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Synthesis and Crystal Structure of $\{[Au_2(dien)_2]^{2+}\}_n$ (dien = diethylenetriamine), an Infinite Linear Polymer based on Weak Gold–Gold Contacts

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The complex $\{[Au_2(dien)_2][BF_4]_2\}_n$ (dien = diethylenetriamine) has been synthesised and characterised by IR and NMR spectroscopy; the crystal structure of its ethanol solvate revealed that the molecular cation has a 16-atom ring structure and an interesting polymeric structure based on weak gold–gold contacts which extends infinitely in the (111) direction.

The development of gold(I) chemistry has been influenced by the generalisation that gold is a typical Class B metal (or soft) Lewis acid, and shows a much greater tendency to form complexes with sulfur or phosphorus than with oxygen and nitrogen ligands. There are therefore an abundance of gold(I) phosphine complexes which are very commonly used as reagents in organometallic and cluster chemistry[1,2] and, more importantly, for the basis of drugs for the treatment of rheumatoid arthritis.[3] In contrast the chemistry of gold(I) with nitrogen ligands has been neglected. The first structurally characterised gold(I) complex co-ordinated to two nitrogen donor ligands was reported by Sadler and co-workers[4] in 1978 and was found to exhibit therapeutic properties as an anti-inflammatory drug similar to the gold(I) thiolates. The compounds [AuCl(pip)] (pip = piperidine) and [AuCl(py)] (py = pyridine) have also been structurally characterised and show interesting structural differences.[5,6] We have recently reported the synthesis and structural characterisation of $[Au(NH_3)_2]^+$.[7] Since there is great interest in the development of new water soluble anti-arthritic and anti-tumour agents of gold(I), we have synthesised a variety of novel gold(I) compounds with nitrogen ligands. In this communication we describe the synthesis, isolation and spectroscopic characterisation of $\{[Au_2(dien)_2][BF_4]_2\}_n$ [dien = $NH_2(CH_2)_2NH(CH_2)_2NH_2$] and the crystal structure of its ethanol solvate.

The compound $\{[Au_2(dien)_2][BF_4]_2\}_n$ is formed very rapidly when dien (0.022 g) is added dropwise to a solution of $[Au(NCPh)_2]^+$ [8] (0.10 g) in MeCN (10 cm^3) at room temperature. After stirring for 45 min the colourless solution was reduced to dryness and washed with CH_2Cl_2. The resultant residue was recrystallised from MeCN–Et_2O to give a colourless crystalline solid in 80% yield based on gold. The compound is slightly photosensitive, but may be stored indefinitely under nitrogen at −25 °C in the dark.

Single crystals suitable for X-ray crystallography were grown by crystallising the compound from EtOH.† The crystal structure of $\{[Au_2(dien)_2][BF_4]_2\cdot EtOH\}_n$ shows that the nitrogen atoms of the ligand are not simultaneously co-ordinated to a single gold cation. The dien acts as a bidentate ligand and pairs of them link adjacent centrosymmetrically related gold(I) centres to form 16-membered macrocyclic dimers. The structure contains two crystallographically independent C_i symmetric macrocycles. These are linked *via* weak Au–Au interactions [3.312(1) Å], to form chains that extend in the crystallographic (111) direction, Fig. 1. Each macrocycle is self-filling [the transannular Au(1)–Au(1a) and Au(2)–Au(2a) distances are 4.54 and 4.62 Å respectively] and has a virtually identical conformation, there being a retention of

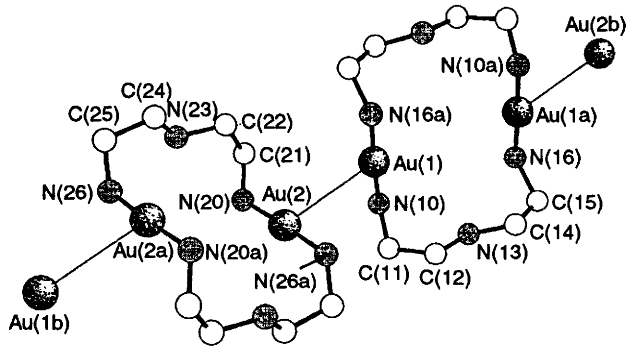

Fig. 1 A pair of weakly linked crystallographically independent macrocyclic dimers in the structure of $\{[Au_2(dien)_2][BF_4]_2\cdot EtOH\}_n$. Selected bond and contact distances (Å): Au(1)–Au(2) 3.312(1), Au(1)–N(10) 2.027(10), Au(1)–N(16a) 2.053(11), Au(2)–N(20) 2.030(10) and Au(2)–N(26a) 2.046(10)

