Table 2. *Bond distances* (Å) *and angles* (°) *for the* Cu *coordination sphere*

Cu–N(1)	1·963 (3)	Cu–O(18)	2·039 (3)
Cu–N(11)	2·002 (4)	Cu–O(20)	2·488 (3)
Cu–O(14)	1·990 (2)	Cu–O(17)	2·473 (3)
N(11)–Cu–N(1)	83·5 (1)	O(18)–Cu–O(14)	89·2 (1)
O(14)–Cu–N(1)	94·4 (1)	O(18)–Cu–O(17)	78·4 (1)
O(14)–Cu–N(11)	175·1 (1)	O(20)–Cu–N(1)	134·9 (1)
O(17)–Cu–N(1)	95·2 (1)	O(20)–Cu–N(11)	87·9 (1)
O(17)–Cu–N(11)	128·0 (1)	O(20)–Cu–O(14)	90·5 (1)
O(17)–Cu–O(14)	56·5 (1)	O(20)–Cu–O(17)	123·8 (1)
O(18)–Cu–N(1)	169·4 (1)	O(20)–Cu–O(18)	54·9 (1)
O(18)–Cu–N(11)	93·7 (1)		

Cu–O distances [mean value 2·480 (7)] are larger than the equatorial distances [mean 2·014 (24) Å]. The Cu–N(1) bond distance [1·963 (3) Å] is similar to those obtained in other compounds [weighted mean of literature values 1·96 (1) Å (Palenik, 1964; Hoy & Morris, 1967; Williams & Wallwork, 1967], while it is shorter than the Cu–N(11) bond distance [2·002 (4) Å] due to the sp^2 character of N(1); this produces a lengthening of the Cu–O bond distance opposite to N(1).

This work was sponsored by a grant from the Universidad de Barcelona.

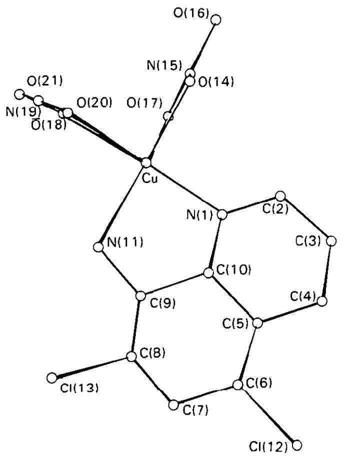

Fig. 1. A view of the complex with the numbering of the atoms.

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Triply Bridged Thiolate Complexes of Oxotungstate(V): Structures of Tetraphenylphosphonium μ-Chloro-bis(μ-phenylthiolato)-bis[dichlorooxotungstate(V)] (I), $[Ph_4P][Cl_2OW(\mu\text{-}Cl)(\mu\text{-}SC_6H_5)_2WOCl_2]$, and Tetraphenylarsonium μ-Chloro-bis(μ-p-tolylthiolato)-bis[dichlorooxotungstate(V)] (II), $[Ph_4As][Cl_2OW(\mu\text{-}Cl)\{\mu\text{-}S(p\text{-}C_6H_4CH_3)\}_2WOCl_2]$

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(*Received* 22 *May* 1984; *accepted* 18 *September* 1984)

Abstract. (I): $M_r = 1134{\cdot}71$, triclinic, $P\bar{1}$, $a = 10{\cdot}8421\ (8)$, $b = 11{\cdot}242\ (1)$, $c = 16{\cdot}491\ (1)$ Å, $\alpha = 98{\cdot}384\ (7)$, $\beta = 98{\cdot}119\ (6)$, $\gamma = 100{\cdot}267\ (7)°$, $V = 1927{\cdot}6\ (4)$ Å^3, $Z = 2$, $D_m = 1{\cdot}94\ (1)$, $D_x = 1{\cdot}955$ g cm^{-3}, $F(000) = 1084$, μ(Mo $K\alpha$) = 68·30 cm^{-1}, $\lambda = 0{\cdot}71069$ Å, $T = 295\ (1)$ K, $R = 0{\cdot}036$ for 6066 unique reflections. (II): $M_r = 1206{\cdot}71$, tetragonal, $P\bar{4}$, $a = 16{\cdot}173\ (1)$, $c = 7{\cdot}8566\ (8)$ Å, $V = 2055{\cdot}1\ (3)$ Å^3, $Z = 2$, $D_m = 1{\cdot}94\ (1)$, $D_x = 1{\cdot}950$ g cm^{-3}, $F(000) = 1152$, μ(Mo $K\alpha$) = 72·13 cm^{-1}, $T = 295\ (1)$ K, $R = 0{\cdot}049$ for 1430 unique reflections. The anions consist of a greatly distorted confacial bioctahedral framework in which there is a weakly bound μ-Cl atom *trans* to two terminal O atoms. The R groups (phenyl, p-tolyl) on the bridging thiolato ligands adopt the relatively unusual axial–axial configuration.

