Solvent mediated disruption of intermolecular association in phosphinegold(I) thiolates: the relative importance of carboxylic acid dimer formation on crystal structure

Douglas R. Smyth,[a] Beverly R. Vincent[b] and Edward R. T. Tiekink*[a]

[a] *Department of Chemistry, The University of Adelaide, Australia 5005. E-mail: edward.tiekink@adelaide.edu.au*
[b] *Molecular Structure Corporation, 9009 New Trails Drive, The Woodlands, Texas 77381-5290, USA*

The crystal and molecular structures of [Au$_2$(2-Hmba)$_2$(μ-PPh$_2$(CH$_2$)$_2$Ph$_2$P)] (**1**) and its 1 : 2 adduct with DMSO (**1**·2DMSO) are reported. In **1**, a two-dimensional structure is found mediated, in part, by carboxylic acid dimer formation within the layers. In the di-solvate, these functionalities are not available as they are involved in hydrogen-bonding contacts to DMSO. Nevertheless, a two-dimensional structure is also formed showing that carboxylic acid dimer formation is not pivotal in determining the crystal structure in these systems.

Introduction

The importance of hydrogen bonding interactions in the design of crystal structure is undisputed for both organic systems and coordination chemistry.[1] The consistency and reliability of their formation enables the crystal engineer to predict the nature of molecular association with some confidence when designing solid-state aggregates. In this context, this contribution describes the results of a study of two phosphinegold(I) thiolates in which the thiolate ligand contains a pendant carboxylic acid functionality that is potentially available for hydrogen bonding.

Interest in the chemistry of phosphinegold(I) 2-mercaptobenzoates, R$_3$PAu(2-Hmba), stems from their actual and putative pharmacological activity, namely anti-arthritic[2] and anti-tumour.[3] Their solid state chemistry and that of related phosphinegold(I) thiolates is of some interest as often aurophilic interactions (with Au···Au 3.0 ± 0.2 Å) serve to stabilise their molecular and crystal structures. The importance of such Au···Au associations for gold(I) systems is evidenced by research which has shown that individual associations impart stability in the order of 6–11 kcal mol^{-1} which is comparable to that imparted by hydrogen-bonding interactions.[4] An area of research receiving particular attention at present is an investigation of complementarity or even competition between aurophilic interactions on the one hand and association *via* hydrogen bonding on the other.[5] In a recent contribution describing some chemistry of triorganophosphinegold(I) 2-mercaptobenzoates, an interesting solution behaviour was noted in that some ^{1}H NMR resonances of the thiolate ligand proved to be solvent (*i.e.*, d$_6$-DMSO and CDCl$_3$) dependent. This behaviour was rationalised in terms of *inter*molecular hydrogen bonding interactions between the carboxylic acid group and the solvent in the case of d$_6$-DMSO and *intra*molecular carboxylic acid···sulfur interactions in the case of CDCl$_3$. Unfortunately, only solvent-free crystals could be obtained and hence, related systems were investigated in order to ascertain the influence of solvent upon the crystallisation of these species. It was thought of interest to ascertain whether the solution behaviour was manifested in the adoption of different structures in the solid state. In this communication, the crystal and molecular structures of

[Au$_2$(2-Hmba)$_2$(μ-PPh$_2$(CH$_2$)$_2$Ph$_2$P)] (**1**) and its 1 : 2 adduct with DMSO (**1**·2DMSO) are reported. This study shows that the overall crystal structure is similar for the two complexes despite the absence of the carboxylic acid dimer motif in the di-solvate.

Results and discussion

Crystals of **1** were obtained from vapour diffusion of diethylether into a dichloromethane solution of the compound. The molecular structure of **1** is shown in Fig. 1 and selected interatomic parameters are given in Table 1. The dinuclear molecule is situated about a crystallographic centre of inversion so that the conformation about the PPh$_2$(CH$_2$)$_2$Ph$_2$P (dppe) ligand is *anti*. The independent gold atom exists in the expected linear geometry defined by the sulfur and phosphorus atoms. The coordination geometry and magnitudes of the key geometric parameters about gold match those found in related systems.[3b,6]
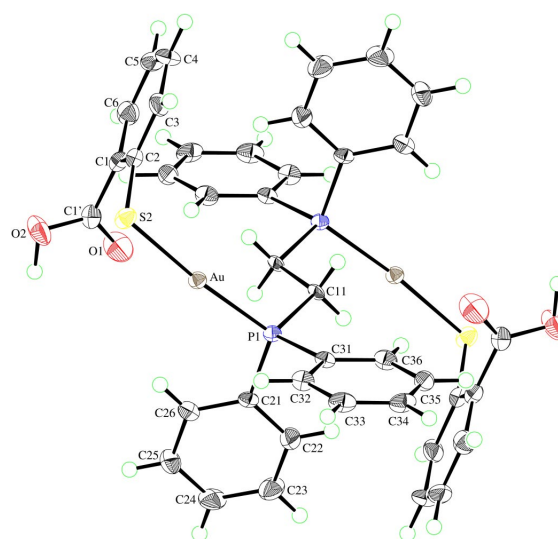

