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Self-assembly of a chiral phosphinegold(I) building block into a two-dimensional netsheet based on a hydrogen bond between one Cl^- anion and three hydroxy groups, co-ordination and aurophilicity interactions†

Ji-Cheng Shi,*[a] Bei-Sheng Kang[a,b] and Thomas C. W. Mak[c]

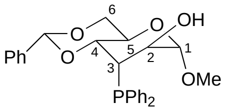
[a] *State Key Laboratory of Structural Chemistry and Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fijian, Fuzhou 350002, China*
[b] *Department of Chemistry, Zhongshan University, Guangzhou, Guangdong 510275, China*
[c] *Department of Chemistry, The Chinese University of Hong Kong, Shatin, New Territories, Hong Kong*

The trigold(I) complex $[\{Au(mbpa)\}_3S]Cl$ **2** [mbpa = methyl 4,6-*O*-benzylidene-3-deoxy-3-(diphenylphosphino)-α-D-altropyranoside] has been obtained from the compound [Au(mpba)Cl] **1** and L-cysteine. Complex **2** crystallizes in space group $P6_6$ with $a = 15.165(2)$, $c = 18.897(3)$ Å and $Z = 2$, $R = 0.030$, $R' = 0.050$. The crystal structure shows that the Au_3S core is a perfect trigonal pyramid with angles Au–S–Au and P–Au–S of 88.7 and 179.6°, respectively, and that the chiral building blocks $[\{Au(mpba)\}_3S]^+$ assemble through triple hydrogen bonding between one hydrogen-bond acceptor, Cl^-, and three hydrogen-bond donors [$Cl\cdots O(2)$ 3.017(10) Å], and form infinite two-dimensional netsheets. The netsheets align in the same direction. A relativistic interaction of the d^{10} closed shell of gold(I) was revealed by NMR studies. Complex **2** displays a strong bright white emission at 495 nm when excited at 303 nm at room temperature, where the lowest-energy transition is of metal-to-ligand charge-transfer (Au→S) type.

Gold(I) complexes have an unusual structural chemistry based on non-classical intermolecular gold(I)–gold(I) contacts.[2] Recently Schmidbaur and co-workers[3] have found that the (phosphine)gold(I) cation can ligate to main-group elements such as carbon and nitrogen with co-ordination numbers as high as five and six and gives certain interesting structures. The novel bonding configurations are caused by the contraction of the 6s orbital of the gold(I). Theoretical descriptions of the gold(I)–gold(I) attraction which requires the inclusion of electron correlation and relativistic effects have been carried out.[4]

The photochemistry of gold(I) complexes has attracted a great deal of attention over the last few years.[5] The relationship between the emission and the gold(I)–gold(I) interaction is an interesting subject of experimental[6] and theoretical studies.[7] Recently, Fackler and co-workers[6a] and Bruce and co-workers[6b] have concluded that luminescence in gold(I) complexes cannot be used as a diagnostic test for the presence of the interaction, but the interaction, in some cases, can shift the emission maximum to lower energies. It has been observed[8] that the strength of the interaction is influenced by the electronic and steric effects of the phosphine ligands in the trigold(I) cations $[\{Au(PR_3)\}_3S]^+$. However, the photochemical consequences have not been seen so far.[9]

The control of molecular assembly by hydrogen bonding is a major tool in crystal engineering.[10] A common feature in the work of Whitesides,[11] Lehn,[12] Hamilton,[13] and Mingos[14] and their co-workers is to use complementary hydrogen-bonding groups structurally related to those found in nucleic acid–base pairs, in order to persuade building blocks to aggregate in the desired manner. The use of F^- or Cl^- as hydrogen-bond acceptor to link to two or three hydrogen-bond donors through hydrogen-bonding interactions is much rarer in the supramolecular systems, although it has some merits: (*a*) to balance charge and to introduce a Coulomb attraction to increase packing forces, (*b*) to avoid the problem[14] of the poor solubility of starting materials encountered in the systems of complementary triple hydrogen bonds. The ionic type of aggregation will often be met in supramolecular systems containing transition-metal ions. It is very important to incorporate transition-metal ions into such systems to introduce the magnetic, optical and conductive properties characteristic of these ions into materials with potentials for non-linear optical, conducting, and ferromagnetic properties.[10a] The gold(I)–gold(I) interactions arising mainly from relativistic effects[2] are comparable to hydrogen bonds in bond energy.[15] Accordingly, it is an intriguing approach[16] to take advantage of 'aurophilicity' to associate appropriate gold(I) building blocks into cluster-like and/or polymeric structures.[17]



