Synthesis and Structural Characterisation of [(pta)₃Au]₂Au₂(i-mnt)₂·0.5Me₂CO·0.5MeCN; an Example of Unsupported Au^{I}···Au^{I} Interactions with [Au(pta)₃]⁺, giving a Non-linear Tetranuclear Chain {pta = phosphatriazaadamantane, i-mnt = [S₂C₂(CN)₂]²⁻}

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The water soluble complex [Au(pta)₃]Cl reacts with K₂[i-mnt] to give a non-linear, tetranuclear Au chain complex with an unprecedented structure.

As Schmidbaur has written,[1] 'gold chemistry is different'; the title complex illustrates another example of this statement as it has been found to be both strongly luminescent and water soluble.

Structural studies have demonstrated that gold(I) phosphine complexes with linear,[2] [AuL₂]⁺, (L = phosphine), trigonal planar,[3] [AuL₃]⁺ and distorted tetrahedral[4] coordination, [AuL₄]⁺, are readily formed. Indeed, the potentially tetra-coordinating tripodal ligand tris[2-(diphenylphosphino)ethyl]-amine, NP₃, gives[4] a well-characterized Au(NP₃)PF₆ salt with trigonal planar AuP₃ coordination and no detectable Au–N bonding. However, with a bidentate phosphine ligand, the di-gold(I) complex [Au₂(Me₂PCH₂PMe₂)₃](BF₄)₂ 0.5C₇H₈ is formed, which shows[3b] essentially trigonal planar AuL₃ coordination but also a short 3.05 Å Au···Au separation. This structure suggests that the [AuL₃]⁺ species might participate in Au···Au bonding even in unbridged systems.

Trigonally coordinated Au^{I} complexes generally display a strong visible luminescence,[5] as do MeCN solutions of the trigonal [AuL₃]⁺ cation, L = triphenylphosphine, to which an excess of phosphine is added.[6] The [AuL₂]⁺ and [AuL₄]⁺ complexes are not luminescent under ligand based UV excitation.

In an attempt to find a phosphine ligand which would produce a mononuclear [AuL₃]⁺ species soluble in water, we were attracted to the phosphatriazaadamantane, pta, ligand. This phosphine 1, first reported[7a] in 1974, has been shown by Darensbourg et al.[7b] to be slightly more basic than PMe₃, has a Tolman cone angle 102° smaller than PMe₃, and to form water soluble organometallic complexes. Thus, [Au(pta)₃]⁺ complexes may be expected to produce stable, optically luminescent gold(I) complexes in aqueous solution.† Furthermore, hydrogen bonding of the coordinated and protonated pta ligands should lead to the enhanced formation of crystalline products, including large clusters, suitable for structural

characterization. Indeed, these properties have been realized in several compounds that will be described elsewhere. Here we describe a tetranuclear Au₄ chain complex which displays a remarkable coordination about two of the four gold(I) centres.

The complex (pta)₃AuCl was synthesized by reacting pta (3 equiv.) with (tht)AuCl, tht = tetrahydrothiophene, in MeCN. Addition of K₂(i-mnt) in MeCN–MeOH gives a yellow solution from which the title compound **3** is isolated.‡ Crystals, mp 225 °C with decomp., suitable for diffraction were obtained from MeCN–acetone. Data were collected and the structure was solved routinely from an initial location of the Au atoms on a Patterson map. The molecular structure is given in Fig. 1. There are no close intermolecular contacts.

The [Au₂(i-mnt)₂]²⁻ moiety bonded to the two [Au(pta)₃]⁺ units in **3** has been structually characterized previously[8] with non-interacting [(Buⁿ)₄N]⁺ cations. It is a planar species with a short, 2.79 Å, Au···Au distance. The geometry of this unit