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† Crystal data: $[C_{10}H_{26}Au_2N_6][BF_4]_2\cdot CH_3CH_2OH$, M = 819.97, triclinic, a = 9.0480(8), b = 11.7375(13), c = 12.5152(12) Å, α = 94.114(10), β = 109.461(8), γ = 106.267(8)°, space group $P\bar{1}$, Z = 2, D_c = 2.302 g cm^{-3}, μ(Mo-Kα) = 12.463 mm^{-1}, $F(000)$ = 764, T = 150(2) K, final $R1$ = 0.0403, $wR2$ = 0.0933 for 2377 independent observed reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta \leqslant 45°$], $w^{-1} = \sigma^2(F_o)^2 + (0.0597P)^2$ where $P = (F_o^2 + 2F_c^2)/3$. Data were measured on a Siemens P4/PC diffractometer with graphite-monochromated Mo-Kα radiation using ω scans. The structure was solved by the heavy-atom method. Both the BF_4^- anions and the included EtOH molecules are disordered and partial occupancy alternative orientations were identified. The N–H hydrogen atoms on N(13) and N(23) could not be located; pairs of 50% occupancy hydrogen atoms were included in tetrahedral positions on these two centres. All non-hydrogen atoms except the carbon atom of the disordered ethanol CH_3 group were refined (using F^2 data) anisotropically using absorption corrected data. Computations were carried out using SHELXTL 5.03.[9]

Atomic coordinates, bond lengths and angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

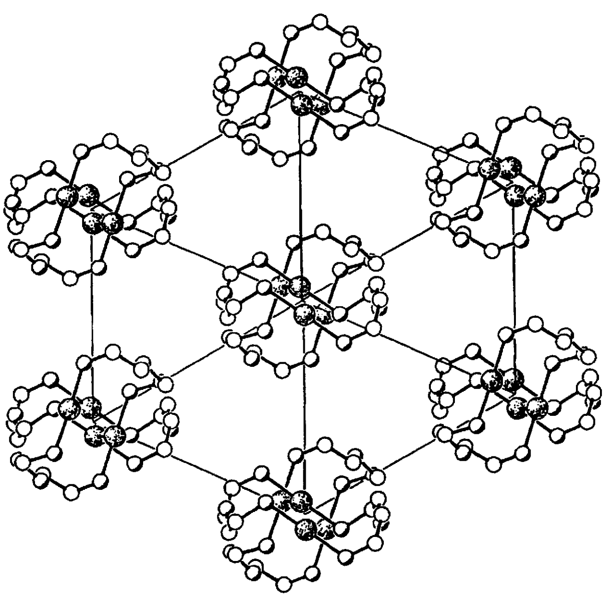

Fig. 2 The pseudo close-packed hexagonal array of polymer chains viewed down the (111) direction (The interleaving BF_4^- anions and EtOH solvent molecules have been omitted for clarity.)

gauche and *anti* geometries about the C–C and C–N bonds respectively, for each ligand. The co-ordination geometries at the gold(I) centres are in each case essentially linear [178.0(4) at Au(1) and 177.2(4)° at Au(2)]. This preference of gold(I) to adopt a linear geometry outweighs the chelating effect and co-ordination of the dien to a single gold(I) centre.[10] Adjacent macrocycles are rotated by *ca.* 74° with regard to each other about the Au(1)–Au(2) linkage. The AuAu ··· AuAu chains are non-linear there being fold angles within each chain of 161 and 139° at Au(1) and Au(2), respectively. The chains of macrocycles are parallel and packed to form an approximately close-packed hexagonal array, Fig. 2.