mbpa

The compound methyl 4,6-*O*-benzylidene-3-deoxy-3-(diphenylphosphino)-α-D-altropyranoside (mbpa) has been prepared for asymmetric catalysis[18] and its gold(I) complexes have attracted our interest because many of them possess high antitumour activity.[19] In addition to the importance of thiolate ligands in the formation of gold drugs, binding of gold(I) to thiolate functions in proteins is expected to play a key role in the molecular pharmacology of gold.[20] Herein we report the formation of a trigold(I) complex $[\{Au(mbpa)\}_3S]Cl$ **2** from the reaction of [Au(mbpa)Cl] **1** and L-cysteine, and the luminescence of these complexes at room temperature.

Experimental

Elemental analyses were performed by the Chemical Analysis Division of this Institute. Infrared spectra were measured on a

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† Chiral phosphine ligands derived from sugars. Part 9.[1]

Bio-Rad FTS-40 spectrometer (in KBr discs, 4000–200 cm^{-1}), Raman spectra on a Nicolet 910 Fourier-transform spectrometer using a Raman 1064 nm laser source at a resolution of 2 cm^{-1} with 300 scans and NMR spectra on a Varian Unity-500 spectrometer operating at 499.98 MHz for ^1H, 125.71 MHz for ^{13}C and 202.36 MHz for ^{31}P. Chemical shifts are expressed in parts per million (ppm) downfield from internal $SiMe_4$ (^1H and ^{13}C) or external 85% H_3PO_4 (^{31}P) standards as positive values. Emission and excitation spectra were measured at room temperature with a Shimadzu RF-540 spectrofluorometer using a xenon lamp. They were not corrected for instrumental response. Pseudo-potential *ab initio* calculations were performed on a VAX 11/785 computer using the GAUSSIAN 92 package.[4b,21] The Au–S and Au–P distances and the Au–S–Au and P–Au–S angles were fixed at the values found from the crystal structure. L-Cysteine was used as received.

Preparations

The compound [Au(mbpa)Cl] **1** was prepared by the literature method.[19] NMR ($CDCl_3$): ^1H, δ 8.10–6.70 (m, 15 H, aryl H), 5.41 (s, 1 H, PhC*H*], 5.06 [m, 1 H, H(5)], 4.67 [m, 1 H, H(4)], 4.60 [s, 1 H, H(1)], 4.31 [dd, 1 H, H(6e)], 3.80 [t, 1 H, H(6a)], 3.77 [m, 1 H, H(3)], 3.73 [d, 1 H, H(2)] and 3.44 (s, 3 H, CH_3); ^{13}C, δ 101.9 (Ph*C*H)], 99.0 [C(1)], 75.4 [C(4)], 69.2 [C(6)], 69.1 [C(2)], 60.6 [C(5)], 54.1 (CH_3) and 41.0 [C(3)]; ^{31}P, δ 28.3. IR (KBr): ν(O–H) 3518m, 3453m; ν(C=C) 1450m; ν(aryl–P) 1439s; ν(alkyl–P) 1396m; ν(C–O–C) 1327m, 1311w and 1292m; ν(Au–P) 392m; ν(Au–Cl) 316s cm^{-1}.