3

1

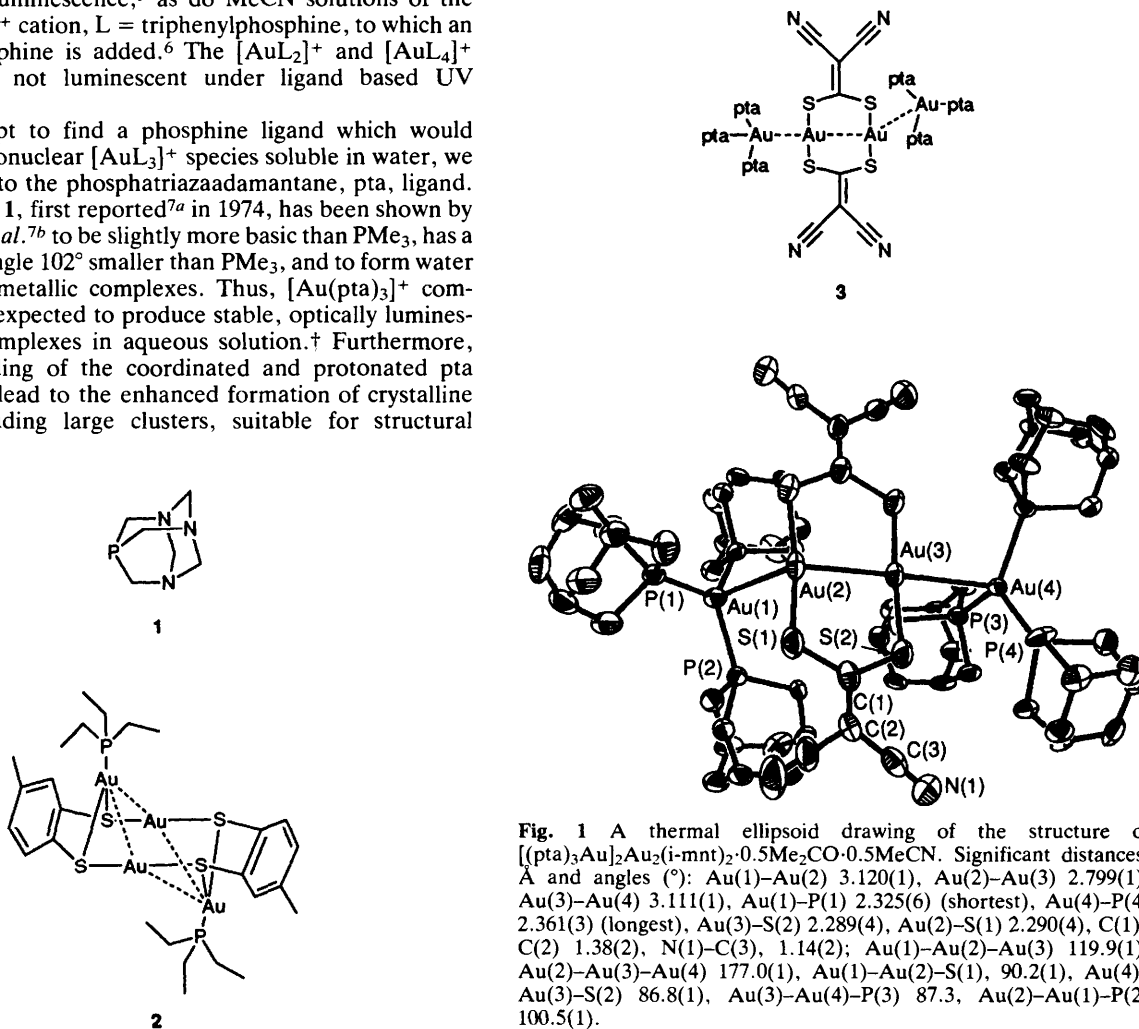

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Fig. 1 A thermal ellipsoid drawing of the structure of [(pta)₃Au]₂Au₂(i-mnt)₂·0.5Me₂CO·0.5MeCN. Significant distances, Å and angles (°): Au(1)–Au(2) 3.120(1), Au(2)–Au(3) 2.799(1), Au(3)–Au(4) 3.111(1), Au(1)–P(1) 2.325(6) (shortest), Au(4)–P(4) 2.361(3) (longest), Au(3)–S(2) 2.289(4), Au(2)–S(1) 2.290(4), C(1)–C(2) 1.38(2), N(1)–C(3), 1.14(2); Au(1)–Au(2)–Au(3) 119.9(1), Au(2)–Au(3)–Au(4) 177.0(1), Au(1)–Au(2)–S(1), 90.2(1), Au(4)–Au(3)–S(2) 86.8(1), Au(3)–Au(4)–P(3) 87.3, Au(2)–Au(1)–P(2) 100.5(1).