Fig. 1 Molecular structure and atomic numbering scheme for **1**. Click on the image or here to view the 3D crystal structure.

Table 1 Selected geometric parameters (Å, °) for **1**

Au–S(2)	2.308(2)	Au–P(1)	2.250(2)
S(2)–C(2)	1.783(6)	P(1)–C(11)	1.822(5)
P(1)–C(21)	1.827(5)	P(1)–C(31)	1.803(7)
C(1')–O(1)	1.233(5)	C(1')–O(2)	1.289(7)
S(2)–Au–P(1)	174.99(5)	Au–S(2)–C(2)	98.5(5)
Au–P(1)–C(11)	112.7(2)	Au–P(1)–C(21)	114.0(2)
Au–P(1)–C(31)	114.1(1)		

The thiolate ligand is not coplanar with the S–Au–P chromophore, as seen in the magnitude of the Au–S(2)–C(2)–C(1) torsion angle of 69.1(5)°. Nor is the carboxylic acid residue coplanar with the aromatic ring: O(1)–C(1')–C(1)–C(2) is –113.2(7)°. These relationships between the various residues are similar to that found in the structure of [Ph$_3$PAu(2-Hmba)]^{3b,6} and presumably arise in order to facilitate intermolecular interactions.

Views of the unit cell contents for **1** are shown in Fig. 2 and 3 from which it may be seen that there are several types of intermolecular interactions leading to a layer structure. The carboxylic acid groups associate *via* the familiar carboxylic dimer motif so that O(2)–H···O(1)^i is 1.64 Å, O(2)···O(1)^i is 2.640(6) Å and the angle subtended at H is 157°; symmetry operation *i*: –*x*, 1 – *y*, 1 – *z*. Each molecule is involved in two such interactions so that chains of hydrogen-bonded molecules are formed, running parallel to the *a*-axis (Fig.

2). Whereas there is no evidence for aurophilic interactions in the structure, rectangular (Au···S)$_2$ units are formed (Fig. 3) as has been seen previously in other phosphinegold(ı) thiolate structures.[7] Thus, centrosymmetrically related pairs of molecules associate *via* Au···S interactions of 3.341(2) Å corresponding to Au···Au separations of 4.194(2) Å (symmetry operation: –*x*, 1 – *y*, –*z*). The Au···S interactions, coupled with the hydrogen-bonding scheme, lead to the formation of a 2D network that stacks along *b*. Within the layers there is overlap between isolated pairs of phosphorus-bound phenyl rings containing the C(31)–C(36) atoms; symmetry operation: 1 – *x*, 1 – *y*, –*z*. However, the average separation between the rings is calculated to be 3.81 Å which is at the upper end of the range given for π···π interactions.[8] Between the layers thus formed, there are significant hydrophobic intermolecular interactions.
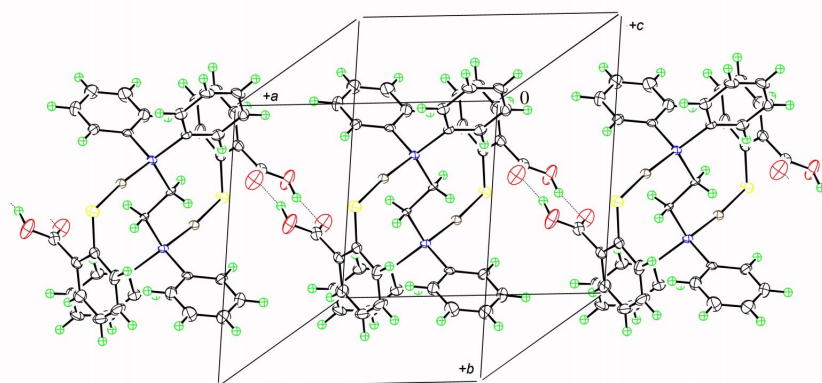

