& Saito, 1970; Loehlin & Fleischer, 1976). The relatively large thermal parameters probably account for the individual deviations from the average. The bond angles approximate to the regular tetrahedral angle (Table 2). No orientational disorder of the O atoms is observed.

All six H atoms bonded to the N atoms participate in intermolecular hydrogen bonding (Table 2). Five act as donors to the O atoms in the carbonate group and perchlorate anion, and one donates to the O atom of the water molecule. The two H atoms from the water are also involved in intermolecular hydrogen bonding.

References

BUCKINGHAM, D. A., CRESSWELL, P. J., DELLACA, R. J., DWYER, M., GAINSFORD, G. J., MARZILLI, L. G., MAXWELL, I. E., ROBINSON, W. T., SARGESON, A. M. & TURNBULL, K. R. (1974). *J. Am. Chem. Soc.* **96**, 1713–1725.

BUCKINGHAM, D. A., DWYER, M., GAINSFORD, G. J., JANSON, V., MARZILLI, L. G., ROBINSON, W. T., SARGESON, A. M. & TURNBULL, K. R. (1975). *Inorg. Chem.* **14**, 1739–1752.

BUCKINGHAM, D. A., FREEMAN, H. C., MAXWELL, I. E. & SARGESON, A. M. (1970). *Inorg. Chem.* **9**, 1921–1925.

BUCKINGHAM, D. A., MARZILLI, P. A. & SARGESON, A. M. (1967). *Inorg. Chem.* **6**, 1032–1041.

DELLACA, R. J., JANSON, V., ROBINSON, W. T., BUCKINGHAM, D. A., MARZILLI, L. G., MAXWELL, I. E., TURNBULL, K. R. & SARGESON, A. M. (1972). *Chem. Commun.* pp. 57–58.

FREEMAN, H. C., MARZILLI, L. G. & MAXWELL, I. E. (1970). *Inorg. Chem.* **9**, 2408–2415.

FREEMAN, H. C. & MAXWELL, I. E. (1969). *Inorg. Chem.* **8**, 1293–1298.

FREEMAN, H. C. & MAXWELL, I. E. (1970). *Inorg. Chem.* **9**, 649–655.

GEUE, R. J. & SNOW, M. R. (1971). *J. Chem. Soc. A*, pp. 2981–2987.

HOSKINS, B. F. & URBAN, A. J. (1987). Private communication.

ITO, M., MARUMO, F. & SAITO, Y. (1970). *Acta Cryst.* **B26**, 1408–1414.

JOHNSON, C. K. (1976). *ORTEPII.* Report ORNL-3794, revised. Oak Ridge National Laboratory, Tennessee, USA.

LOEHLIN, J. H. & FLEISCHER, E. B. (1976). *Acta Cryst.* **B32**, 3063–3066.

SARGESON, A. M. & SEARLE, G. H. (1965). *Inorg. Chem.* **4**, 45–52.

SARGESON, A. M. & SEARLE, G. H. (1967). *Inorg. Chem.* **6**, 787–796, 2172–2180.

SCHLEMPER, E. O., SEN GUPTA, P. K. & DESGUPTA, T. P. (1983). *Acta Cryst.* **C39**, 1012–1015.

SHELDRICK, G. M. (1976). *SHELX76.* Program for crystal structure determination. Univ. of Cambridge, England.

TORIUMI, K. & SAITO, Y. (1975). *Acta Cryst.* **B31**, 1247–1252.

Structure of Di-μ-tetrasulfido-bis{bis[μ-(dimethylene)diphenylphosphoranyl-C,C']-digold(II)(Au–Au)}

BY LEIGH CHRISTOPHER PORTER

*University of Texas at El Paso, El Paso, TX 79968, USA*

AND JOHN P. FACKLER JR

Laboratory for Molecular Structure and Bonding, Texas A&M University, College Station, TX 77843, USA