changes little upon interaction with $[Au(pta)_3]^+$. Previous attempts to coordinate $[AuL]^+$, L = phosphine, to the $[Au_2(i-mnt)_2]^{2-}$ anion have failed to produce isolable products. However, the related dithiolates formed from toluene-3,4-dithiol[9a] or from benzene-1,2-dithiol[9b] coordinate with $[AuPEt_3]^+$ to give tetranuclear gold(i) clusters in which the $[AuPEt_3]^+$ units coordinate centrosymmetrically to two S atoms (2.32 Å) producing a rectangle of gold(i) atoms separated[9a] from each other by about 3.1 Å, 2.

The structure of 3 (Fig. 1),§ which strongly luminesces orange as a solid under light from a hand held UV source, and yellow orange in acetone, is interesting in that the $[Au(pta)_3]^+$ units interact with each of the two Au atoms of the anion differently and do not bond to S atoms of the $[Au_2(i-mnt)_2]^{2-}$ The $[Au(PPh_3)_3]^+$ cation is known to bond weakly[10] to Cl⁻ and to the S atom of SCN⁻. The Au···Au distances are only slightly longer than the Au···Au distance observed in the $[Au_2(Me_2PCH_2PMe_2)_3](BF_4)_2·0.5C_7H_8$. The $[AuL_3]^+$ presumably behaves as a weak Lewis acid toward the gold atoms in the $[Au_2(i-mnt)_2]^{2-}$. The AuP_3 coordination about both Au(1) and Au(4) is very nearly trigonal planar (δ P–Au–P angles sum to 355.6 and 356.5°, respectively). The Au···Au interactions perturb this trigonal planarity only slightly with Au–Au–P angles ranging from 87 to 102°. The Au(4)–Au(3)–Au(2) angle is nearly linear, 177.0°, but the Au(1)–Au(2)–Au(3) angle is bent to 119.9°. The Au(1)–Au(2) and Au(3)–Au(4) distances are nearly equal at 3.120 and 3.111 Å respectively, while the Au(2)–Au(3) distance, 2.799 Å is nearly unchanged from that found in the isolated anion. The four gold atoms in the structure reside on a mirror plane.

Jones et al[11] described an unusual mixed-valance complex in which one $Au^{III}(C_6F_5)_3$ adds to $Au_2(ylide)_2$ to form a linear Au–Au–Au structure with much shorter Au–Au distances (2.572 and 2.769 Å) than those observed in the title compound. Attempts to add two $Au^{III}(C_6F_5)_3$ units failed to give an X-ray characterisable product and the NMR spectrum in solution was incompatible with the formation of a symmetrical product. The very short Au–Au distance in their compound suggests electron pair bonding between the $Au(C_6F_5)_3$ and a Au atom of the dimer, a result typically associated with Au^{II}–Au^{II} bonding.

In compound 3, the metal–metal interactions of the Au centres of the thiolate species with the three-coordinate Lewis acid $[AuL_3]^+$ are novel, although Lewis acid-base behaviour is well established for Au^I in related systems. The $[AuL_3]^+$ species are well known to bond to an additional phosphine base and other anions as stated above. Indeed, several $[AuL_4]^+$, species, L = pta, have been structurally characterized by us. The best characterised example of Lewis base behaviour in a Au^I dimer is found in the SO_2 adduct to the organometallic ylide dimer, $Au_2(ylide)_2(SO_2)_2$, in which the SO_2 bonds symmetrically to the Au^I centres[12] with a linear S–Au–Au–S axis. The non-linear Au–Au–Au–Au interaction observed in 3 is somewhat reminiscent of the structure[13] of the chain polymer complex $[TlAu(mtp)_2]_n$ mtp = $[Ph_2P(S)CH_2]^-$. In particular, the Au(2) atom (Fig. 1) is structurally similar to the 'sawhorse' geometry found for Tl^I, an ion with a $d^{10}s^2$ configuration. This latter geometry for Au (and Tl^I) is consistent with the presence of a stereochemically active lone pair of electrons, as if the ion were Au⁻, with the atom Au(3)

