Inorganica Chimica Acta, *155* (1989) 227–230

Crystal and Molecular Structure of Chloro-1,4,7-trithiacyclononane Gold(I): Adoption of a Strained [225] Conformation by the Macrocyclic Ligand

DAVID PARKER*, PARTHA S. ROY

Department of Chemistry, University of Durham, South Road, Durham DH1 3LE, U.K.

GEORGE FERGUSON* and MARGARET M. HUNT

Department of Chemistry and Biochemistry, University of Guelph, Guelph, N1G 2W1, Canada

(Received June 10, 1988)

Abstract

The crystal structure of Au($C_6H_{12}S_3$)Cl has been determined by X-ray diffraction methods. Each gold atom adopts an approximately linear geometry, with a bond to one of the sulphur atoms of the [9]-S_3 ligand, which adopts a strained [225] conformation (Au–S = 2.270(3) Å). An infinite, almost linear, gold chain is formed along a crystallographic glide plain with Au- - -Au = 3.3095(4) Å, and Au–$\hat{\text{Au}}$–Au = 176.34(1)°, indicative of fairly weak metal–metal bonding.

Introduction

The coordination chemistry of gold(I) is dominated by the tendency of gold to adopt linear complexes [LAuX] in many of which the gold atoms interact to generate either oligomeric or polymeric chains [1–3]. Such behaviour is not conducive to the formation of macrocyclic complexes of gold(I), although examples of three and four coordinate complexes have been defined [4–6]. During the course of some preliminary work in gold macrocyclic coordination chemistry, we have investigated the reaction of 1,4,7-trithiacyclononane with ClAu[S($CH_2CH_2OH)_2$] – a convenient precursor complex for studies of gold(I) chemistry.

Results and Discussion

Reaction of equimolar quantities of 1,4,7-trithiacyclononane and ClAu[S($CH_2CH_2OH)_2$] in aqueous acetone yielded a colourless precipitate which was recrystallised from acetonitrile. The complex is insoluble in common solvents (e.g. $CHCl_3$, Me_2CO, MeOH), and both the ^1H and ^{13}C NMR spectra (298 K, CD_3CN) revealed only one resonance (δ_H + 3.17 ppm; δ_C 35.8 ppm) consistent with local C_3 symmetry. There was a small coordination shift, $\Delta\delta_H = 0.07$, $\Delta\delta_C = 0.40$ ppm. The ^1H NMR spectrum of the complex in CD_3CN was examined over the temperature range 310 to 230 K. The resonance at 3.17 ppm was observed to broaden as the temperature was lowered but no further signals were observed at the lower temperature limit ($\omega_{1/2}$ = 35 Hz, 235 K). The same degree of line-broadening effect also occurred with different concentrations of the complex. In the presence of a mole equivalent of free ligand the signal due to the free ligand remained sharp while the complex gave a line-broadened signal as before. Such behaviour suggest that in solution the three sulphur atoms are equivalenced by a fast intramolecular exchange process.

The crystal structure of the complex (Fig. 1) revealed that the unique gold atom has only one sulphur atom of the [9]-S_3 macrocycle and a chlorine coordinated in a linear fashion (Cl–Au–S(1) = 176.3(1)°). The gold atom is further weakly coordinated (Table 1) to two adjacent gold atoms (related by a crystallographic *a* glide plane) to produce an infinite, almost linear-array of gold atoms extending along the crystallographic *a* direction (Au–Au = 3.3095(4) Å, Au–$\hat{\text{Au}}$–Au = 175.34(1)°) (Fig. 2).

The gold–gold separation is larger than that in metallic gold (2.884 Å) [7a], but is significantly shorter than two van der Waals radii. Similar distances between gold(I) atoms have been observed in the chain structures of [($C_3H_7NH_2$)Au(C≡CPh)] (3.274 Å) [7b], and [AuCl(PCl_3)] (3.14 Å) [7c], and in [(piperazine)AuCl] (3.30 Å) [3] in which an Au_4 square has been located. It seems likely that these short contacts are due to the ease of packing linear molecules to form gold chains, rather than to any significant bonding interactions [7e]. An infinite chain of gold atoms, similar to that reported here, has also been found in iodo(tetrahydrothiophene)gold(I) [2]. In that case, each gold atom was bound in turn to two iodine and two thioether ligands, and the gold–gold separations were some-

---

*Authors to whom correspondence should be addressed.