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0108-2701/85/010047-06$01.50 © 1985 International Union of Crystallography

Introduction. The chemistry of oxomolybdenum(V) has been extensively explored, yielding a wide variety of well characterized structural units (see, for example: Stiefel, 1977; Boyd, Dance, Landers & Wedd, 1979). In contrast, there are relatively few analogues in the chemistry of tungsten(V), particularly with dimeric species (Dori, 1981). It has been suggested (Dilworth, Neaves, Dahlstrom, Hyde & Zubieta, 1982), based on structural evidence, that the triply bridged geometry for Mo^V shown in Fig. 1 is comparatively common and versatile. Recently Wedd and co-workers (Hanson, Brunette, McDonell, Murray & Wedd, 1981; Bradbury, Masters, McDonell, Brunette, Bond & Wedd, 1981) were able to synthesize tungsten anions of the type $[W_2O_2(SR)_6(OMe)]^-$ (M=W; L, X, Y = SPh, S-*p*-tolyl, or SePh; and Z = OMe in Fig. 1) and studied these complexes using spectroscopic and electrochemical techniques. The almost simultaneous publication of the preparation and structure of the anion $[Cl_2OW(\mu\text{-}Cl)(\mu\text{-}S^tBu)_2WOCl_2]^-$ (III) (L, Z = Cl; X, Y = S^tBu) by our laboratory (Patel, Boorman, Kerr & Moynihan, 1982) confirmed the gross geometry of these complexes as that shown in Fig. 1. Interestingly, it was found that (III) differed from previous structures in the disposition of the R groups of the bridging thiolates. In view of the fact that Mo compounds with X, Y = SR have an aryl R substituent, it was of interest to us to characterize such a tungsten analogue. This paper describes the preparation and structures of salts of the anion $[Cl_2OW(\mu\text{-}Cl)(\mu\text{-}SR)_2WOCl_2]^-$ where R = Ph (I), *p*-tolyl (II) and compares the structures to those previously reported.

Experimental. The neutral compounds $(Me_2S)Cl_3W(\mu\text{-}SR)_2WCl_3(SMe_2)$ (R = phenyl or *p*-tolyl) were prepared as described previously (Boorman, Ball, Moynihan, Patel & Richardson, 1983). In an attempt to convert these into the corresponding chloroanions, $[Cl_4W(\mu\text{-}SR)_2WCl_4]^{2-}$, they were reacted with Ph_4PCl (I) or Ph_4AsCl (II) in CH_2Cl_2. After standing for several hours the solution changed from orange-red to green, and upon addition of hexane (278 K) yielded a small quantity of reddish-brown crystals of the title complexes. The source of oxygen is believed to be moisture contained in the Ph_4PCl and Ph_4AsCl reagents.