The short Au(1)–Au(2) contacts observed here contrast with the dimers $\{[Au(NH_2Pr^i)(C\equiv CPh)]_2\}_n$[11] and $\{[Au(Pr^iO)_2PS_2]_2\}_n$[12] which have short Au–Au contacts within the dimer and between dimers. This difference can be attributed to the larger bite angle of the outer nitrogen atoms of dien. The Au–N distances are in the range 2.053(11)–2.027(10) Å and do not differ significantly from the distances reported for $[Au(NH_3)_2]^+$ and the gold dimers mentioned above. There are two EtOH molecules of crystallisation within the unit cell and together with BF_4^- anions they participate in a complex network of hydrogen bonds with adjacent nitrogen atoms from the dien. The only Cu^I–dien complex to have been structurally characterised, $[Cu(dien)(CO)]^+$,[13] has the dien acting as a tridentate ligand forming a distorted tetrahedral geometry around the Cu. Surprisingly no Ag^+–dien analogues have been reported. Bond distances and angles within the dien ligand do not differ significantly from values previously reported for the square-planar Au^{3+}–dien complex $[Au(dien)Cl]^{2+}$,[14] although the conformation differs greatly.

The FAB mass spectrum of $\{[Au_2(dien)_2][BF_4]_2\}_n$ shows a parent ion peak which can be attributed to $[Au_2(dien)_2]^{2+}$ (m/z = 300, 45%), and $[Au(dien)_2]^+$ (m/z = 403, 10%). The IR spectrum of the ethanol-free sample (KBr disc) shows bands at 3334, 3287, 3193 and 3099 [ν(N–H)], 2947 and 2833 [ν(C–H)], 1084 [ν(B–F)] and 534 and 522 cm^{-1} [ν(Au–N)]. The ^{13}C NMR spectrum shows two (1:2:1) triplets at δ 49.1 and 45.3, $^1J(^{13}C-H)$ = 134 and 142 Hz, respectively, which are attributed to the chemically inequivalent CH_2 groups.

These results taken together with those recently reported[7,8,10] suggest that the chemistry of gold(I) with nitrogen ligands is more varied and structurally interesting than previously thought.

Acknowledgements

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References

1 R. J. Puddephatt, *Comprehensive Organometallic Chemistry*, eds. G. Wilkinson, F. G. A. Stone and E. W. Abel, Pergamon, Oxford, 1st edn., 1984, p. 765.

2 K. P. Hall and D. M. P. Mingos, *Prog. Inorg. Chem.*, 1984, **32**, 237.

3 R. V. Parish and S. N. Cottrill, *Gold Bull.*, 1987, **20**, 3 and refs. therein.

4 N. A. Malik, P. J. Sadler, S. Neidle and G. L. Taylor, *J. Chem. Soc., Chem. Commun.*, 1978, 711.

5 J. J. Guy, P. G. Jones, M. J. Mays and G. M. Sheldrick, *J. Chem. Soc., Dalton Trans.*, 1977, 8.

6 V. H.-N. Adams, W. Hiller and J. Strähle, *Z. Anorg. Allg. Chem.*, 1982, **485**, 81.

7 D. M. P. Mingos, J. Yau, S. Menzer and D. J. Williams, *J. Chem. Soc., Dalton Trans.*, 1995, 319.

8 D. M. P. Mingos and J. Yau, *J. Organomet. Chem.*, 1994, **479**, C16.

9 G. M. Sheldrick, SHELXTL 5.03, University of Göttingen, 1995.

10 D. M. P. Mingos, J. Yau and H. R. Powell, *Polyhedron*, in the press.

11 P. W. R. Corfield and H. M. M. Shearer, *Acta Crystallogr.*, 1967, **23**, 156.

12 S. L. Lawton, W. J. Rohrbaugh and G. T. Kokotailo, *Inorg. Chem.*, 1972, **9**, 2227.

13 M. Pasquali, F. Marchetti and C. Floriani, *Inorg. Chem.*, 1978, **17**, 1684.

14 G. Nardin, L. Randaccio, G. Annibale, G. Natile and B. Pitteri, *J. Chem. Soc., Dalton Trans.*, 1980, 220.

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