Letter

Synthesis and crystal structure of $[Au_2(N\text{-}Ts[9]aneNS_2)Cl_2]_2$ {N-Ts[9]aneNS$_2$ = 7-(toluenesulfonyl)-7-aza-1,4-dithiacyclononane} incorporating Au···Au and π–π interactions

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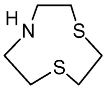
Reaction of AuCl(tht) (tht = tetrahydrothiophene) with N-Ts[9]aneNS$_2$ {N-Ts[9]aneNS$_2$ = 7-(toluenesulfonyl)-7-aza-1,4-dithiacyclononane} affords the tetranuclear Au(I) species $[Au_2(N\text{-}Ts[9]aneNS_2)Cl_2]_2$ which exhibits Au···Au and π–π interactions leading to an overall infinite chain structure.

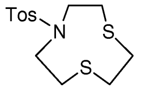
The co-ordination of Au(I) by thioether crowns is well documented.[1–3] The Au(I) centre usually adopts a distorted tetrahedral geometry as in $[Au([9]aneS_3)_2]^{+}$[1] and $[Au([18]aneS_6)]^{+}$,[2] whereas linear co-ordination is observed in Au([9]aneS$_3$)Cl[3] where only one thioether donor is bound to Au(I). Ligation of amines to Au(I) fragments is known,[4] but is much less common than ligation with sulfur due to Au(I) being a typical class B/soft metal ion.[5] Although co-ordination of [18]aneN$_2$S$_4$ to Au(I) leads to an unstable product which decomposes to form elemental gold, its methylated analogue, Me$_2$[18]aneN$_2$S$_4$, gives a stable species $[Au(Me_2[18]aneN_2S_4)]^+$ in which only the thioether donors are co-ordinated to the metal.[2] Little has been reported[6] on the interaction of Au centres with mixed N/S donor macrocycles such as [9]aneN$_2$S and [9]aneNS$_2$, and we therefore undertook a study of the interaction of Au(I) with [9]aneNS$_2$.

Initial reactions of AuCl(tht) (tht = tetrahydrothiophene) with [9]aneNS$_2$ in 2 : 1 and 1 : 1 stoichiometries resulted in the formation of insoluble products, probably polymeric species, which could not be characterised fully. We have found previously that thioether crowns can form extended polymers with d^{10} metal ions.[7] In light of this, the macrocyclic precursor, N-Ts[9]aneNS$_2$ [7-(toluenesulfonyl)-7-aza-1,4-dithia cyclononane], was used in the hope that the tosyl group would make the resulting product more soluble. Also, the protection afforded to the amino group might be expected to inhibit reduction of Au(I) to the metal.

Reaction of AuCl(tht) with N-Ts[9]aneNS$_2$ in a 2 : 1 molar ratio in CH$_2$Cl$_2$ resulted in a colourless solution. Addition of Et$_2$O yielded a white solid which was collected by filtration and dried. Microanalytical and spectroscopic data for the complex are consistent with the stoichiometry Au$_2$(N-Ts[9]aneNS$_2$)Cl$_2$.† Crystals of the dichloromethane hemisolvate suitable for X-ray diffraction‡ were obtained by the slow diffusion of Et$_2$O vapour into a solution of the complex in CH$_2$Cl$_2$.