Single crystals of (I) and (II), 0·31 × 0·20 × 0·18 and 0·26 × 0·14 × 0·10 mm, mounted on an Enraf–Nonius CAD-4F automated diffractometer, graphite-monochromatized Mo *Kα* radiation. D_m by flotation, $CCl_4/CHBr_3$. Lattice parameters from least-squares refinement of 25 accurately centred reflections in range of $14 < \theta < 20°$ and $10 < \theta < 18°$. Ambiguity in space groups resolved using E values (K curve) and successful solution of structures. Data measured using $\omega/2\theta$ scan, scan range $1{\cdot}5(0{\cdot}58 + 0{\cdot}347 \tan\theta)°$ and $1{\cdot}5(0{\cdot}64 + 0{\cdot}347 \tan\theta)°$. Three standard reflections [050, $\bar{1}\bar{2}\bar{5}$, $20\bar{6}$ for (I) and $\bar{1}70$, 520, 004 for (II)] measured every 1500 s of X-ray exposure time showed no decay. Data collected: ($\pm h$, $\pm k$, $-l$), max. indices 14, 14, 21 to $\theta_{max} = 27{\cdot}5°$ for (I) and ($\pm h$, $\pm k$, $+l$) to $\theta = 17{\cdot}5°$ and ($+h$, $+k$, $+l$) to $\theta_{max} = 25{\cdot}0°$, max. indices 19, 19, 9 for (II). 9397 reflections measured, 8805 unique, 5424 unobserved $[I < 3\sigma(I)]$ for (I) and 2875 measured, 1949 unique, 938 unobserved $[I < 3\sigma(I)]$ for (II). Data corrected for background, Lorentz, polarization and absorption effects; (I): crystal faces {100}, {010}, {001}, {01$\bar{1}$}, {10$\bar{1}$}, Gaussian method (Coppens, 1965), 10 × 10 × 16 grid, transmission factors 0·272 to 0·396; (II): crystal faces {110}, (0$\bar{1}$1), (01$\bar{1}$), Gaussian, 12 × 12 × 6 grid, transmission factors 0·202 to 0·412. Structures solved using Patterson and difference Fourier syntheses, refined by full-matrix least squares based on F; $\sum w(|F_o| - |F_c|)^2$ minimized; w defined as $[\sigma^2(F_o)]^{-1}$ with $\sigma(F_o)$ derived from counting statistics; *XRAY76* system of computer programs (Stewart, 1976); H atoms located by difference Fourier map but included in idealized positions [sp^2, d(C—H) = 0·95 Å; sp^3, d(C—H) = 1·00 Å] with isotropic thermal parameters set to 1·1 times that of the bonded atom, H parameters not refined; all non-H anisotropic in (I); W, As, Cl, S anisotropic, O, C isotropic in (II). Model for (I) converged with: 6066 observations [observed reflections plus those for which $I_c > 3\sigma(I_o)$], 433 variables, $R = 0{\cdot}036$, $R_w = 0{\cdot}044$, max. $\Delta/\sigma = 0{\cdot}02$, $S = 0{\cdot}95$, isotropic extinction parameter = 2·1 (8) × 10^{-4}, max. residual electron density ±1·88 e Å^{-3}; (II): 1430 observations [including those for which $I_c > 3\sigma(I_o)$], 126 variables, $R = 0{\cdot}049$, $R_w = 0{\cdot}041$, max. $\Delta/\sigma = 0{\cdot}10$, isotropic extinction parameter not refined, max. residual electron density ±2·57 e Å^{-3}. Scattering factors were those of Cromer & Mann (1968) for non-H and Stewart, Davidson & Simpson (1965) for H atoms. Anomalous-dispersion corrections were included for non-H atoms (*International Tables for X-ray Crystallography*, 1974).

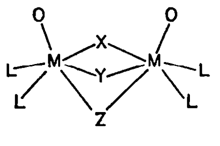

Fig. 1. Triply bridged geometry of bis[oxometal(V)] complexes.

Discussion. Atomic parameters are given in Tables 1 and 2.* Selected bond lengths and angles are given in Table 3 for (I) and Table 4 for (II). Perspective views of

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* Tables containing the remaining bond lengths and angles, anisotropic thermal parameters, H-atom coordinates and isotropic thermal parameters and structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39727 (55 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

the anions with atomic labelling schemes are presented in Figs. 2 and 3 for (I) and (II) respectively.

The structures consist of distinct anions and cations with no unusual interionic contacts. Crystallographic symmetry is imposed on (II); a twofold axis passes through the bridging Cl atom and bisects the W—W bond in the anion and two independent cations sit on sites of $\bar{4}$ symmetry. The W—W distances in both (I) and (II) are indicative of weak, formal single bonds as predicted for these d^1 systems and discussed in the paper on (III) (Patel, Boorman, Kerr & Moynihan, 1982).

Although the structures can be described as being approximately confacial bioctahedral, they are significantly distorted from this geometry by the presence of the two terminal oxo groups. As can be seen in Table 5, W—Cl bond lengths show a pronounced difference between the terminal (*t*) and bridging (*br*) ligands. Such a structural feature is common in binuclear chloro-complexes but is typically much less. For example, in the anion $[Cl_3W(\mu\text{-}Cl)(\mu\text{-}SPh)_2WCl_3]^{2-}$ (Ball, Boorman, Moynihan, Patel, Richardson, Collison & Mabbs, 1983) the values are $W—Cl_t(av.) = 2{\cdot}391\ (5)$ and $W—Cl_{br} = 2{\cdot}439\ (6)$ Å and in $W_2Cl_9^{3-}$ (Watson & Waser, 1958) the averages are $W—Cl_t = 2{\cdot}40$ and