being square planar Au^{III} (d^8 electronic configuration). However, there is no precedence for Au⁻ in any coordination compound, even though the ion is a well established species. Calculations are underway to examine the electronic structure of this unprecedented coordination for a Au^I complex. In a related result for two coordinate $(XAuPH_3)_2$ compounds, Pyykkö recently concluded that the relativistic aurophilic attraction[14] is directly correlated with the softness of the X ligand.

Footnotes

† Crystalline $[Au(pta)_3]Cl·xH_2O$ luminesces in water and methanol. Details of this study will be reported elsewhere.

‡ Satisfactory elemental analysis was obtained (C, N and H).

§ Crystal data: monoclinic, $P2_1/m$, a = 9.759(2), b = 19.025(3), c = 18.107(3) Å, β = 101.010(10)°, Z = 2, μ = 9.167 mm⁻¹, Mo-Kα radiation, 4493 unique reflections, 3264 with $F > 4σ(F)$ used in refinement, R = 0.035, R_w = 0.034; Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

References

1 H. Schmidbaur, Interdisc. Sci. Rev., 1992, 17, 213.
2 R. J. Staples, C. King, Md. N. I. Khan, R. E. Winpenny and J. P. Fackler, Jr., Acta. Crystallogr., Sect. C, 1993, 49, 472.
3 (a) P. Jones, J. Chem. Soc., Chem. Commun., 1980, 1031; (b) W. Bensch, M. Plelati and W. Ludwig, J. Chem. Soc., Chem. Commun., 1986, 1762.
4 Md. N. I. Khan, R. J. Staples, C. King and J. P. Fackler, Jr., Inorg. Chem., 1993, 32, 5800.
5 C. King, Md. N. I. Khan, R. J. Staples and J. P. Fackler, Jr., Inorg. Chem., 1992, 31, 3236; T. M. McClesky and H. B. Gray, Inorg. Chem., 1992, 31, 1733.
6 R. C. Elder, E. H. Keller Zeiher, M. Onady and R. R. Whittle, J. Chem. Soc., Chem. Commun., 1981, 900.
7 (a) D. Daigle, A. B. Pepperman Jr. and S. L. Vail, J. Heterocycl. Chem., 1974, 11, 407; (b) J. R. DeLerno, L. M. Trefnas, M. Y. Darensbourg and R. J. Majeste, Inorg. Chem., 1976, 15, 815.
8 Md. N. I. Khan, S. Wang and J. P. Fackler, Jr., Inorg. Chem., 1989, 28, 3579.
9 (a) R. Dávila, A. Elduque, T. Grant, R. J. Staples and J. P. Fackler, Jr., Inorg. Chem., 1993, 32, 1749; (b) M. Nakamoto, A. Schier and H. Schmidbaur, J. Chem. Soc., Chem. Commun., 1993, 1347.
10 P. G. Jones, G. M. Sheldrick, J. A. Muir, M. M. Muir and L. B. Pulgar, J. Chem. Soc., Dalton Trans., 1982, 2123.
11 R. Uson, A. Laguna, M. Laguna, M. T. Tartón and P. G. Jones, J. Chem. Soc., Chem. Commun., 1988, 740.
12 C. King, D. D. Heinrich, G. Garzon, J-C. Wang and J. P. Fackler, Jr., J. Am. Chem. Soc., 1989, 111, 2300.
13 S. Wang, John P. Fackler, Jr., C. King and J.-C. Wang, J. Am. Chem. Soc., 1988, 110, 3308; S. Wang, G. Garzon, C. King, J-C. Wang and J. P. Fackler, Jr., Inorg. Chem., 1989, 28, 4623.
14 P. Pyykkö, J. Li and N. Runeberg, Chem. Phys. Lett., in the press.