[9]aneNS$_2$



N-Ts[9]aneNS$_2$

The structure contains two Au$_2$(N-Ts[9]aneNS$_2$)Cl$_2$ units linked across a crystallographic inversion centre by two equivalent Au···Au interactions [Au···Au 3.1155(5) Å] (Fig. 1). The macrocyclic ring has a strained [225] conformation[8] similar to that observed by Parker and co-workers in Au([9]aneS$_3$)Cl.[3] While the Au···Au distance is longer than that found in metallic gold (2.884 Å),[9] it is shorter than twice the van der Waals radius for gold (3.32 Å)[10] and comparable to those of known Au···Au interactions, some of which have been calculated as having bond strengths lying between those of the strongest hydrogen-bonds and those of the weakest covalent bonds (42–46 kJ mol^{-1}).[11] The FAB mass spectrum of the complex shows a fragmentation peak corresponding to $[Au_2L_2Cl]^+$ at m/z 1064. Each Au(I) centre is bound to a Cl$^-$ anion and one thioether donor in an almost linear fashion [S(1)–Au(1)–Cl(1) 171.27(5), S(4^i)–Au(2)–Cl(2) 178.86(5)°], the Au···Au interactions being orthogonal to these bonds [Cl(1)–Au(1)–Au(2) 89.47(4), Cl(2)–Au(2)–Au(1) 96.13(4)°] (Fig. 1).

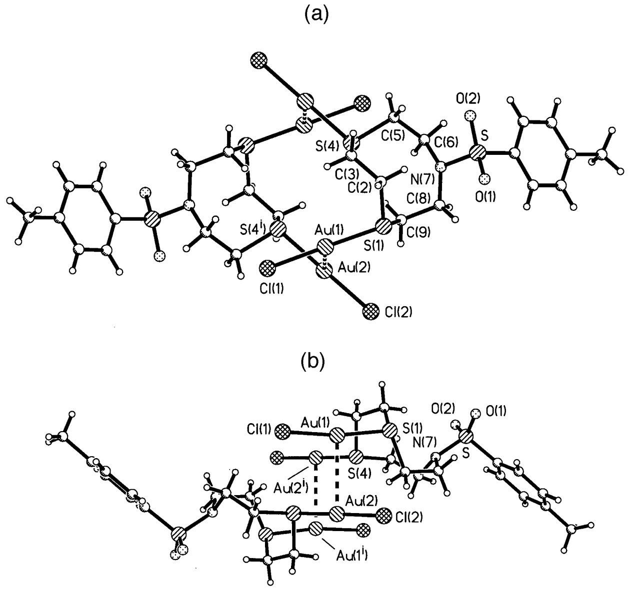


Fig. 1 Two views (a) and (b) of the tetranuclear fragment of $[Au_2(N\text{-}Ts[9]aneNS_2)Cl_2]_2$. Selected bond lengths (Å) and angles (°): Au(1)···Au(2) 3.1155(5), Au(1)–S(1) 2.2581(14), Au(2)–S(4^i) 2.2711(13), Au(1)–Cl(1) 2.2664(15), Au(2)–Cl(2) 2.2770(14), S(1)–Au(1)–Cl(1) 171.27(5), S(1)–Au(1)–Au(2) 98.73(3), Cl(1)–Au(1)–Au(2) 89.47(4), S(4^i)–Au(2)–Cl(2) 178.86(5), S(4^i)–Au(2)–Au(1) 84.72(3), Cl(2)–Au(2)–Au(1) 96.13(4) ($i = -x + 2, -y, -z$).

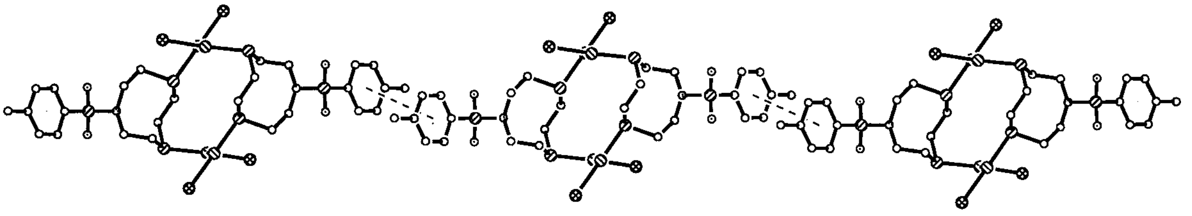


Fig. 2 Crystal packing of $\{Au_2(N\text{-}Ts[9]aneNS_2)Cl_2\}_\infty$. The π–π interactions (dashed lines) give a centroid–centroid distance of 4.14 Å and an interplanar distance of 3.48 Å.

