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The Structure of a Large Ring Gold Complex

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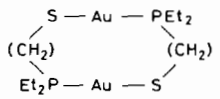
In the course of a study of a number of lipid soluble gold(I) complexes for possible application to arthritis therapy, Weinstock and his coworkers prepared the unusual complex di-μ-(diethylphosphinoethylthio)digold, $(AuSCH_2CH_2PEt_2)_2$ (I) [1]. Molecular weight and mass spectral studies clearly indicated that I was a dimer and the following structure was proposed [1].



I

Furthermore, analysis of the mass spectral fragmentation pattern led Weinstock *et al.* to propose an Au–Au interaction in the complex [1]. We will now report an X-ray diffraction study which confirms the predicted structure and supports the proposed Au–Au interaction.

Experimental

Crystals of I suitable for X-ray diffraction study were obtained from Smith, Kline & French Laboratories. Preliminary photographic studies were followed by precise lattice parameter determination and intensity data collection on the Syntex $P2_1$ automatic diffractometer using monochromated MoKα X-rays (λ = .71069 Å). Systematic conditions of relection of hkl, h + k = 2n, and h0l, l = 2n, left the choice of space group ambiguous as Cc or C2/c; however, the subsequent structural analysis was consistent with a space group of C2/c. The pertinent crystal data for $(AuSCH_2CH_2PEt_2)_2$ are a = 21.626(4), b = 8.547(7), c = 18.12(1) Å, β = 145.16(7)°, V = 1912 Å^3, M = 692.4 g/mol, Z = 4 molecules/unit cell, d(calculated) = 2.37, d(measured by flotation in aqueous ZnBr) = 2.26 g/cm^3. The Au position was determined by Patterson analysis and the other atoms except for H were located by successive Fourier syntheses. Several criteria were used to distinguish P from S including Fourier peak height, isotropic temperature factors and Au–X–C (X = S or P) bond angles as well as the presence of the ethyl groups. Anisotropic temperature factors were assigned to Au, P, and S in the final cycles of block diagonal least squares refinement whereas isotropic temperature factors were employed for C. The conventional R index ($\Sigma||F_o| - |F_c||/\Sigma|F_o|$) is .088 for 811 observed reflections.

Results and Discussion

The molecular structure is given in the Fig. 1 and the atomic coordinates are listed in Table I. The molecule has symmetry C_2 consistent with the space group C2/c and Z = 4. Selected interatomic distances are listed in Table II as are selected bond angles in Table III.

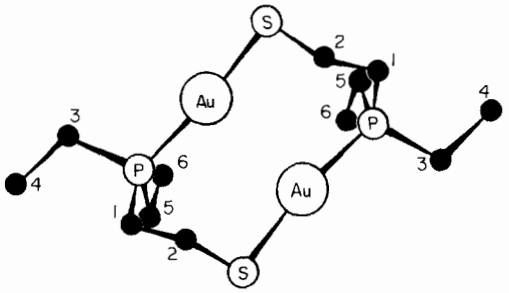


Figure 1. The molecular structure of I. The numbered atoms are carbon.

TABLE I. Atomic Coordinates.[a]

Atom	x	y	z
Au	0.3765(2)	0.5368(4)	0.1447(3)
P	0.3448(13)	0.4777(22)	−0.0065(15)
S	0.3898(14)	0.6107(26)	0.2803(17)
C(1)	0.384(6)	0.632(9)	−0.028(7)
C(2)	0.485(6)	0.727(9)	0.094(7)
C(3)	0.201(5)	0.439(9)	−0.160(6)
C(4)	0.330(5)	0.067(8)	0.277(6)
C(5)	0.406(4)	0.292(7)	0.013(5)
C(6)	0.385(5)	0.157(7)	0.045(6)

aEstimated standard deviations are given in parentheses.

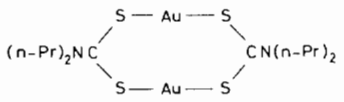
TABLE II. Important Interatomic Distances.

Atoms	Distance, Å
Au–Au	3.104
Au–P	2.27
Au–S	2.31
P–C(1)	1.79
S–C(2)	1.83
C(1)–C(2)	1.54

TABLE III. Important Bond Angles.

Atoms	Angles, degrees
S–Au–P	173.5
Au–P–C(1)	112.4
Au–S–C(2)	103.8
P–C(1)–C(2)	115.8
S–C(2)–C(1)	113.7

This structure may be viewed as containing a ten-membered ring; however, consideration of the short Au–Au contact (3.104 Å) invites a description involving two fused six-membered rings. Weinstock has already proposed an Au–Au interaction based on mass spectral data [1] and has made a comparison with di-μ-(N,N-di-n-propyldithiocarbamato)digold (II).



II

In the crystal structure reported for II [2] the Au–Au contact is only 2.76 Å compared with 2.884 Å in the metal [3]. The Au–Au contact in I where the large ring consists of 10 atoms appears to be weaker than in II where the large ring consists of 8 atoms. However, Au–Au attraction in I is evidenced by a P–Au–S bond angle of 173.5° in which the Au's are pulled toward each other rather than a strictly linear coordination for the Au(I). Interatomic distances between Au atoms considered to be bonded of 2.67–3.16 Å have been reported for low-valent gold cluster compounds [4]. The Au, S and P atoms in I are not coplanar and the dihedral angle between the two planes defined by each Au and its coordinating atoms is 29.5°.

More information on the nature of this ring system is desirable and dynamic nuclear magnetic resonance studies are in progress to investigate possible fluxional behavior.

Acknowledgment

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