[{Au(mbpa)}$_3$S]Cl 2. To a solution of L-cysteine hydrochloride (17.5 mg, 0.1 mmol) in MeOH (10 cm^3) containing NaOMe (10.8 mg, 0.2 mmol) was added a solution of compound **1** (68.2 mg, 0.1 mmol) in CH_2Cl_2 (10 cm^3) and stirred for 10 h at room temperature under a nitrogen atmosphere. The solvent was removed under reduced pressure. The residue was taken up in hot dimethylformamide and filtered while hot. The filtrate was kept at room temperature for a few weeks to give colourless crystals of **2** (14.1 mg, yield 21.0% based on **1**), m.p. 190 °C (decomp.). NMR [$CDCl_3$–$(CD_3)_2SO$ (1 : 1, v/v)]: ^1H, δ 8.19–6.35 (m, 15 H, aryl H), 5.42 (s, 1 H, PhC*H*), 5.08 [m, 1 H, H(5)], 4.75 [m, 1 H, H(4)], 4.51 [s, 1 H, H(1)], 4.39 [dd, 1 H, H(3)], 4.31 [dd, 1 H, H(6e)], 3.92 [d, 1 H, H(2)] and 3.80 [t, 1 H, H(6a)]; ^{13}C, δ 100.8 (Ph*C*H), 100.2 [C(1)], 75.1 [C(4)], 69.2 [C(6)], 68.1 [C(2)], 61.0 [C(5)], 53.8 (CH_3) and 29.5 [C(3)]. ^{31}P, δ 26.9. IR (KBr): ν(O–H) 3457m, 3224m; ν(C=C) 1452m; ν(aryl–P) 1437s; ν(alkyl–P) 1389m; ν(C–O–C) 1324m, 1307m, 1289m; ν(Au–P) 384m; ν(Au–S) 314s cm^{-1}.

Crystallography

A single crystal of compound **2** suitable for X-ray diffraction was obtained directly from the reaction solution. Reflection data were collected at 294 K on a Rigaku AFC 7R diffractometer with Mo-Kα radiation (λ 0.710 73 Å), using the ω-scan technique ($4.0 < 2θ < 55.0°$) for a crystal with dimensions 0.20 × 0.25 × 0.50 mm, mounted on a glass fibre. Details of the crystal data are summarized in Table 1. Crystal and instrument stabilities were monitored with a set of three standard reflections measured every 100; in all cases no significant variations were found. The intensity data collected were corrected for Lorentz-polarization and absorption (empirically).The structure was solved by the Patterson method and refined on *F* by full-matrix least squares. All calculations were performed on an IBM PC/486 computer with the Siemens SHELXTL-PC program package.[22] Of the 1746 reflections collected, 1312 with $F \geqslant 4.0\sigma(F)$ were used in the solution and refinement. Final refinements of all the non-hydrogen atoms except those of the phenyl rings are anisotropic, the carbon atoms of the phenyl rings were fixed as a rigid group with C–C bond distances of 1.395 Å, and hydrogen atoms (which were calculated geometrically) as fixed isotropic contributions.