Fig. 2 A view of the unit cell contents for **1** emphasising the association mediated by carboxylic acid dimer formation. Click on the image or here to view the 3D crystal structure.
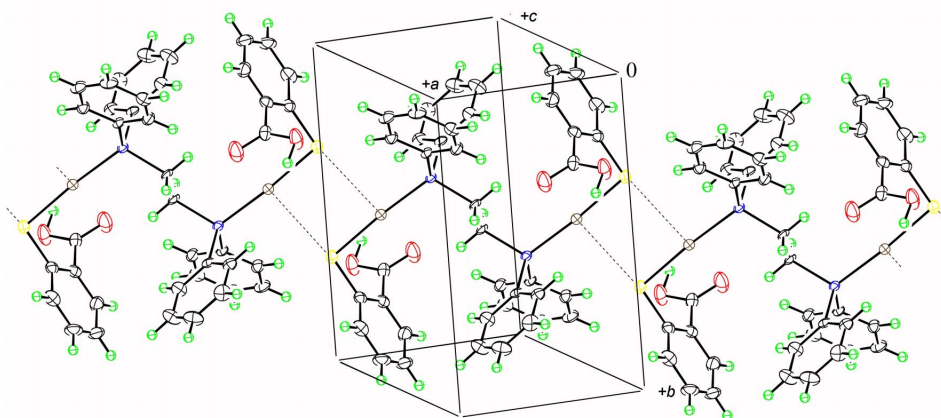

Fig. 3 A view of the unit cell contents for **1** emphasising the association mediated by the formation of (Au···S)$_2$ rectangles. Click on the image or here to view the 3D crystal structure.

**Table 2** Selected geometric parameters (Å, °) for **1**·2DMSO

Au(1)-S(1)	2.307(3)	Au(2)-S(2)	2.309(3)
Au(1)-P(1)	2.256(3)	Au(2)-P(2)	2.258(3)
S(1)-C(2)	1.77(1)	S(2)-C(12)	1.77(1)
P(1)-C(21)	1.824(9)	P(2)-C(41)	1.83(1)
P(1)-C(31)	1.82(1)	P(2)-C(51)	1.81(1)
P(1)-C(61)	1.820(7)	P(2)-C(62)	1.821(7)
S(1)-Au(1)-P(1)	176.8(1)	S(2)-Au(2)-P(2)	177.90(9)
Au(1)-S(1)-C(2)	99.1(4)	Au(2)-S(2)-C(12)	104.0(4)
Au(1)-P(1)-C(21)	113.3(4)	Au(2)-P(2)-C(41)	113.7(3)
Au(1)-P(1)-C(31)	112.1(3)	Au(2)-P(2)-C(51)	113.5(4)
Au(1)-P(1)-C(61)	113.7(4)	Au(2)-P(2)-C(62)	114.2(4)

Fig. 4 highlights the key intermolecular interactions between successive layers. Centrosymmetrically related pairs of thiolate rings approach each other at distances indicative of $\pi \cdots \pi$ interactions so that the average separation between the rings is calculated to be 3.35 Å; symmetry operation: $-x$, $-y$, $-z$. Two such associations occur for each dinuclear unit, one on either side of the molecule. In addition to these there are C–H$\cdots\pi$ interactions between the layers. These occur between translationally related thiolate C(5)–H and phosphine–C(21)–C(26) rings (symmetry operation: x, $1 + y$, z). The H$\cdots$ring centroid distance is 2.75 Å and the C(5)–H$\cdots$centroid angle is 156°. Each molecule is involved in one donor and one acceptor C–H$\cdots\pi$ interaction on the surface of each side of the layer.
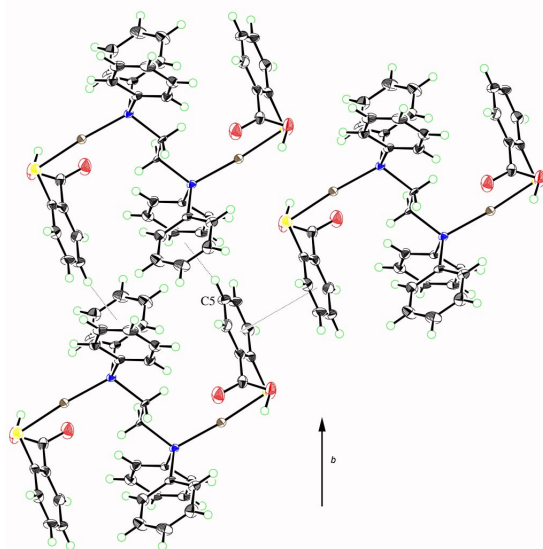
Fig. 4 Detail of interlayer association in **1**. Click on the image or here to view the 3D crystal structure.