0020-1693/89/$3.50

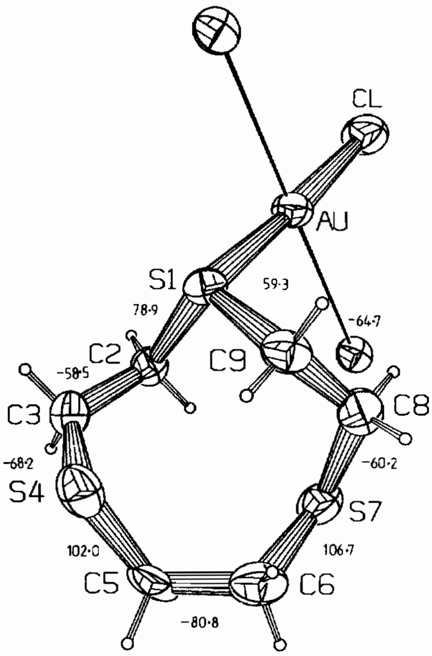

Fig. 1. A view normal to the Au–Au–Au chain. For clarity, the atoms are shown as bare ellipsoids at the 20% probability level, and the torsion angles are also given.

TABLE 1. Selected Molecular Dimensions for ([9]-S_3·AuCl)[a]

Bond distance (Å)		Bond angles (°)	
Au–Au(I)	3.3095(4)	Au(II)–Au–Au(I)	176.34(1)
Au–Cl	2.267(3)	Au(II)–Au–Cl	100.85(8)
Au–S(1)	2.270(3)	Cl–Au–S(1)	176.3(1)
S(1)–C(2)	1.838(10)	Au(I)–Au–Cl	81.65(8)
C(2)–C(3)	1.504(15)	Au–S(1)–C(2)	106.2(3)
		Au(II)–Au–S(1)	75.56(6)
		Au–S(1)–C(9)	106.4(4)

[a] e.s.d.s are given in parentheses. The Roman numerals refer to the following equivalent positions: (I) $\frac{1}{2} + x, y, \frac{1}{2} - z$; (II) $-\frac{1}{2} + x, y, \frac{1}{2} - z$.

what shorter (2.980(2); 2.967(2) Å) and non-linear (Au–Âu–Au = 161.25(4)° and 155.46(4)°). The gold–chlorine (2.267(3) Å) and gold–sulphur (2.270(3) Å) distances are similar to those reported in some analogous linear complexes e.g. in chloro-(*N*-propyl-1,3-imidazoline-2-thione-S)gold(1), Au–Cl = 2.27(1) Å and Au–S = 2.25(1) Å [8]; in Ph_3P–Au–Cl, Au–Cl = 2.279(3) Å [9]; in $(PhO)_3PAuCl$, Au–Cl = 2.273(3) Å [10]; in bis(ethylenethiourea)gold(1) chloride hydrate, Au–S = 2.279(3) Å [11]. The geometry at S(1) is pyramidal and the ligand dimensions (mean C–S = 1.82(1), C–C = 1.50(2) Å) are unexceptional.

Analysis of the torsion angle data (Fig. 1) shows that the 1,4,7-trithiacyclononane ligand adopts a rather stained conformation with an approximate two-fold axis passing through S(1) and the C(5)–C(6) band. The conformation may be considered to be a [225] form (following Dale's analysis) [12], rather than the more common and less strained [333] or [234] conformations previously reported for [9]-S_3 [13] and [9]-N_2S [14] macrocyclic complexes. In these more common conformations, at least two of the donor atoms are bound to the metal. The gold complex is the first structure reported with this cycle in which [9]-S_3 behaves as a monodentate ligand, and which adopts this strained conformation.

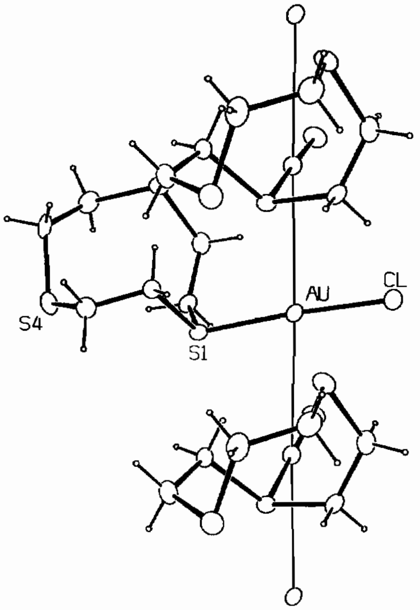

Fig. 2. A view of the [9]-S_3AuCl unit with two adjacent gold atoms, showing the numbering scheme. Thermal ellipsoids are at the 50% level.