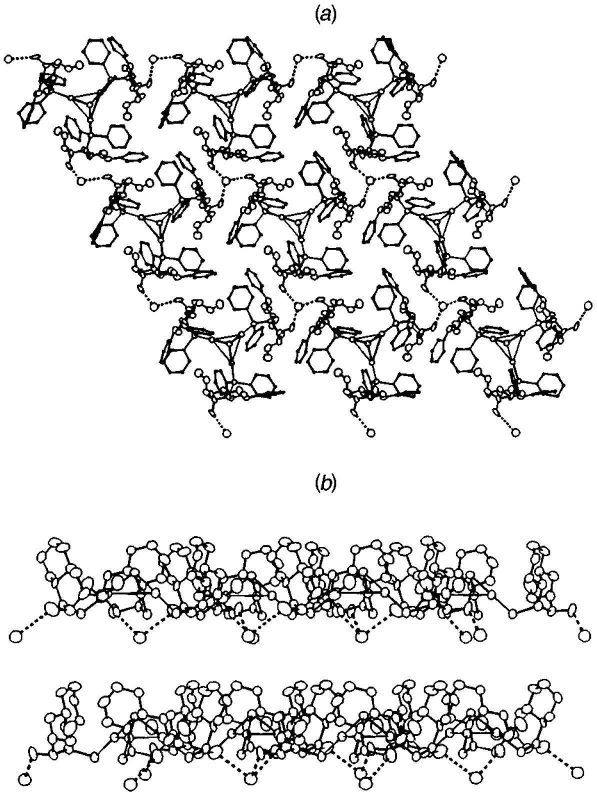

Fig. 1 Packing of complex **2** in the lattice; in (*b*) all the phenyl rings are omitted for clarity

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/470.

Results and Discussion

Synthesis

The reaction of equimolar quantities of [Au(mbpa)Cl] **1** in CH_2Cl_2 with L-$HSCH_2CH(NH_2)CO_2Na$ in MeOH gives a low yield (21.0%) of [{Au(mbpa)}$_3$S]Cl **2**, as a colourless crystalline product, which decomposes at 190 °C without melting. Analogues of complex **2** have been prepared through the reaction of $[\{Au(PR_3)\}_3O]^+$ or $[Au(PR_3)]^+$ with bis(trimethylsilyl) sulfide[8] or hydrogen sulfide.[23] Jones *et al.*[24] have reported that [Au(PPh$_3$)Cl] abstracts a sulfur atom from $Et_4P_2S_2$ to give μ$_3$-sulfido-tris[(triphenylphosphine)gold(I)] hexafluorophosphate $[\{Au(PPh_3)\}_3S]PF_6$. Since attempts to isolate and identify the organic product of C–S bond cleavage were unsuccessful, the mechanism of [Au(mbpa)Cl] abstracting a sulfur atom from L-cysteine to form the trigold(I) complex remains unclear. Cleavage of the C–S bond of ethane-1,2-dithiolate (edt) with the late transition-metal ions (Ni^{2+} or Co^+) has been observed and afforded compounds $[Ni(tpdt)(PPh_3)]$[25a] (tpdt = 3-thiapentane-1,5-dithiolate) and $[Co_7S_6(PPh_3)_6Br]$,[25b] respectively, in which the tpdt ligand arose from the condensation of two edt and loss of a sulfur atom. Isab and Sadler[26] have found that ligands exchange between a medicine myocrisin and cysteine *in vivo* when the latter is injected.

Crystal structure

As can be seen from Fig. 1, each Cl^- anion links to three $[\{Au(mbpa)\}_3S]^+$ cations through hydrogen bonds between the

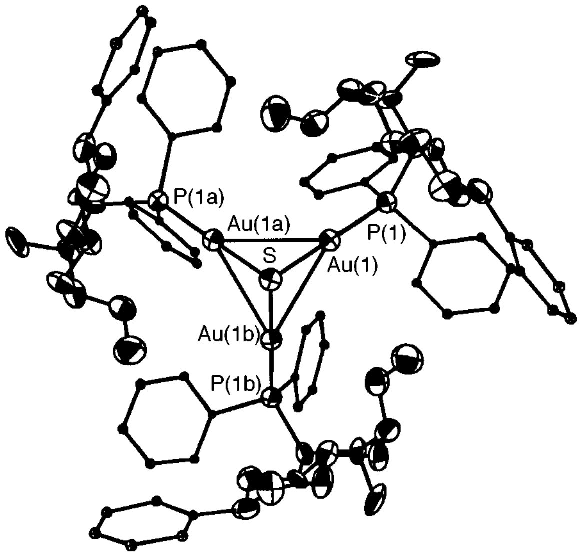

Fig. 2 Structure of the cation $[\{Au(mbpa)\}_3S]^+$ of complex **2**. Hydrogen atoms are omitted for clarity.