As reported in an earlier study on related monomeric species,[3b] a solvent dependence is found in the ^{1}H NMR spectra of **1**. In particular, there is a significant shift in the resonance assigned to H6 of the thiolate ligand (Fig. 1). In CDCl$_3$ solution, this resonance is found at δ 8.31 and is shifted upfield by almost 1 ppm when the spectrum is measured in d$_6$-DMSO solution (7.37). In the earlier study, these differences were ascribed to different conformations of the thiolate ligand owing to the interaction of the carboxylic acid group with the solvent in the case of d$_6$-DMSO. Structural evidence is now afforded for the

assignment as crystals of the 1 : 2 adduct between **1** and DMSO, *i.e.* **1**·2DMSO, have been characterised.The molecular structure of **1**·2DMSO, isolated from the vapour diffusion of diethylether into a DMSO solution of the complex, is illustrated in Fig. 5 and selected geometric parameters are collected in Table 2. To a first approximation, the overall conformation of the molecule is as found for **1** although there is no molecular symmetry in **1**·2DMSO. The geometric parameters are also comparable between the two structures. Thus, with the exception of the Au(2)–S(2)–C(12) angle, which at 104.0(4)° has opened up by *ca.* 5° compared to the other Au–S–C angles, all bond distances and angles are equal within experimental error. The conformation of the thiolate ligand with respect to the S–Au–P chromophore and that of the carboxylic acid group to the ring are in essential agreement with those found in the unsolvated molecule: the Au–S–C–C torsion angles are –76(1)° and 74(1)°, respectively and the O–C–C–C angles are 112(2)° and –93(1)°, respectively. The obvious difference between the structures is found in the association of two molecules of DMSO.
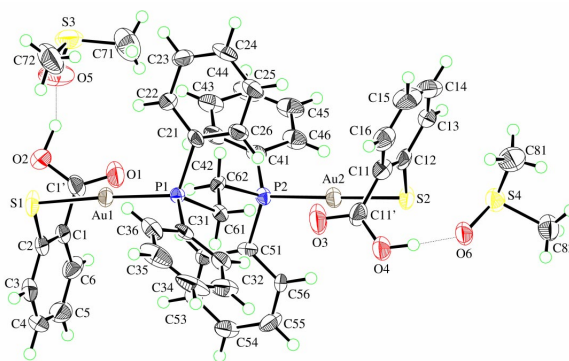
Fig. 5 Molecular structure and atomic numbering scheme for **1**·2DMSO. The C(33) and C(52) atoms are not labelled. Click on the image or here to view the 3D crystal structure.