Abstract. [{Au(CH$_2$)$_2$P(C$_6$H$_5$)$_2$}$_2$S$_4$]$_2$, $M_r = 1897 \cdot 2$, triclinic, $P\bar{1}$, $a = 12 \cdot 048$ (3), $b = 13 \cdot 243$ (3), $c = 10 \cdot 756$ (3) Å, $\alpha = 113 \cdot 42$ (2), $\beta = 110 \cdot 92$ (2), $\gamma = 85 \cdot 40$ (2)°, $V = 1467 \cdot 1$ (8) Å^3, $Z = 1$, $D_x = 2 \cdot 147$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 10 \cdot 4$ mm^{-1}, $F(000) = 896$, $T = 298$ K, $R = 0 \cdot 0674$ and $wR = 0 \cdot 0940$ for 137 variable parameters and 2062 reflections with $I > 3\sigma(I)$. The unit cell contains one centrosymmetric molecule consisting of two dimeric Au^{II} ylides linked together by pairs of four-atom polysulfide bridges forming a 12-atom heterocyclic ring. The Au—Au distance is 2·671 (2) Å and the Au—S bond lengths range from 2·34 (2) to 2·41 (2) Å.

Introduction. We recently described the syntheses and X-ray crystal structures of two unusual products obtained from reactions involving the addition of either H$_2$S or NaS$_2$ to the Au^{II} ylide dimer, [Au(CH$_2$)$_2$P(C$_6$H$_5$)$_2$Br]$_2$ (Fackler & Porter, 1986). The products obtained from these reactions were unexpected: instead of simply substituting the axial Br$^-$ ligands with HS$^-$, we obtained instead two compounds in which pairs of Au^{II} ylide dimers were linked by four- and five-atom polysulfide bridges. One of these adducts, the more symmetrical of the two consisting of pairs of Au^{II} ylide dimers linked by a pair of four-atom polysulfide bridges, crystallized with two molecules of water per unit cell,

presumably as a result of using an aqueous solution of Na$_2$S. We have since repeated these reactions using the Au^{II} ylide benzoate dimer, [Au(CH$_2$)$_2$-P(C$_6$H$_5$)$_2$C$_6$H$_5$CO$_2$]$_2$, and have succeeded in obtaining in good yield another {[Au(CH$_2$)$_2$P(C$_6$H$_5$)$_2$]$_2$S$_4$}$_2$ product, the structure of which we now report.
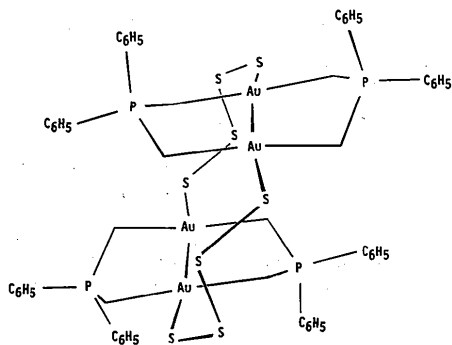
Experimental. The dinuclear Au^I starting material, [Au(CH$_2$)$_2$P(C$_6$H$_5$)$_2$]$_2$, was prepared by a modification of the literature procedure (Schmidbaur & Franke, 1975). [Au(CH$_2$)$_2$P(C$_6$H$_5$)$_2$C$_6$H$_5$CO$_2$]$_2$ was prepared by procedures that have been previously described (Porter & Fackler, 1986). The sulfur-bridged Au^{II} complex was obtained by infusing a THF solution of [Au(CH$_2$)$_2$P(C$_6$H$_5$)$_2$C$_6$H$_5$O$_2$]$_2$ with H$_2$S, whereupon a deep-red color rapidly developed. Crystallization from a CH$_2$Cl$_2$/diethyl ether solution yielded numerous thin red plates with an approximate yield of 70% calculated on the basis of the amount of ylide used. A small, fairly regularly shaped crystal of approximate dimensions 0·1 × 0·1 × 0·02 mm was selected and mounted on the end of a glass fiber in a random orientation. Triclinic symmetry was suggested on the basis of interaxial angles and confirmed by a Delaunay reduction procedure. Refined cell parameters determined from the setting angles of 20 reflections with $20 < 2\theta < 25°$. Data collection was carried out at ambient temperature using a Nicolet $R3/m$ diffractometer utilizing the ω-scanning technique in bisecting geometry and graphite-monochromated Mo $K\alpha$ radiation. Scan-rate variable, 2–30° min^{-1}; scan range, 1·8° in ω. Three standards (0$\bar{1}$0, 001, $\bar{1}$00) measured every 100 data showed no significant variation over the period of data collection. During the process of data reduction, several reflections were deleted from the reflection set. 3556 unique reflections ($\pm h$, $\pm k$, $+l$; h_{max} = 12, k_{max} = 14, l_{max} = 11) with $0 < 2\theta < 45°$ [(sinθ)/λ_{max} = 0·538 Å^{-1}] were obtained and corrected for Lorentz and polarization effects. Absorption corrections applied empirically on the basis of azimuthal scans of seven strong reflections spanning a range of 2θ values (minimum and maximum transmission factors 0·244 and 0·858, respectively). Struc-