The structure of the complex in acetonitrile solution is different from that defined in the solid state. The NMR data suggest that the gold atom is bound to three equivalent sulphurs, or that there is rapid intermolecular exchange on the NMR time scale (298 down to 230 K) of the three sulphur donors. Reaction of the gold complex with aromatic thiols in acetonitrile (e.g. *para*-thiocresol) leads to quantitative formation of the corresponding polymeric gold thiolate complex $[Au(SAr)]_n$ [1c].

Experimental

Proton NMR spectra were recorded on a Bruker AC 250 (250 MHz); carbon-13 spectra were recorded on a Bruker AC-250 (62.9 MHz). Chemical shifts are given in ppm relative to $SiMe_4$ (0 ppm). Infrared spectra were recorded as KBr discs using a Perkin-Elmer 297 spectrophotometer. Commercial solvents were distilled from an appropriate drying agent under nitrogen, prior to use according to standard procedures. Thiodiglycol and 1,4,7-trithiacyclononane were purchased from Aldrich Chemical Co.

Chloro-1,4,7-trithiacyclononane Gold(I)

To a solution of potassium tetrachloro-aurate dihydrate (0.1 g, 0.24 mmol) in aqueous acetone (4 cm^3; 1:1) at 2 °C was added thiodiglycol (0.06 g, 0.48 mmol) in acetone (1 cm^3). After thirty minutes a colourless solution formed, to which a solution of 1,4,7-trithiacyclononane (0.065 g, 0.36 mmol) in acetone (6 cm^3) was added. An immediate white precipitate was obtained, which was filtered, washed with acetone (3 × 1 cm^3) and dried *in vacuo* over P_2O_5, 0.08 g (80%). *Anal.* Found: C, 17.0; H, 2.52; S, 23.1; Cl, 8.53. Calc. for $AuC_6H_{12}ClS_3$: C, 17.4; H, 2.91; Cl, 8.60; S, 23.3%. $\delta_H(CD_3CN)$ 3.17(s); $\delta_C(CD_3CN)$ 35.8 ppm. IR: ν(Au–S) 350 cm^{-1}, ν(Au–Cl) 330 cm^{-1}. Colourless prisms, suitable for X-ray analysis were grown from a saturated solution of the gold complex in acetonitrile, at −4 °C.

The corresponding bromo complex may be obtained in an analogous manner, (82% yield). The complex is soluble in acetonitrile but decomposes quickly to leave a gold mirror. *Anal.* Found: C, 15.5; H, 2.60; S, 21.0. Calc. for $AuC_6H_{12}BrS_3$: C, 15.7; H, 2.65; S, 21.0%. IR (KBr) ν(Au–S) 350 cm^{-1}.

Crystal Data

$C_6H_{12}AuClS_3$, $M = 412.8$, orthorhombic, a = 6.616(1), b = 7.593(1), c = 21.198(5) Å, V = 1064.8(5) Å^3, $Z = 4$, D_c = 2.57 g cm^{-3}, μ(Mo Kα) = 145.6 cm^{-1}, $F(000)$ = 768. Space group P_nma or $P_n2(1)a$ from the symstematic absences ($0kl$, $k + l$, = $2n + 1$; $hk0$, $h = 2n + 1$); $P_n2(1)a$ chosen after consideration of intensity statistics and confirmed by the successful analysis and refinement.

Data Collection and Processing

Data were collected with a small colourless crystal (0.11 × 0.20 × 0.40 mm) on a CAD 4 diffractometer, using the $\omega/2\theta$ scan mode to a maximum 2θ of 54°, with graphite monochromated Mo Kα radiation; 1249 unique reflections were measured and after correction for Lorentz, polarisation and absorption effects, the 916 reflections with $I > 3\sigma(I)$ were labelled observed and used in the structure solution and refinement.

Structure Analysis and Refinement

The x and z coordinates of the Au atom were determined from an analysis of the three-dimensional Patterson function (the Au y coordinate was set at zero to define the origin (Table 2). Initial heavy-atom phasing was slightly complicated by the Au atom lying very close to $x = 0$, $z = 0.25$, but careful selection of atomic sites from the Au-phased Fourier summation, revealed the structure. Refinement was by full-matrix least-squares calculations with all non-hydrogen atoms allowed anisotropic motion. Hydrogen atoms were visible in early difference maps and were included (but not refined) as riding atoms with C–H = 0.95 Å in the final rounds of refinement. The weights used in the least-squares calculations were based on the counting statistics and an extinction correction was also made ($g = 3.0 \times 10^{-7}$). At convergence, $R = 0.0238$, $R_w = 0.0323$, and the shift/error ratio was less than 0.001. At an intermediate stage in the refinement, calculations with the opposite hand, lead to R factors which were 0.5% higher than those for the chosen model; at the conclusion of the analysis, refinement with the opposite hand led to values of R and R_w of 0.030 and 0.041 respectively. A final difference map had two small peaks (0.9 e Å^{-3}) 0.9 Å from Au, but was otherwise featureless. All calculations were performed on a PDP11/73 computer system using the SDP-Plus system of programs [15].