Table 1. *Positional parameters* ($\times 10^4$) *and* B_{eq} ($\times 10$) *for the non-hydrogen atoms of* $[Ph_4P][Cl_2OW(\mu\text{-}Cl)(\mu\text{-}SPh)_2WOCl_2]$

$$B_{eq} = \tfrac{8}{3}\pi^2 \textstyle\sum_i \sum_j U_{ij} a^*_i a^*_j \mathbf{a}_i . \mathbf{a}_j.$$

	x	y	z	B_{eq}(Å^2)
W(1)	2263·1 (4)	−688·1 (4)	1744·5 (3)	36
W(2)	1636·4 (4)	1018·8 (4)	3027·5 (3)	38
Cl(1)	1059 (3)	1041 (3)	1442 (2)	47
Cl(2)	910 (3)	−1985 (3)	584 (2)	66
Cl(3)	3627 (3)	−410 (3)	750 (2)	68
Cl(4)	−327 (3)	1474 (4)	3285 (2)	80
Cl(5)	2267 (4)	3193 (3)	3390 (2)	65
S(1)	3617 (3)	1250 (2)	2469 (2)	39
S(2)	326 (3)	−985 (3)	2365 (2)	44
P(1)	5616 (2)	5826 (2)	1971 (2)	33
O(1)	2956 (7)	−1593 (6)	2291 (4)	48
O(2)	2222 (6)	511 (7)	3875 (4)	49
C(1)	4913 (9)	1142 (9)	3211 (6)	34
C(2)	5938 (11)	2116 (10)	3369 (7)	48
C(3)	7004 (11)	2115 (13)	3958 (9)	59
C(4)	7059 (11)	1184 (14)	4389 (8)	58
C(5)	6023 (11)	201 (11)	4245 (7)	51
C(6)	4959 (9)	175 (10)	3681 (6)	39
C(11)	364 (11)	−2004 (12)	3117 (7)	53
C(12)	831 (13)	−3067 (13)	3008 (9)	74
C(13)	746 (21)	−3852 (24)	3571 (17)	128
C(14)	209 (33)	−3636 (34)	4255 (21)	156
C(15)	−303 (20)	−2598 (25)	4350 (12)	107
C(16)	−213 (14)	−1758 (15)	3786 (9)	80
C(21)	5517 (10)	6077 (9)	3063 (6)	38
C(22)	4523 (11)	6562 (11)	3315 (7)	56
C(23)	4449 (13)	6813 (12)	4152 (8)	62
C(24)	5343 (14)	6568 (14)	4715 (8)	68
C(25)	6331 (14)	6066 (16)	4490 (8)	81
C(26)	6420 (11)	5821 (12)	3659 (7)	55
C(31)	4017 (9)	5388 (9)	1401 (6)	32
C(32)	3619 (10)	5968 (9)	760 (6)	39
C(33)	2360 (11)	5596 (11)	343 (7)	52
C(34)	1564 (11)	4688 (12)	549 (8)	54
C(35)	1938 (11)	4116 (11)	1196 (9)	60
C(36)	3168 (10)	4472 (9)	1634 (7)	49
C(41)	6409 (8)	7187 (8)	1672 (6)	31
C(42)	6887 (11)	7101 (10)	931 (7)	48
C(43)	7362 (11)	8155 (11)	652 (7)	50
C(44)	7423 (10)	9268 (9)	1107 (8)	49
C(45)	6984 (11)	9386 (9)	1849 (7)	47
C(46)	6463 (10)	8337 (9)	2130 (7)	42
C(51)	6484 (9)	4618 (9)	1755 (5)	31
C(52)	5879 (9)	3455 (9)	1351 (6)	36
C(53)	6581 (13)	2545 (9)	1263 (7)	49
C(54)	7866 (12)	2774 (11)	1533 (8)	52
C(55)	8461 (10)	3945 (12)	1932 (7)	52
C(56)	7785 (10)	4883 (9)	2023 (7)	44

Table 2. *Positional* ($\times 10^4$) *and isotropic thermal* ($B_{eq} \times 10$, $U \times 10^3$) *parameters for the non-hydrogen atoms of* $[Ph_4As][Cl_2OW(\mu\text{-}Cl)\{\mu\text{-}S(p\text{-}tolyl)\}_2WOCl_2]$

For W, As, Cl and S atoms $B_{eq} = \tfrac{8}{3}\pi^2 \sum_i \sum_j U_{ij} a^*_i a^*_j \mathbf{a}_i . \mathbf{a}_j$.