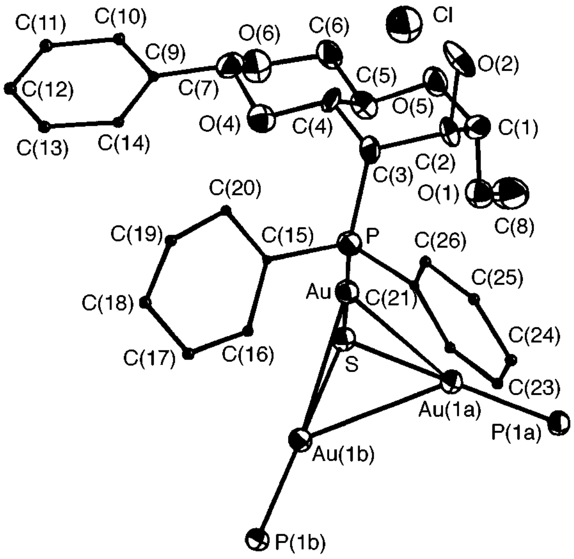

Fig. 3 Partial view of compound **2** with the atom labelling of the chiral phosphine ligand

OH group of the altropyranose ring [Cl···O(2) 3.017(10) Å], to form an infinite two-dimensional net structure. This results in a novel two-dimensional netsheet. Each netsheet is in the same direction as shown in Fig. 1(*b*). All Au, S or Cl atoms in the same sheet are coplanar, and the distance of two planes composed of the same atoms in adjacent sheets is equal to *c*/2 (9.446 Å). The phenyl rings of the adjacent sheets interlock each other, although there are no π-stacking effects.

The structure of the cation of complex **2** shown in Fig. 2 has a crystallographically imposed C_3 axis which is perpendicular to the Au_3 plane and passes through the μ_3-S atom. The Au_3S core shows a perfect trigonal-pyramidal structure with the sulfur atom occupying the apical position. In comparison with those reported,[8,24,27] the angle Au–S–Au is the nearest to 90° (deviation of 1.3°), indicating that the sulfur atom uses its p orbital to form bonds with three Au atoms which are each linked to the phosphorus atom of the chiral phosphine of mbpa to make a linear two-co-ordinate geometry at gold(I) [179.6(1)°]. To our knowledge, the angle P–Au–S is also the nearest to 180° among those reported.[8,24,27]

The Au–P [2.269(4) Å] and Au–S [2.325(3) Å] bond lengths (Table 2) are similar to those in $[\{Au(PPh_3)\}_3S]^+$ (average 2.266 and 2.327 Å, respectively),[24] but shorter than those in $[\{Au(PPh_3)\}_3S]^{2+}$ (average 2.270 and 2.399 Å, respectively)[27] and longer than those in $[Au(mbpa)(NC_5H_4S\text{-}2)]$ **3** (2.256 and 2.303 Å, respectively),[19] as expected.

Table 1 Crystal data for $[\{Au(mbpa)\}_3S]Cl$ **2**

Formula	$C_{78}H_{81}Au_3ClO_{15}P_3S$
M	2009.7
Colour	Colourless
Crystal system	Hexagonal
Space group	$P6_3$ (no. 173)
a/Å	15.165(2)
c/Å	18.897(3)
U/Å^3	3760(2)
Z	2
D_c/g cm^{-3}	1.775
F(000)	1968
η	−1.00(7)
μ/mm^{-1}	6.030
h, *k*, *l* Ranges	0–17, 0–19, 0–24
Goodness of fit	1.09
R^a	0.030
R'^b	0.050
$(\Delta/\sigma)_{max}$	0.214
Final difference peak, hole/e Å^{-3}	0.49, −0.50

[a] $R = (\Sigma||F_o| - |F_c||)/\Sigma|F_o|$. [b] $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$; $w^{-1} = \sigma^2(F) + 0.0002F^2$.