ture solution carried out using the SHELXTL collection of crystallographic software, and refined using the SHELXTL PC crystallographic software package (Sheldrick, 1978, 1990). Au-atom positions determined from a sharpened Patterson map; remaining non-H atoms located on difference Fourier maps. Au, S, and P atoms refined anisotropically; phenyl rings refined as rigid idealized hexagons using H atoms included in idealized positions with fixed isotropic thermal parameters (U = 0·08 Å^2). Scattering factors, including terms for anomalous dispersion, taken from International Tables for X-ray Crystallography (1974, Vol. IV). Refinement based on F using weights of the form $w^{-1} = [\sigma^2(F) + 0·0025(F^2)]$. Convergence to conventional R values of $R = 0·0674$ and $wR = 0·094$ with a goodness-of-fit of 1·49 obtained from 137 variable parameters and 2062 reflections with $I > 3\sigma(I)$. No reflections had intensities beyond the range for valid coincidence correction. For the final cycle, maximum shift/$\sigma = 0·000$ with minimum and maximum residual electron densities of $-1·18$ and $+5·81$ e Å^{-3} in the vicinity of Au(1).

Discussion. The asymmetric unit of this cell consists of one half of a centrosymmetric dimer. A view of the structure illustrating the atomic numbering scheme is presented in Fig. 1; in Fig. 2 a stereoview packing diagram of the complex is shown. Atomic positional parameters and equivalent isotropic thermal parameters for all non-H atoms are presented in Table 1.* Bond distances and angles are summarized in Table 2.

The overall structures of the two Au ylide dimers in this complex are best described as being eight-membered heterocyclic rings containing two Au centers linked by a metal–metal bond with a conformation closely resembling that of a twist-boat by analogy with the various conformations typically seen in cyclohexane. The Au^{II} atoms have square-planar coordination geometries and are bridged symmetrically by the P ylide ligands. The observed internuclear Au-atom separation in this structure measures 2·671 (2) Å, consistent with the presence of a metal–metal bond. Bond angles about the Au centre show some variation, ranging from a minimum of 82·1 (12)° for S(4)—Au(2)—C(3) to a maximum of 94·6 (10)° for S(4)—Au(2)—C(2). Bonds to the C atoms of the ylide ligands also exhibit some variation and range from a minimum of 2·09 (4) to a

---

maximum of 2·13 (3) Å for Au(2)—C(3) and Au(2)—C(2), respectively.

Structural features of the polysulfide groups in the compound described here are similar to those observed in other transition-metal complexes containing large polysulfide ligands (Muller & Diemann, 1987). Some of the S atoms appeared to suffer from some degree of disorder and/or high-amplitude thermal motion. A difference Fourier map calculated using a model from which these atoms were deleted, however, showed no evidence for alternate positions, thus indicating that the refined positions were the principal contributors (at least 90%) to the electron density in those regions.

The geometry of this complex is essentially identical to the product obtained from the reaction of [Au(CH₂)₂P(C₆H₅)₂Br]₂ with Na₂S in which two molecules of water were present in the unit cell (Fackler & Porter, 1986). The observed S—S bond lengths for the anhydrous structure range from a minimum of
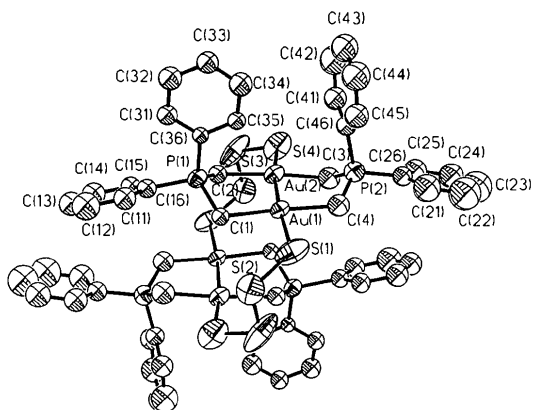