	x	y	z	B_{eq} or U (Å^2)
W	629·3 (7)	4370·9 (7)	1501·2 (14)	27
As(1)	0	0	5000	40
As(2)	5000	5000	5000	39
Cl(1)	0	5000	4263 (10)	35
Cl(2)	1981 (5)	4373 (5)	2680 (11)	52
Cl(3)	621 (5)	3012 (5)	2665 (11)	52
S	852 (5)	5869 (4)	1430 (9)	34
O	744 (9)	4262 (9)	−571 (14)	24 (3)
C(1)	1232 (14)	6209 (15)	−562 (30)	27 (7)
C(2)	1820 (17)	6839 (17)	−423 (36)	46 (8)
C(3)	2155 (19)	7168 (18)	−1857 (40)	63 (10)
C(4)	1941 (15)	6952 (15)	−3526 (42)	45 (7)
C(5)	1328 (16)	6336 (16)	−3587 (41)	55 (8)
C(6)	980 (19)	5965 (18)	−2118 (32)	50 (9)
C(7)	2307 (19)	7263 (19)	−5077 (46)	76 (11)
C(11)	405 (20)	882 (20)	6681 (48)	80 (10)
C(12)	937 (22)	626 (21)	7934 (45)	78 (12)
C(13)	1224 (18)	1239 (21)	8930 (38)	71 (11)
C(14)	1033 (20)	2017 (21)	8624 (48)	85 (11)
C(15)	589 (23)	2254 (24)	7372 (47)	92 (13)
C(16)	202 (17)	1708 (18)	6251 (40)	58 (9)
C(21)	4157 (18)	4553 (18)	6488 (46)	68 (9)
C(22)	4329 (23)	4064 (24)	7845 (49)	92 (14)
C(23)	3764 (22)	3764 (20)	8911 (41)	80 (11)
C(24)	2985 (20)	3988 (19)	8556 (48)	79 (10)
C(25)	2708 (23)	4408 (23)	7312 (47)	90 (13)
C(26)	3316 (20)	4766 (18)	6170 (43)	73 (10)

Table 3. *Selected bond lengths* (Å) *and angles* (°) *for the anion* $[Cl_2OW(\mu\text{-}Cl)(\mu\text{-}SPh)_2WOCl_2]^-$

W(1)–W(2)	2·8824 (7)		
W(1)–S(1)	2·436 (2)	W(2)–S(1)	2·441 (3)
W(1)–S(2)	2·455 (3)	W(2)–S(2)	2·449 (3)
W(1)–Cl(1)	2·596 (3)	W(2)–Cl(1)	2·606 (3)
W(1)–Cl(2)	2·361 (3)	W(2)–Cl(4)	2·358 (4)
W(1)–Cl(3)	2·375 (4)	W(2)–Cl(5)	2·379 (3)
W(1)–O(1)	1·663 (8)	W(2)–O(2)	1·671 (7)
S(1)–C(1)	1·762 (10)	S(2)–C(11)	1·809 (14)
W(2)–W(1)–S(1)	53·84 (7)	W(1)–W(2)–S(1)	53·69 (6)
W(2)–W(1)–S(2)	53·90 (6)	W(1)–W(2)–S(2)	54·10 (7)
W(2)–W(1)–Cl(1)	56·53 (6)	W(1)–W(2)–Cl(1)	56·18 (7)
W(2)–W(1)–Cl(2)	129·03 (10)	W(1)–W(2)–Cl(4)	131·67 (9)
W(2)–W(1)–Cl(3)	132·00 (9)	W(1)–W(2)–Cl(5)	130·82 (9)
W(2)–W(1)–O(1)	102·2 (3)	W(1)–W(2)–O(2)	100·4 (3)
S(1)–W(1)–Cl(2)	153·8 (1)	S(1)–W(2)–Cl(4)	156·6 (1)
S(1)–W(1)–Cl(3)	82·1 (1)	S(1)–W(2)–Cl(5)	82·1 (1)
S(1)–W(1)–O(1)	96·9 (2)	S(1)–W(2)–O(2)	95·0 (3)
S(2)–W(1)–Cl(2)	82·6 (1)	S(2)–W(2)–Cl(4)	83·4 (1)
S(2)–W(1)–Cl(3)	160·9 (1)	S(2)–W(2)–Cl(5)	158·7 (1)
S(2)–W(1)–O(1)	94·2 (3)	S(2)–W(2)–O(2)	94·0 (2)
Cl(1)–W(1)–Cl(2)	88·3 (1)	Cl(1)–W(2)–Cl(4)	92·3 (1)
Cl(1)–W(1)–Cl(3)	96·1 (1)	Cl(1)–W(2)–Cl(5)	93·9 (1)
Cl(1)–W(1)–O(1)	158·6 (3)	Cl(1)–W(2)–O(2)	156·6 (3)
Cl(2)–W(1)–O(1)	106·5 (2)	Cl(4)–W(2)–O(2)	104·9 (3)
Cl(3)–W(1)–O(1)	101·0 (3)	Cl(5)–W(2)–O(2)	104·1 (2)
Cl(2)–W(1)–Cl(3)	82·0 (1)	Cl(4)–W(2)–Cl(5)	81·2 (1)
S(1)–W(1)–S(2)	107·64 (9)	S(1)–W(2)–S(2)	107·69 (9)
S(1)–W(1)–Cl(1)	72·85 (9)	S(1)–W(2)–Cl(1)	72·59 (9)
S(2)–W(1)–Cl(1)	72·11 (10)	S(2)–W(2)–Cl(1)	72·02 (9)
W(1)–S(1)–W(2)	72·47 (7)	W(1)–S(2)–W(2)	72·00 (8)
W(1)–S(1)–C(1)	116·1 (3)	W(1)–S(2)–C(11)	113·0 (4)
W(2)–S(1)–C(1)	111·7 (4)	W(2)–S(2)–C(11)	108·1 (3)
W(1)–Cl(1)–W(2)	67·30 (7)		