Table 2 Selected atomic distances (Å) and angles (°) for $[\{Au(mbpa)\}_3S]Cl$ **2**

Au(1)–S	2.325(3)	Au(1)–P(1)	2.269(4)
Au(1)–Au(1a)	3.251(1)	P(1)–C(15)	1.835(17)
P(1)–C(21)	1.811(15)	P(1)–C(3)	1.846(12)
Cl···O(2)	3.017(10)		
S–Au(1)–P(1)	179.6(1)	S–Au(1)–Au(1a)	45.6(1)
P(1)–Au(1)–Au(1a)	134.2(1)	P(1)–Au(1)–Au(1b)	134.8(1)
Au(1)–Au(1a)–Au(1b)	60.0(1)	Au(1)–S–Au(1a)	88.7(2)
Au(1)–P(1)–C(15)	112.4(4)	Au(1)–P(1)–C(21)	112.8(5)
Au(1)–P(1)–C(3)	118.8(5)		

Similar to those in free mbpa,[28] the altropyranose ring and the 4,6-*O*-benzylidene ring in complex **2** adopt a distorted chair conformation. The average torsion angles are ±57 (altropyranose ring) and ±61° (4,6-*O*-benzylidene ring) and ±55 (altropyranose ring) and ±60° (4,6-*O*-benzylidene ring) for free mbpa.[28] The torsion angles P–C(3)–C(2)–O(2) and O(2)–C(2)–C(1)–O(1) for **2** are 161 and 171°, respectively, indicating that the substituents PPh_2, OH and OMe are in pseudo-axial positions. The torsion angles C(21)–P–C(3)–C(2) and C(15)–P–C(3)–C(4) (173 and 147°) are comparable to those of free mbpa (173 and 152°).

Spectroscopic studies

As can be seen from the ^1H and ^{13}C NMR data compiled in the Experimental section, the resonances of the altropyranose ring of compound **2** are very similar to those of **1**, except for those of H(3) and C(3). The chemical shift of H(3) is δ 4.39 for **2** and 3.77 for **1**, and that of C(3) is δ 29.5 for **2** and 41.0 for **1**. This suggests that: (*a*) the conformation of the altropyranose ring of **2** is very similar to that of **1**, and the formation of the Au_3S core does not affect the conformation; (*b*) the Au_3S core perturbs the electron distribution of the phosphinoaltrose ligand only locally at C(3), although significantly in comparison to that in **1**, (*c*) the gold(I) in the Au_3S core is electron rich, compared to that in AuCl, which may be in part from the interaction of the d^{10} closed shell of gold(I). The latter is also confirmed by the $^{31}P\text{-}\{^1H\}$ NMR data, which show a single peak at δ 26.9 for three phosphorus atoms, shifted upfield by 1.4 and 2.4 ppm in comparison to the starting material **1** and the mononuclear P–Au–S compound $[Au(mbpa)(NC_5H_4S\text{-}2)]$ **3**,[19] respectively.

The ν(Au–P) and ν(Au–S) absorptions in the IR spectrum

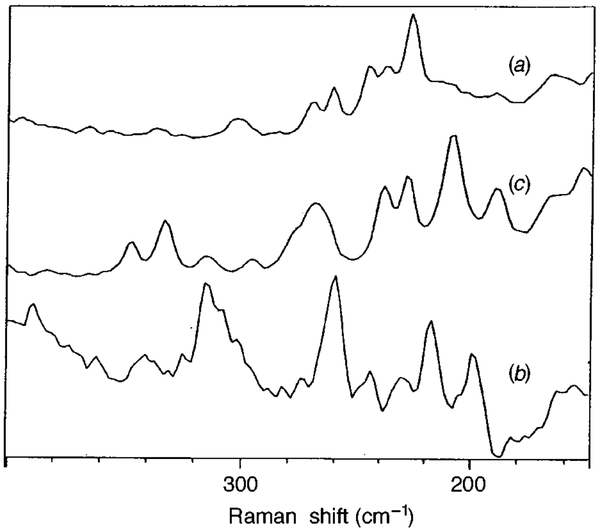

Fig. 4 Raman spectra of (*a*) free mbpa, (*b*) complex [Au(mbpa)Cl] **1** and (*c*) complex [{Au(mbpa)}$_3$S]Cl **2**