Each carboxylic acid group forms a hydrogen bond to a molecule of DMSO. One such contact, O(2)–H$\cdots$O(5), involves the familiar *syn* arrangement of the O–H and carbonyl atoms whereas O(4)–H$\cdots$O(6) features an *anti* disposition of these atoms. The O(2)–H$\cdots$O(5) separation is 1.50 Å corresponding to O(2)$\cdots$O(5) of 2.55(1) Å and the angle subtended at the hydrogen is 155°. For the second interaction, the O(4)–H$\cdots$O(6) separation is 1.59 Å, O(4)$\cdots$O(6) is 2.53(1) Å and the angle is 173°. The presence of the hydrogen bonds between the complex and
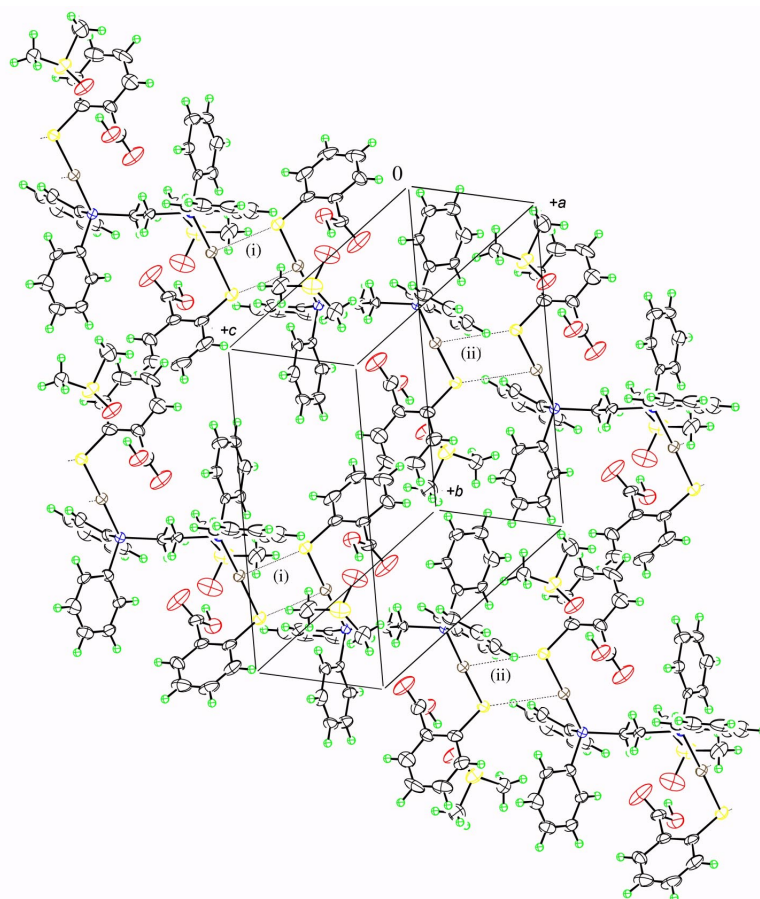
Fig. 6 View of unit contents in **1**·2DMSO showing the formation of alternating ribbons of (Au···S)$_2$ rectangles. Click on the image or here to view the 3D crystal structure.
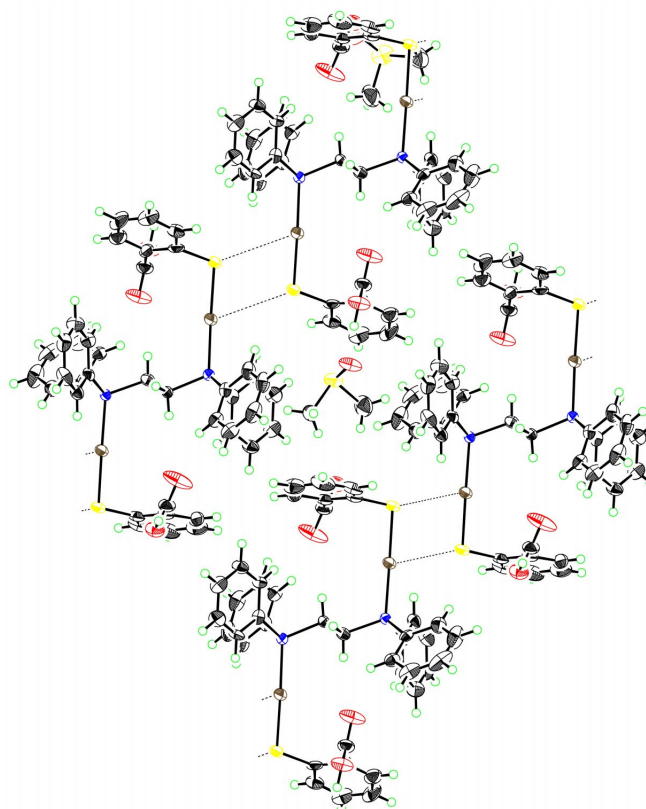

Fig. 7 Association between four complex molecules mediated by a DMSO molecule in **1**·2DMSO. Click on the image or here to view the 3D crystal structure.

DMSO molecules precludes association between molecules *via* carboxylic acid interactions as found in **1**. However, it is of interest that despite the absence of hydrogen bonding between complex molecules, a 2D network is still formed for **1·2DMSO**.

In **1·2DMSO**, the layers are parallel to the (011) plane. Associations in this plane occur *via* rectangular (Au···S)$_2$ units as found for **1**, however, in **1·2DMSO** these are not equivalent as one such association is significantly shorter than the other. Thus, the Au(1) atom is separated from a symmetry related S(1) atom by 3.349(3) Å [–1 – x, –y, 1 – z; labelled (i) in Fig. 6] whereas Au(2) is separated from symmetry related S(2) by 3.683(2) Å [1 – x, 1 – y, –z; labelled (ii) in Fig. 6]. As shown in Fig. 6, rows of molecules arise due to these (Au···S)$_2$ interactions of alternating strength. The next most notable intermolecular contact within the layer is of the type C–H···π, there being no evidence for significant π···π interactions. These involve DMSO-bound hydrogens such that C(82)–H···ring centroid of C(51)–C(56) is 2.82 Å and the C(82)–H···centroid angle is 132° (symmetry operation: 1 – x, 1 – y, –z). Cohesion between the layers is afforded by a combination of π···π and C–H···π contacts.