Fig. 1. A perspective view of the {[Au(CH₂)₂P(C₆H₅)₂]₂S₄}₂ adduct illustrating the atomic numbering scheme. Thermal ellipsoids have been drawn at the 50% probability level. H atoms have been omitted for clarity.
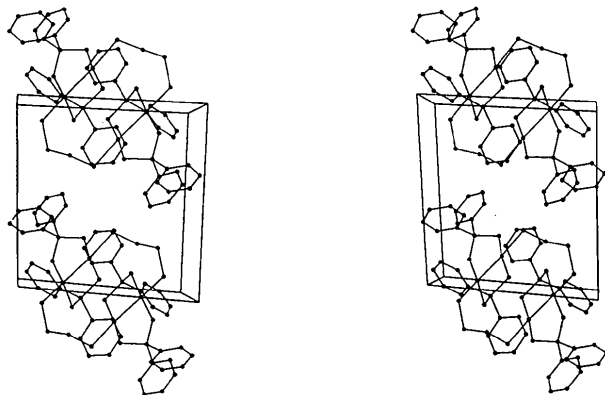

Fig. 2. A stereoview packing diagram projected down the crystallographic c axis.

Table 1. *Atomic coordinates* ($\times 10^4$) *and equivalent isotropic displacement coefficients* ($\text{Å}^2 \times 10^3$)

Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
Au(1)	2688 (1)	248 (1)	4425 (1)	44 (1)
Au(2)	4248 (1)	1759 (1)	4794 (12)	50 (1)
S(1)	1444 (9)	−1038 (11)	4499 (12)	92 (7)
S(2)	1765 (10)	−2578 (10)	3718 (13)	94 (7)
S(3)	6940 (11)	2761 (15)	4617 (13)	133 (10)
S(4)	5590 (11)	3276 (11)	5388 (13)	105 (8)
P(1)	3641 (7)	−415 (8)	1759 (9)	47 (4)
P(2)	2468 (7)	2756 (8)	6494 (9)	55 (5)
C(1)	3176 (24)	−1000 (24)	2750 (30)	40 (7)
C(2)	4738 (25)	667 (26)	3027 (31)	49 (8)
C(3)	3990 (29)	2831 (31)	6689 (38)	70 (10)
C(4)	2110 (29)	1368 (28)	6049 (36)	62 (9)
C(11)	3566 (15)	−2477 (19)	−446 (24)	62 (9)
C(12)	4001	−3305	−1411	100 (14)
C(13)	5125	−3145	−1430	77 (11)
C(14)	5813	−2158	−484	72 (10)
C(15)	5378	−1331	481	54 (8)
C(16)	4254	−1490	501	47 (8)
C(21)	1257 (21)	3338 (21)	8394 (29)	99 (14)
C(22)	1082	3982	9688	141 (20)
C(23)	1851	4909	10691	139 (19)
C(24)	2796	5192	10401	89 (12)
C(25)	2971	4547	9107	79 (11)
C(26)	2202	3620	8104	54 (8)
C(31)	2095 (16)	−319 (14)	−846 (18)	50 (8)
C(32)	1151	97	−1665	65 (10)
C(33)	512	919	−985	55 (9)
C(34)	818	1323	516	65 (10)
C(35)	1763	907	1335	41 (7)
C(36)	2401	85	654	33 (6)
C(41)	2017 (15)	3871 (20)	4668 (25)	67 (10)
C(42)	1277	4327	3722	108 (15)
C(43)	50	4067	3142	87 (12)
C(44)	−438	3353	3507	100 (14)
C(45)	301	2897	4453	72 (10)
C(46)	1529	3157	5033	51 (8)

Table 2. *Bond lengths* (Å) *and bond angles* (°)