$W—Cl_{br} = 2{\cdot}48$ Å. The abnormally long $W—Cl_{br}$ bond is a feature of both Mo and W oxo complexes (Dilworth, Neaves, Dahlstrom, Hyde & Zubieta, 1982; Bunzey, Enemark, Gelder, Yamanouchi & Newton, 1977) and can be ascribed to the *trans*-weakening influence of the oxo ligands.

Table 4. *Selected bond lengths* (Å) *and angles* (°) *for the anion* $[Cl_2OW(\mu\text{-}Cl)\{\mu\text{-}S(p\text{-}tolyl)\}_2WOCl_2]^-$

W–W′	2·878 (2)	W–Cl(2)	2·375 (9)
W–S	2·450 (7)	W–Cl(3)	2·380 (8)
W–S′	2·427 (8)	W–O	1·65 (1)
W–Cl(1)	2·604 (7)	S–C(1)	1·77 (2)
W′–W–S	53·5 (2)	Cl(1)–W–Cl(3)	92·2 (2)
W′–W–S′	54·2 (2)	Cl(1)–W–O	155·4 (5)
W′–W–Cl(1)	56·4 (1)	Cl(2)–W–O	106·4 (5)
W′–W–Cl(2)	130·5 (2)	Cl(3)–W–O	106·3 (5)
W′–W–Cl(3)	130·4 (2)	Cl(2)–W–Cl(3)	81·8 (3)
W′–W–O	98·9 (5)	S–W–S′	107·6 (2)
S–W–Cl(2)	82·7 (3)	S–W–Cl(1)	71·9 (2)
S–W–Cl(3)	157·3 (3)	S′–W–Cl(1)	72·3 (2)
S–W–O	93·8 (5)	W–S–W′	72·3 (2)
S′–W–Cl(2)	156·6 (3)	W–S–C(1)	112·2 (8)
S′–W–Cl(3)	81·7 (3)	W′–S–C(1)	114·4 (8)
S′–W–O	94·0 (5)	W–Cl(1)–W′	67·1 (2)
Cl(1)–W–Cl(2)	92·0 (2)		

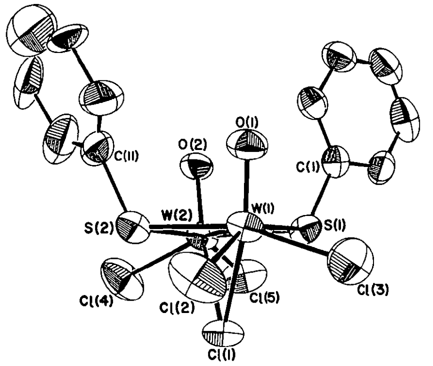


Fig. 2. An *ORTEP* view (Johnson, 1965) of the anion $[Cl_2OW(\mu\text{-}Cl)(\mu\text{-}SPh)_2WOCl_2]^-$, showing the atomic numbering scheme. (Thermal ellipsoids at 50% probability level.)

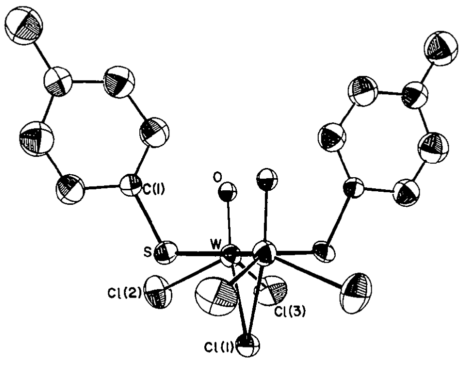
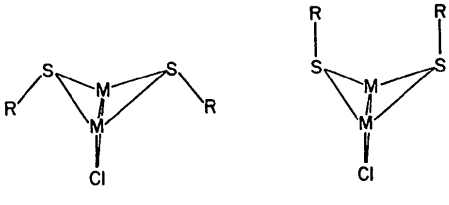


Fig. 3. An *ORTEP* view of the anion $[Cl_2OW(\mu\text{-}Cl)\{\mu\text{-}S(p\text{-}tolyl)\}_2WOCl_2]^-$, showing the atomic numbering scheme. (Thermal ellipsoids at 50% probability level.)