Between the layers, centrosymmetrically related pairs of C(41)–C(46) rings have an average separation of 3.67 Å indicative of π···π interactions; symmetry operation: –x, 1 – y, –z. The next closest π···π interaction occurs between a pair of C(31)–C(36) rings with an average separation of 3.81 Å and symmetry operation: –x, –y, 1 – z. Several C–H···π contacts are formed between the layers, involving both phenyl- and DMSO-bound hydrogen atoms. The C(45)–H atom is 2.85 Å from the ring centroid of C(21)–C(26) (the angle at H is 137° and symmetry operation: –x, 1 – y, –z). The DMSO molecule associated with the carboxylic acid group with the *anti* conformation forms a total of three close C–H···π contacts, one as described above. The second interaction involving C(81)–H(83) is formed with the C(21)–C(26) ring (2.72 Å, 153° and –x, 1 – y, 1 – z) and the shortest C–H···π distance of 2.58 Å occurs between C(82)–H(86) and a translationally related aromatic ring of the thiolate ligand (132° and 1 + x, 1 + y, z). It would appear that this DMSO molecule serves to link four complex molecules as shown in Fig. 7 and detailed in Fig. 8, however, the importance of methyl–H intermolecular associations is still controversial.

The differences in the nature of intermolecular interactions formed by the carboxylic acid groups are clearly seen in the infrared spectra (KBr discs). In **1**, ν(C=O) is observed at 1683 cm^{-1} consistent with carboxylic acid dimer formation whereas in **1·2DMSO** two distinct bands are observed at 1684 and 1718 cm^{-1}. The density of the solvent free crystal of 1.972 g cm^{-3} is greater than that of 1.869 g cm^{-3} for **1·2DMSO** suggesting a more efficient packing in **1**. This conclusion is supported by the melting behaviour for the two crystals. Crystals of **1** melt with decomposition in the range 198–202 °C whereas those of **1·2DMSO** commence melting at 155 °C, owing to loss of solvent which can be seen to condense higher up in the capilliary tube.

Conclusion

The conclusion from the study of the two structures described herein is that layer structures are found in each case, *i.e.* even in the situation where carboxylic acid dimer formation has been precluded. This only serves to indicate that a stable crystal lattice is a composite of a wide variety

of intermolecular interactions and the disruption of one type of intermolecular interaction, even involving hydrogen
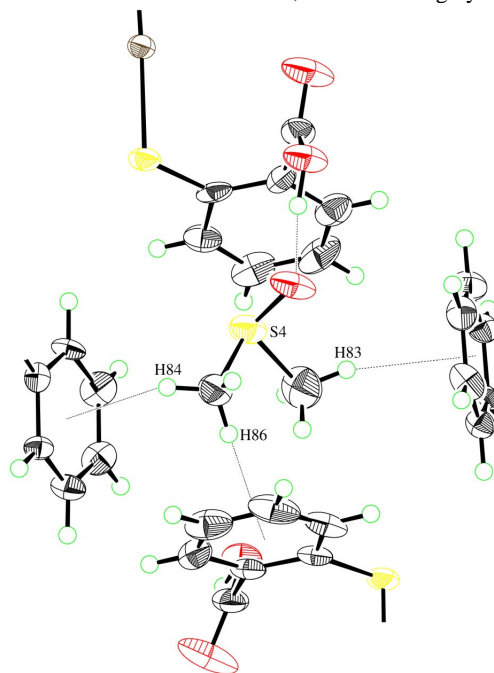

Fig. 8 Detail of association between association between a DMSO molecule and four residues in **1·2DMSO**. Click on the image or here to view the 3D crystal structure.

bonds, may not necessarily alter the 'global' crystal structure.