Au(1)—Au(2)	2·671 (2)	Au(1)—S(1)	2·399 (15)
Au(1)—C(1)	2·134 (29)	Au(1)—C(4)	2·093 (35)
Au(2)—S(4)	2·413 (15)	Au(2)—C(2)	2·129 (31)
Au(2)—C(3)	2·085 (37)	S(1)—S(2)	1·938 (18)
S(2)—S(3A)	1·998 (18)	S(3)—S(4)	2·033 (20)
P(1)—C(1)	1·791 (41)	P(1)—C(2)	1·767 (27)
P(1)—C(16)	1·850 (23)	P(1)—C(36)	1·811 (20)
P(2)—C(3)	1·776 (38)	P(2)—C(4)	1·753 (39)
P(2)—C(26)	1·781 (30)	P(2)—C(46)	1·825 (28)

Au(2)—Au(1)—S(1)	170·9 (3)	Au(2)—Au(1)—C(1)	92·6 (9)
S(1)—Au(1)—C(1)	92·7 (10)	Au(2)—Au(1)—C(4)	92·4 (11)
S(1)—Au(1)—C(4)	82·4 (12)	C(1)—Au(1)—C(4)	175·1 (15)
Au(1)—Au(2)—S(4)	172·7 (3)	Au(1)—Au(2)—C(2)	92·7 (10)
S(4)—Au(2)—C(2)	94·6 (10)	Au(1)—Au(2)—C(3)	90·6 (12)
S(4)—Au(2)—C(3)	82·1 (12)	C(2)—Au(2)—C(3)	172·8 (11)
Au(1)—S(1)—S(2)	116·2 (7)	S(1)—S(2)—S(3A)	103·8 (7)
S(4)—S(3)—S(2A)	103·2 (9)	Au(2)—S(4)—S(3)	112·1 (7)
C(1)—P(1)—C(2)	107·7 (15)	C(1)—P(1)—C(16)	109·4 (14)
C(2)—P(1)—C(16)	110·7 (13)	C(1)—P(1)—C(36)	111·6 (12)
C(2)—P(1)—C(36)	110·9 (13)	C(16)—P(1)—C(36)	106·5 (10)
C(3)—P(2)—C(4)	105·5 (18)	C(3)—P(2)—C(26)	112·7 (13)
C(4)—P(2)—C(26)	110·5 (18)	C(3)—P(2)—C(46)	110·8 (18)
C(4)—P(2)—C(46)	109·5 (13)	C(26)—P(2)—C(46)	107·9 (12)
Au(1)—C(1)—P(1)	111·0 (15)	Au(2)—C(2)—P(1)	113·4 (18)
Au(2)—C(3)—P(2)	110·6 (14)	Au(1)—C(4)—P(2)	114·2 (23)
P(1)—C(16)—C(11)	118·5 (7)	P(1)—C(16)—C(15)	121·5 (7)
P(2)—C(26)—C(21)	119·9 (9)	P(2)—C(26)—C(25)	120·1 (9)
P(1)—C(36)—C(31)	121·3 (6)	P(1)—C(36)—C(35)	118·7 (6)
P(2)—C(46)—C(41)	119·1 (8)	P(2)—C(46)—C(45)	120·1 (8)

1·94 (2) Å for S(1)—S(2) to a maximum of 2·03 (2) Å for S(3)—S(4). These values are well within the range normally observed in polysulfide linkages and compare well with those reported for orthorhombic sulfur (S—S = 2·06 Å).

It is interesting to note that the addition of H_2S to $[Au(CH_2)_2P(C_6H_5)_2Br]_2$ produces as the principal product the less symmetrical complex possessing four- and five-atom polysulfide bridges in good yield. In contrast, addition of H_2S to the Au^{II} benzoate derivative, $[Au(CH_2)_2P(C_6H_5)_2C_6H_5CO_2]_2$, produces a very symmetrical product containing two four-atom polysulfide bridges in nearly quantitative yield. The linear S—Au—Au—S geometry undoubtedly plays a role in determining the most stable ring size; however, the reasons underlying the preferential formation of the product containing two four-atom S bridges over that containing both four- and five-atom S bridges remain unclear at this point.

References

FACKLER, J. P. JR & PORTER, L. C. (1986). *J. Am. Chem. Soc.* **108**, 2750–2751.

