Å].[6b] Both Au···Cl distances are significantly shorter than that modelled for the EXAFS of **1**, and may be due to a different conformation of the molecule in the sample prepared herein, crystallised from dichloromethane/diethyl ether. The XRPD pattern of this sample (ESI†) showed it to be partially amorphous, and a comparison of the experimental diffractogram with the calculated patterns from the two reported crystal structures (ESI†) shows clear differences in the diffraction patterns. The two calculated patterns are also very different from each other, indicating that the inclusion of a different solvent (acetonitrile or acetone) and/or a different Au···Cl distance significantly affects the diffraction pattern. Although it is not possible to extract specific structural information from the experimental XRPD, the discrepancies between this and the calculated patterns support the presence of a different conformation, which may be due to an elongated Au···Cl distance or the inclusion of a different solvent. On recrystallisation of the sample in the presence of acetonitrile, the XRPD pattern remained similar and the EXAFS of the solid again indicated a long Au···Cl distance of 3.13 Å, similar to that of the sample obtained from dichloromethane/diethyl ether.

Good agreement between the crystal structure[7] and the solid state EXAFS data was found for **2**. However, in solution the feature associated with the anion coordination was absent. In addition, a N atom at 2.88 Å improved the fit significantly for the dissolved complex as determined by the χ^2 statistical test, indicating the formation of a solvato species in MeCN (Scheme 1). The χ^2 values with and without N coordination were 2.54×10^{-6} and 2.87×10^{-6}, respectively. Coordination of MeCN has been proposed for these types of complexes to explain their optical behaviour, with the yellow emission (λ_{max} = 570–595 nm) that the compounds exhibit in solution being attributed to $[Au_2(dppm)_2(MeCN)_2]^{2+}$.[13] No experimental data is available for the Au···N distance; however, *ab initio* calculations predict a distance of 2.583 Å[13] which is shorter than that determined herein by EXAFS. Given the higher coordinating ability of chloride with respect to MeCN and that the core of **1** and **2** are the same, the fact that the chloride is not seen on dissolving **1** in chloroform but MeCN is found in **2** is surprising. Although the chloride in **1** on dissolution may be dissociated, it is also possible that it remains mainly associated with the cation but with an elongated Au···Cl distance and is not observed in the EXAFS. The low value obtained for the molar conductivity (2.1 Ω^{-1} mol^{-1} cm^2) of **1** in chloroform (0.8×10^{-3} M) indicates that the amount of chloride ions in solution is not significant, and agrees with previous studies[6a] that found complex **1** only slightly dissociated in polar solvents.

The EXAFS and crystallographic studies showed excellent agreement for the Au–P and Au–S or Au–Cl bond distances in complexes **3–5**. The two first shells modelled for the EXAFS



Scheme 1

spectra of **3** and **5** consisted in one P and one S atom at similar distances from Au. It was not possible to distinguish each element by EXAFS and these shells can be exchanged with no significant difference in the fit obtained. In the crystal structure of complex **4**,[11] a weak Au···O contact at 3.097 Å is present. This shell could not be fitted to the EXAFS data with any statistical significance. The aurophilic interaction was included as a third shell in the models, and could be reliably fitted for the three solid-state spectra. However, in solution, a Au···Au contact could be modelled with confidence only in the case of complex **5**.

Loss of low-energy luminescence (λ_{max} = 620 nm) upon dissolution has been observed for complex **4**,[11] in agreement with the loss of Au···Au contacts shown in the EXAFS. Complex **5** also shows low-energy solid-state emission (λ_{max} = 624 nm) likely to be related to the aurophilic contact. As in the case of **4**, such emission is not seen in solution, despite the presence of aurophilicity indicated by EXAFS results. However, it is known that the emission from similar complexes can be strongly concentration dependant[14] and the solutions used for optical studies were more dilute (*ca.* 10^{-3} M) compared with that used for EXAFS (*ca.* 3×10^{-2} M). Further studies to clarify the structural and optical properties of **5** and analogous complexes are currently underway.

Given the relative flexibility of the diphosphine ligand in **5** compared with that in **4**, and the 'semi-supported' character of the aurophilic interaction, the presence of Au···Au contacts in dissolved **5** is unexpected. However, it has been observed that greater flexibility in the diphosphine bridge can actually favour aurophilic contacts in solution in the related compound $[(AuCl)_2(\mu\text{-dpephos})]$, which has a solid-state Au···Au interaction of 3.0038(6) Å.[11] Optical and NMR studies indicated that this contact remained in solution, and this has been attributed to the ability of dpephos to accommodate the Au···Au moiety without significant distortion of the phosphine's backbone, which remains similar to that of the free ligand (*e.g.*, the angle between the phenyl rings is 67° in free dpephos and 61° in $[(AuCl)_2(\mu\text{-dpephos})]$, whereas the distance between the P atoms is *ca.* 4.9 Å in both compounds). The crystal structure of **5** (Fig. 1) also shows the phosphine's backbone in a non-distorted conformation (*i.e.*, P–P: 4.96 Å, angle between Ph rings: *ca.* 59°). The more rigid xantphos ligand, however, undergoes significant distortion upon coordination, as indicated by the crystal structure of **4**,[11] and such constraint may favour the loss of the aurophilic contact on dissolution.

In many of the *pseudo*-radial distribution functions (see ESI†) features at *ca.* 4.5 Å are observed which may be related to the presence of small amounts of colloidal gold formed by decomposition during the EXAFS experiment. Although metallic gold may be fitted to the data, the additional shells are not statistically significant and less than 5% of the gold is in this form. Even with the inclusion of gold, the parameters obtained for previous shells are not significantly affected.

In conclusion, EXAFS studies have provided for the first time Au···Au distances in solution (**1**, **2**, **5**), allowing a deeper understanding of the luminescent behaviour of the compounds.

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Notes and references

‡ All EXAFS spectra were recorded at the Daresbury SRS on stations 9.2 and 16.5. The scans were averaged using EXCALIB, which was also used to convert the raw data into energy *versus* absorption data. EXBROOK was used to remove the background and analysis of the EXAFS data was performed using EXCURV98 on the raw data.[15] The best statistical fits were determined using the reduced χ^2 test (see ESI†).

§ *Crystal Data for* $C_{50}H_{42}P_2S_2OAu_2$ **(5)** - M = 1178.83, triclinic, space group *P*-1, a = 11.295 (3) Å, b = 13.536 (3) Å, c = 15.667 (4) Å, α = 81.769 (5), β = 70.825 (5), γ = 71.182 (5), U = 2139.7 (9) Å^3, Z = 2, $\mu = 7.059$ mm^{-1}, $R_{int} = 0.0705$. A total of 12292 reflections were measured for the angle range $1.7 < 2\theta < 45$ and 7154 independent reflections were used in the refinement. The final parameters were $wR2 = 0.2615$ and $R1 = 0.0964$ [$I > 2\sigma I$]. CCDC 276949. See http://dx.doi.org/10.1039/b508863a for crystallographic data in CIF or other electronic format.

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