Additionally, the crystal structure determination also shows the presence of π–π interactions in the solid state (Fig. 2), with the aromatic rings of neighbouring dimeric units lying parallel to each other and separated by a perpendicular distance of 3.48 Å. The ring centroids lie 4.14 Å apart and are offset by 2.24 Å relative to one another, as is typically observed in aromatic π–π stacking.[12] While these interactions may not persist in solution, they obviously have a significant role to play in the overall geometry of the complex in the solid state. Such interactions, together with hydrogen-bonding, has allowed Munakata and co-workers to form[13] infinite linear chains of Cu(I) quinoline-2-thione complexes. The same author has also observed π–π stacking playing a considerable role in the structure of many polymeric complexes.[14] Additionally, π–π stacking, together with Ag···Ag interactions, has played a vital role in the construction of a polymeric Ag(I) complex of 1,2-*trans*-(4-pyridyl)ethene.[15]

In conclusion, the complex $[Au_2(N\text{-}Ts[9]aneNS_2)Cl_2]_2$ shows interesting π–π and Au···Au interactions which combine to give an overall polymeric motif. With a great variety of tosylated mixed N/S macrocycles available and the replacement of the tosyl group for larger aromatic systems possible, an interesting and varied chemistry is anticipated from this system.

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Notes and references

† Experimental procedure: a solution of 7-(toluenesulfonyl)-7-aza-1,4-dithiacyclononane (0.016 g, 0.05 mmol) in the minimum amount of CH_2Cl_2 (1 cm^3) was added to a stirred solution of AuCl(tht) (0.032 g, 0.10 mmol) in the minimum amount of CH_2Cl_2 (1 cm^3). After stirring for 30 min, Et_2O (10 cm^3) was added to the clear solution to afford a white precipitate which was collected by filtration. Yield 0.034 g, 86% (Calc. for $C_{13}H_{19}Au_2Cl_2NO_2S_3$: C, 19.96; H, 2.45; N, 1.79. Found: C, 19.77; H, 2.46; N, 1.53%). FAB mass spectrum (nitrobenzyl alcohol matrix): *m/z* 1064 ($Au_2L_2Cl^+$, 10%), 977 ($Au_3LCl_2{}^+$, 18%), 831 ($AuL_2{}^+$, 42%), 746 (Au_2LCl^+, 27%), 514 (AuL^+, 100%). ^1H NMR ($CDCl_3$, 300 MHz, 293 K): δ 7.60 (d, $J = 8.3$, 2H, Ar), 7.37 (d, $J = 8.4$ Hz, 2H, Ar), 3.51 (br s, 4H), 3.45, (br s, 8H), 2.46 (s, 3H, $ArCH_3$).

‡ Crystal data for **1**: $C_{13}H_{19}Au_2Cl_2NO_2S_3\cdot 0.5CH_2Cl_2$, $M = 824.77$, triclinic, space group $P\bar{1}$, $a = 7.977(1)$, $b = 11.053(1)$, $c = 12.455(1)$ Å, $\alpha = 107.37(1)$, $\beta = 95.23(1)$ $\gamma = 90.33(1)°$, $U = 1043.08(18)$ $Å^3$, $Z = 2$, $\mu = 14.741$ mm^{-1}, $T = 203(2)$ K, 9778 reflections collected, 5240 independent reflections [$R_{int} = 0.048$], R_1 [$I > 2\sigma(I)$] = 0.0361, wR_2(all data) = 0.0987. All significant difference electron density features lie within 1.07 Å of Au(1) or Au(2). The CH_2Cl_2 solvent molecule is disordered about a crystallographic inversion centre. CCDC reference number 440/104. See http://www.rsc.org/suppdata/nj/1999/345/ for crystallographic files in ·cif format.

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