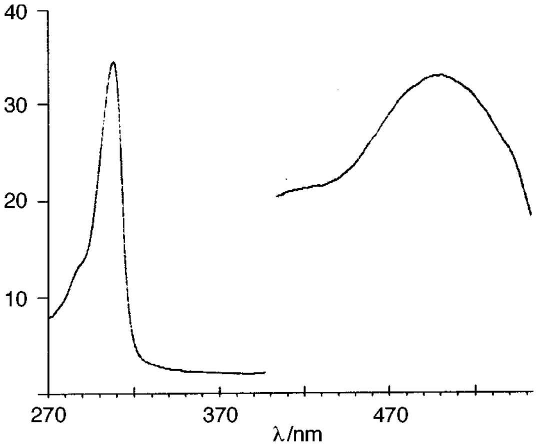

Fig. 5 Uncorrected solid-state excitation and emission spectra for the complex [{Au(mbpa)}$_3$S]Cl **2** at room temperature

of compound **2** appear at 384m and 314m cm^{-1}, respectively, which are comparable to those assigned to compounds [Au(PR$_3$)(SCN)][29] (388–375 and 360–291 cm^{-1}, respectively) and [AuL(X)] (L = mbpa or its 2-PPh$_2$ analogue, X = Cl, pyridine-2-thiolate or benzimidazole-2-thiolate) (395–368 and 326–322 cm^{-1}, respectively).[19]

The Raman spectrum of compound **2** is shown in Fig. 4(*c*). Compared to those of free mbpa [Fig. 4(*a*)] and **1** [Fig. 4(*b*)], the absorptions in the region 300–150 cm^{-1} are similar to each other and may be ascribed to the δ(P–C) mode.[30] The band at *ca.* 315 cm^{-1} of **2** is weaker than that of **1**, attributed to the fact that the ν(Au–Cl) mode is replaced by the ν(Au–S) mode. The Au–P stretching frequency is only observed for **1** at 390 cm^{-1}. The peaks at 200 cm^{-1} for **1** and 190 cm^{-1} for **2** are not from ν(Au–P), but from the splitting of the δ(P–C) mode upon co-ordination of P to Au$^{\mathrm{I}}$.

Of the three complexes **1**–**3**, only **2** luminesces at room temperature in the solid state. It displays a strong bright white emission at 495 nm when excited at 303 nm (Fig. 5). The luminescence spectrum is very similar in bandshape, but the Stokes shift of 12 800 cm^{-1} is nearly twice, to those reported,[6b] which are assigned to phosphorescence by lifetime measurements using time delays. A large Stokes shift with the present complex is indicative of a large distortion in the excited state compared to the ground state and implies that the emission is phosphorescence.[6]

For phosphinegold(I) complexes with arene- or alkanethiolate ligands it is generally accepted that the emission is due to a metal-to-ligand charge transfer (m.l.c.t.) with the excitation from an orbital primarily associated with the sulfur to the metal-based orbital of the excited state.[6] The excited transition of the present trigold(I) complex is also of the S→Au c.t. type, since S^{2-} can be seen as a reducing ligand compared to arene- or alkane-thiolates. This proposed assignment of the emission is confirmed by pseudo-potential *ab initio* calculations, which show that the highest occupied molecular orbital of [{Au(3-mpba)}$_3$S]Cl consists of large contribution from the sulfur 3s and 3p orbitals and the lowest unoccupied molecular orbital from the gold(I) 6p orbital.

This structure is noteworthy because it represents a novel example of a chiral building block containing a cluster-like core assembled through the triple hydrogen bonding between one hydrogen-bond acceptor of the anion and three hydrogen-bond donors. Therefore, this work provides *a new direction* in the design of supramolecular systems containing transition-metal ions using the anionic type of hydrogen-bond acceptor such as F$^-$, Cl$^-$ and NO$_3$$^-$. Further studies with mbpa in related systems are in progress.

Acknowledgements

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