The *R* groups of the bridging thiolato groups of (I) and (II) are found to have the *aa* geometry defined below:



ee *aa*

This geometry is consistent with that previously reported for the analogous Mo compounds $[Cl_2OMo(\mu\text{-}Cl)(\mu\text{-}SPh)_2MoOCl_2]^-$ (Dilworth, Neaves, Dahlstrom, Hyde & Zubieta, 1982) and $[(S_2CNEt_2)OMo(\mu\text{-}Cl)(\mu\text{-}SPh)_2MoO(S_2CNEt_2)]^+$ (Bunzey, Enemark, Gelder, Yamanouchi & Newton, 1977). With the latter Mo complex it should be noted that the *aa* geometry is observed despite the presence of chelating ligands in two pairs of terminal ligand positions which result in a constriction of the S—Mo—S angle. In contrast, (III) was found to have the *ee* configuration, which would be expected to be more stable on steric grounds (Dahl & Wei, 1963).

An analysis of the structures by least-squares planes (Table 5) facilitates an explanation for the *aa* geometry in (I) and (II). The W_2S planes can be considered and compared to the 120° angle between them expected for a pure confacial bioctahedral framework. The interplanar angles of 175·9 (3) and 176·7 (5)°, for (I) and (II) respectively, are such that the S atoms are more widely separated than in the case of a confacial bioctahedral framework. The structure of (III) shows the same features but is somewhat more folded along the W---W vector [164·4 (5)°] bringing the μ-S atoms closer together. Such a distortion would be expected to lower the energy of the *aa* isomer by reducing the repulsion between substituents on the S atoms. This is achieved so successfully for (I) and (II) that it allows the SPh planes to lie approximately at right angles (I) or antiparallel (II) (Table 5, Figs. 1, 2) rather than parallel as in a graphite-like arrangement. As seen in Table 5, S(1)···Cl(1) and S(2)···Cl(1) contacts become significantly shorter than the van der Waals radii of ~ 3·6 Å, particularly when *R* = phenyl.

The structural features discussed above would be consistent with an alternative description to that of confacial bioctahedral, namely that the anions consist of two distorted square-pyramidal species sharing an edge; the μ-Cl^- ion would then be considered as being loosely coordinated to both W atoms to complete the octahedra:

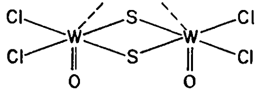


Table 5. *Comparison of the geometry of* $[Cl_2OW(\mu\text{-}Cl)(\mu\text{-}SPh)_2WOCl_2]^-$(I), $[Cl_2OW(\mu\text{-}Cl)\{\mu\text{-}S(p\text{-}tolyl)\}_2WOCl_2]^-$(II), $[Cl_2OW(\mu\text{-}Cl)(\mu\text{-}S^tBu)_2WOCl_2]^-$(III), $[(S_2CNEt_2)OW(\mu\text{-}Cl)(\mu\text{-}SPh)_2WO(S_2CNEt_2)]^+$(IV), *and* $[Cl_2OMo(\mu\text{-}Cl)(\mu\text{-}SPh)_2MoOCl_2]^-$(V)

br = bridging, *t* = terminal, av. = average, *a* = axial, *e* = equatorial.