Experimental

Complex **1** was prepared by the reaction of [(AuCl)$_2$(µ-dppe)] with two molar equivalents of 2-H$_2$mba and KOH in ethanolic solution using a procedure similar to that in the literature.[3b] Yield, 0.216 g (85%). **1**, mp 198–202 °C (dec.); **1·2DMSO** 155 °C (lost solvent). C$_{40}$H$_{34}$Au$_2$O$_4$P$_2$S$_2$ found: C 43.56, H 3.22; calc: C 43.73, H 3.12. **1·2DMSO**, C$_{44}$H$_{46}$Au$_2$O$_6$P$_2$S$_4$ found: C 42.17, H 3.49; calc: C 42.11, H 3.69. IR (KBr, cm^{-1}): **1**, 1683(vs) ν(C=O); **1·2DMSO**, 1718(s) and 1684(s) ν(C=O). Selected NMR data (d$_6$-DMSO): δ(^{1}H) = 12.71 [b, 2H, COOH]; 7.68–7.78 [m, 10H, o-PhH & H3 – refer to Fig. 1 for atom labels]; 7.44–7.57 [m, 12H, m/p-PhH]; 7.37 [dd, $^3J_{HH}$ = 7.5 Hz, $^4J_{HH}$ = 1.8 Hz, 2H, H6]; 6.92–7.03 [m, 4H, H4 & H5]; 2.95 [d, $^2J_{HP}$ = 4.8 Hz, 4H, CH$_2$]. δ(^{13}C) = 169.6 [CO$_2$H]; 141.6 [C2]; 135.4 [C1]; 135.1 [C3]; 133.1 [t, $^2J_{CP}$ = 6.7 Hz, o-PhC]; 131.9 [p-PhC]; 129.4 [d, $^1J_{CP}$ = 53.1 Hz, i-PhC]; 129.3 [t, $^3J_{CP}$ = 5.6 Hz, m-PhC];128.8 [C4]; 128.3 [C6]; 123.0 [C5]; 22.7 [CH$_2$]. δ(^{31}P) = 35.6. **1** (CDCl$_3$): δ(^{1}H) = 8.31 [d, $^3J_{HH}$ = 6.6 Hz, 2H, H6]; 7.73 [dd, $^3J_{HH}$ = 7.5 Hz, $^4J_{HH}$ = 1.8 Hz, 2H, H3]; 7.42–7.66 [m, 20H, PhH]; 7.19–7.31 [m, 4H, H4 & H5], 2.60 [s, 4H, CH$_2$].

Intensity data were measured at 173 K on a Rigaku AFC7R for **1** and a Rigaku/MSC Mercury CCD area detector for **1·2DMSO** employing Mo-Kα radiation. Crystallographic details are given in Table 3. The data were corrected for Lorentz and polarisation effects and for absorption; **1**[9] and **1·2DMSO**.[10] The structures were solved with DIRDIF92 PATTY[11] and refined on F (teXsan[12]) with reflections satisfying $I \geq 3.0\sigma(I)$. Carbon-bound hydrogens were included in their calculated positions. Positions for O–H atoms were located from difference Fourier syntheses for the CO$_2$H atom in **1** and for the *syn*-H in **1.DMSO**; the

Table 3 Crystallographic data for **1** and **1**·2DMSO[a]

Chemical formula	$C_{40}H_{34}Au_2O_4P_2S_2$	$C_{44}H_{46}Au_2O_6P_2S_4$
Formula weight	1098.7	1255.0
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a/Å	10.701(3)	11.8235(3)
b/Å	11.238(5)	14.133(2)
c/Å	8.837(5)	16.2301(6)
α/°	109.31(4)	71.019(1)
β/°	112.70(3)	61.6720(5)
γ/°	83.83(3)	88.529(1)
V/Å^3	925.0(8)	2230.4(2)
Z	1	2
D_x/g cm^{-3}	1.972	1.869
μ/mm^{-1}	8.190	6.899
Reflections collected	4463	24774
θ_{max}/°	27.5	26.4
Independent reflections	4237	9073
Reflections with $I \geq 3.0\sigma(I)$	3612	5173
Final R, R_w	0.034, 0.038	0.041, 0.043
ρ_{max}/e Å^{-3}	2.08	2.48

[a] Click here for full crystallographic data (CCDC no.1350/28).

anti-H was included in its calculated position for **1**·2DMSO. In order to confirm their assignments, the O–H atoms were refined but not in the final cycles. Residual electron density peaks were located near gold atoms in each case. Programs used in the analysis: teXsan,[12] PLATON[13] and ORTEP.[14]

Acknowledgements

References

1 *e.g*., (*a*) C. B. Aakeröy and K. R. Seddon, *Chem. Soc. Rev*., 1993, 397; (*b*) G. R. Desiraju, *Angew. Chem., Int. Ed. Engl*., 1995, **34**, 2311; (*c*) C. B. Aakeröy, *Acta Crystallogr., Sect. B*, 1997, **B53**, 569; (*d*) D. Braga, F. Grepioni, P. Sabatino and G. R. Desiraju, *Organometallics*, 1994, **13**, 3532; (*e*) D. Braga, F. Grepioni and G. R. Desiraju, *Chem. Rev*., 1998, **98**, 1375.