TABLE 2. Atomic Coordinates[a]

Atom	x	y	z	B (Å)^2
Au	0.01324(4)	0.0	0.24751(1)	2.925(6)
Cl	0.0704(5)	0.2150(4)	0.1755(1)	4.27(6)
S1	−0.0652(4)	−0.2154(4)	0.3176(1)	2.84(4)
S4	0.0255(4)	−0.5668(4)	0.4194(1)	3.91(6)
S7	0.4025(4)	−0.1957(4)	0.4125(1)	3.84(6)
C2	0.1139(14)	−0.3959(13)	0.3029(4)	2.7(2)
C3	0.0548(17)	−0.5650(10)	0.3349(5)	3.7(2)
C5	0.2782(16)	−0.5359(13)	0.4480(5)	3.8(3)
C6	0.3360(17)	−0.3534(17)	0.4713(5)	4.3(3)
C8	0.1841(17)	−0.0498(14)	0.4114(5)	3.6(2)
C9	−0.0169(13)	−0.1252(16)	0.3953(5)	2.1(2)

[a] e.s.d.s given in parentheses. The y coordinate was fixed to define the origin. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as: $4/3[a^2B_{11} + b^2B_{22} + C^2B_{33} + ab(\cos\gamma)B_{12} + ac(\cos\beta)B_{13} + bc(\cos\alpha)B_{23}]$.

Acknowledgements

We thank Celltech plc for support and NSERC (Canada) for research support via operating grants.

References

1 (a) R. J. Puddephat, *The Chemsitry of Gold*, Elsevier, Amsterdam, 1978; (b) H. Schmidbaur, *Ang. Chem., Int. Ed. Engl., 15* (1976) 728; (c) A. K. H. Al-Sa'ady, K. Moss, C. A. McAuliffe and R. V. Parish, *J. Chem. Soc., Dalton Trans.*, (1984) 1609.

2 S. Ahrland, B. Noren and A. Oskarsson, *Inorg. Chem., 24* (1985) 1330.

3 J. J. Guy, P. E. Jones, M. J. Mays and G. M. Sheldrick, *J. Chem. Soc., Dalton Trans.*, ((1976) 8.

4 R. S. Nyholm, *Nature (London), 168* (1951) 705.

5 R. V. Parish and J. D. Rush, *Chem. Phys. Lett., 63* (1979) 37; P. G. Jones, *Gold Bull., 14* (1981) 102.

6 S. J. Berners-Price, M. A. Mazid and P. J. Sadler, *J. Chem. Soc., Dalton Trans.*, (1984) 969; P. A. Bates and J. M. Waters, *Inorg. Chim. Acta, 81* (1984) 151.

7 (a) D. N. Batchelder and R. O. Simons, *J. Appl. Phys., 36* (1965) 2864; (b) P. W. R. Corfield and H. M. M. Shearer, *Acta Crystallogr., 23* (1967) 156; (c) G. J. Arai, *Recl. Trav. Chim. Pays-Bas, 81* (1962) 307; (d) R. Hesse and P. Jennische, *Acta Chem. Scand., 26* (1972) 3855.

8 M. S. Hussain and A. A. Isab, *J. Coord. Chem., 14* (1985) 17.

9 N. C. Balzinger, W. E. Bennertt and D. M. Soboroff, *Acta Crystallogr., Sect. B, 32* (1976) 962.

10 P. B. Hitchcock and P. L. Pye, *J. Chem. Soc., Dalton Trans.*, (1977) 1457.

11 P. G. Jones and G. M. Sheldrick, *Acta Crystallogr., Sect. B, 32* (1976) 3321.

12 J. Dale, *Tetrahedron, 30* (1974) 1683.

13 W. N. Setzer, C. A. Ogle, G. S. Wilson and R. S. Glass, *Inorg. Chem., 22* (1983) 266; K. Wieghardt, H.-J. Kuppers and J. Weiss, *Inorg. Chem., 24* (1985) 3067.

14 S. M. Hart, J. C. A. Boeyens, J. P. Michael and R. D. Hancock, *J. Chem. Soc. Dalton Trans.*, (1983) 1601; J. C. A. Boeyens, S. M. Dobson and R. D. Hancock, *Inorg. Chem., 24* (1985) 3073.

15 B. A. Frenz and Associates Inc., *SDP-Plus*, College Station, Tx, U.S.A. and Enraf-Nonius, Delft, The Netherlands, 1983.