MULLER, A. & DIEMANN, E. (1987). *Adv. Inorg. Chem.* **31**, 89–122.

PORTER, L. C. & FACKLER, J. P. JR (1986). *Acta Cryst.* **C42**, 1128–1131.

SCHMIDBAUR, H. S. & FRANKE, R. (1975). *Inorg. Chim. Acta,* **13**, 79–84.

SHELDRICK, G. M. (1978). *SHELXTL. An Integrated System for Solving, Refining and Displaying Crystal Structures from Diffraction Data.* Univ. of Göttingen, Germany.

SHELDRICK, G. M. (1990). *SHELXTL PC. An Integrated System for Solving, Refining and Displaying Crystal Structures from Diffraction Data.* Univ. of Göttingen, Germany.

A Molybdenum(II) Halide Cluster with (E)-Cinnamyl Alcoholate Ligands

BY N. PERCHENEK AND A. SIMON*

Max-Planck-Institut für Festkörperforschung, Heisenbergstrasse 1, D-7000 Stuttgart 80, Germany

Abstract. Single crystals of disodium octa-μ_3-chloro-hexakis[(E)-cinnamyl alcoholato]-*octahedro*-hexamolybdate(II)–acetonitrile–(E)-cinnamyl alcohol (1/3/1), $Na_2[Mo_6Cl_8(OC_9H_9)_6].C_9H_9OH.3CH_3CN$, have been grown from acetonitrile. $M_r = 1961.6$, monoclinic, $C2/c$, $a = 36.244$ (7), $b = 8.430$ (2), $c = 31.679$ (5) Å, $\beta = 127.48$ (2)°, $V = 7681$ (3) Å^3, $Z = 4$, $D_x = 1.696$ Mg m^{-3}, $\lambda(Mo\ K\alpha) = 0.71069$ Å, $\mu = 1.268$ mm^{-1}, $F(000) = 3896$, $T = 213$ K, $R = 0.0531$ for 2905 independent reflections with $F_o > 4\sigma(F_o)$. The compound contains $[Mo_6Cl_8]^{4+}$-cluster units with six terminal (E)-cinnamyl alcoholate ligands, $d_{Mo—Mo}$ ranging from 2.596 (2) to 2.623 (2) Å, $d_{Mo—Cl}$ from 2.480 (4) to 2.508 (5) Å, $d_{Mo—O}$ from 2.012 (1) to 2.09 (2) Å. The sodium ions have distorted tetrahedral environment.

Introduction. The synthesis of salts containing octahedral Mo_6 clusters with methoxy, ethoxy or phenoxy ligands is well known (Nannelli & Block, 1968, 1969) and so are the crystal structures of the methoxy derivatives (Chisholm, Heppert & Huffman 1984). We are interested in the introduction of alcoholate ligands with delocalized π-electron systems into clusters. (E)-cinnamyl alcoholate was chosen as a simple model ligand.

Experimental. The compound was obtained by metathesis of $Na_2Mo_6Cl_8(OCH_3)_6$, prepared according to the procedure given by Nannelli & Block (1968), with (E)-cinnamyl alcohol. A solution of $Na_2Mo_6Cl_8(OCH_3)_6$ in (E)-cinnamyl alcohol was stirred at room temperature for 24 h. The methanol formed in the reaction distilled off continuously under reduced pressure. Removal of excess (E)-cinnamyl alcohol left a yellow powder which was recrystallized from acetonitrile to form small orange columns. A suitable crystal of dimensions $0.10 \times 0.17 \times 0.25$ mm was selected under petroleum, glued to the top of a 0.7 mm glass capillary and immediately transferred to an Enraf–Nonius CAD-4 diffractometer where it was cooled to 213 K in a cold N_2-gas stream. Graphite-monochromatized Mo $K\alpha$ radiation; cell parameters from 25 reflections ($19.0 < 2\theta < 25.2°$); systematic absences consistent with $C2/c$; total of 10 775 reflections measured with $3.0 < 2\theta < 46.0°$ in the range $-39 \le h \le 39$, $0 \le k \le 9$, $-34 \le l \le 34$; intensity variation of two standard reflections $1.09 \ge$