2 (*a*) B. M. Sutton and J. Weinstock, US Patent 3842107, 15 Oct., 1974; *Chem. Abstr*., **82**, 57937h; (*b*) B. M. Sutton and J. Weinstock, US Patent 73-381832, 23 July, 1973; *Chem. Abstr*., **84**, 17559w.

3 (*a*) E. R. T. Tiekink, P. D. Cookson, B. M. Linahan and L. K. Webster, *Metal-Based Drugs*, 1994, **1**, 299; (*b*) D. de Vos, P. Clements, S. M. Pyke, D. R. Smyth and E. R. T. Tiekink, *Metal-Based Drugs*, 1999, **6**, 31.

4 *e.g*., (*a*) H. Schmidbaur, W. Graf and G. Müller, *Angew. Chem., Int. Ed. Engl*., 1988, **27**, 417; (*b*) K. Dziwok, J. Lachmann, D. L. Wilkinson, G. Müller and H. Schmidbaur, *Chem. Ber*., 1990, **123**, 423; (*c*) R. Narayanaswany, M. A. Young, E. Parkhurst, M. Ouelette, M. E. Kerr, D. M. Ho, R. C. Elder, A. E. Bruce and M. R. M. Bruce, *Inorg. Chem*., 1993, **32**, 2506; (*d*) D. E. Harwell, M. D. Mortimer, C. B. Knobler, F. A. L. Anet and M. F. Hawthorne, *J. Am. Chem. Soc*., 1996, **118**, 2679.

5 *e.g*., (*a*) W. Schneider, A. Bauer and H. Schmidbaur, *Organometallics,* 1996, **15**, 5445; (*b*) C. Hollatz, A. Schier and H. Schmidbaur, *J. Am. Chem. Soc*., 1997, **119**, 8115; (*c*) C. Hollatz, A. Schier, J. Riede and H. Schmidbaur, *Chem. Commun*., 1999, 111; (*d*) B.-C. Tzeng, A. Schier and H. Schmidbaur, *Inorg. Chem*., 1999, **38**, 3978; (*e*) K. Nomiya, N. C. Kasuga, R. Noguchi, C. Kato, B. R. Vincent, D. R. Smyth and E. R. T. Tiekink, *Chem. Commun*., submitted.

6 (*a*) P. D. Cookson and E. R. T. Tiekink, *J. Coord. Chem*., 1992, **26**, 313; (*b*) K. Nomiya, N. C. Kasuga, I. Takamori and K. Tsuda, *Polyhedron,* 1998, **17**, 3519.

7 *e.g*., (*a*) M. Preisenberger, A. Bauer, A. Schier and H. Schmidbaur, *J. Chem. Soc., Dalton Trans*., 1997, 4753; (*b*) P. Bishop, P. Marsh, A. K. Brisdon and M. F. Mahon, *J. Chem. Soc., Dalton Trans*., 1998, 675; (*c*) M. Preisenberger, A. Schier and H. Schmidbaur, *Z. Naturforsch*., 1998, **53b**, 781; (*d*) B.-C. Tzeng, J. Zank, A. Schier and H. Schmidbaur, *Z. Naturforsch*., 1999, **54b**, 825.

8 T. Dahl, *Acta Chem. Scand*., 1994, **48**, 95.

9 N. Walker and D. Stuart, *Acta Crystallogr., Sect. A*, 1983, **A39**, 158.

10 *CrystalClear*, *Software for Automated X-ray Imaging Systems*, Molecular Structure Corporation and Rigaku Corporation, Tokyo, 1999.

11 P. T. Beurskens, G. Admiraal, G. Beurskens, W. P. Bosman, S. García-Granda, J. M. M. Smits and C. Smykalla, *The DIRDIF program system, Technical Report of the Crystallography Laboratory*, University of Nijmegen, 1992.

12 *teXsan, Single Crystal Structure Analysis Software*, Version 1.04, Molecular Structure Corporation, The Woodlands, TX, 1997.

13 A. L. Spek, *PLATON, A Multipurpose Crystallographic Tool*, Utrecht University, Utrecht, The Netherlands 2000; http://www.cryst.chem.uu.nl/platon/

14 C. K. Johnson, ORTEP. Report ORNL-5138, Oak Ridge National Laboratory, TN, 1976.