	(I)*	(II)*	(III)†	(IV)‡	(V)§
M–*M* (Å)	2·8824 (7)	2·878 (2)	2·854 (2)	2·822 (2)	2·915 (1)
M–Cl_{br} (Å)	2·601 (3)	2·604 (7)	2·622 (8)	2·61 (1)	2·651 (3)
(*M*–Cl_t) (av.) (Å)	2·368 (4)	2·378 (9)	2·370 (8)	—	2·380 (3)
(*M*–O) (av.) (Å)	1·667 (8)	1·65 (1)	1·66 (2)	1·656 (6)	1·658 (9)
(*M*–S_{br}) (av.) (Å)	2·445 (3)	2·439 (8)	2·418 (8)	2·457 (8)	2·447 (3)
(*M*–S_{br}–*M*) (av.) (Å)	72·24 (8)	72·3 (2)	72·3 (2)	70·09 (7)	73·1 (1)
M–Cl_{br}–*M* (°)	67·30 (7)	67·1 (2)	66·0 (2)	65·35 (7)	66·7 (1)
O–*M*–Cl_{br} (°)	157·6 (3)	155·4 (5)	160·2 (3)	158·2 (2)	155·1 (3)
(O–*M*–S_{br}) (av.) (°)	95·0 (3)	93·9 (5)	90·0 (7)	95·6 (1)	94·4 (3)
Configuration of S_{br}	*aa*	*aa*	*ee*	*aa*	*aa*
S_{br}–Cl_{br} (Å)	2·990 (4), 2·975 (4)	3·14 (1)	3·16 (1), 3·19 (1)	3·020 (5), 2·982 (5)	‖
Angles between planes					
$W_2(S_{br})$ (°)	175·9 (3)	176·7 (5)	164·4 (5)	182·3 (3)	‖
$(S_{br})_2Cl_2$ or $(S_{br})_2S_2$ (°)	144·0 (5)	143·8 (9)	134·0 (9)	145·0 (4)	‖
SR (°)	85·5 (6)	180·0 (9)	—	45·5 (6)	‖
Distance (Å) of *M* from $(S_{br})_2Cl_2$ planes	0·38	0·39	0·26	0·40	0·40

* This work.
† Patel, Boorman, Kerr & Moynihan (1982).
‡ Bunzey, Enemark, Gelder, Yamanouchi & Newton (1977).
§ Dilworth, Neaves, Dahlstrom, Hyde & Zubieta (1982).
‖ Atomic coordinates not provided.

In this model the distortion would be measured by the angles between the S_2Cl_2 planes. Clearly (I) and (II) conform more closely to this description than does (III). Consideration of the S_2Cl_2 planes shows that the W atoms lie out of these planes toward the O atoms as a result of the short W=O bonds.

Two recent examples give an indication of the potentially interesting chemistry associated with the effect of *trans*-weakening in binuclear structures. Firstly, Drew, Mitchell and co-workers (Drew, Baricelli, Mitchell & Read, 1983) have reported the loose coordination of a pyridine (or pyridazine) molecule in the bridging position *trans* to two oxo ligands in the complex *μ*-oxo-*μ*-pyridine-*μ*-sulphido-bis[(*O*,*O*′-diisopropyl phosphorodithioato)oxomolybdenum(V)]. The coordination appears to have been facilitated by a 'crevice' created by the disposition of the alkyl chains of the terminal ligands. Secondly, $[Mo(NC_6H_4CH_3)(\mu\text{-}S)\{S_2CN(i\text{-}C_4H_9)_2\}]_2$ and $[Mo(NC_6H_4CH_3)(\mu_3\text{-}S)\{S_2CN(i\text{-}C_4H_9)_2\}]_4$ were isolated from the same reaction mixture (Wall, Folting, Huffman & Wentworth, 1983), implying an equilibrium between the dimer and tetramer. The tetramer is formed by the coordination of the *μ*-sulphido groups in the dimer to the vacant *trans* site in a second dimer.

The observation in the present study that the nature of the substituent on a bridging thiolato ligand plays a significant part in the determination of the molecular structure in binuclear oxotungstate(V) species could imply a further role in determining the electronic properties and chemical reactivity of these complexes.

We thank the Natural Sciences and Engineering Research Council of Canada for financial support, and Dr K. Ann Kerr for the use of facilities enabling us to carry out the X-ray structure determinations.

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[Methoxy(*p*-tolylimino)methyl](triphenylphosphine)gold(I), $C_{27}H_{25}AuNOP$

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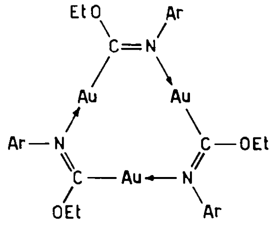
(*Received* 16 *February* 1984; *accepted* 20 *September* 1984)

Abstract. $M_r = 607{\cdot}441$, triclinic, $P\bar{1}$, $a = 21{\cdot}710\ (16)$, $b = 17{\cdot}235\ (12)$, $c = 10{\cdot}316\ (8)$ Å, $\alpha = 77{\cdot}9\ (1)$, $\beta = 104{\cdot}7\ (1)$, $\gamma = 95{\cdot}4\ (1)°$, $V = 3647\ (5)$ Å^3, $Z = 6$, $D_m = 1{\cdot}64$, $D_x = 1{\cdot}659$ Mg m^{-3}, Mo $K\bar{\alpha}$, $\lambda = 0{\cdot}71069$ Å, $\mu = 6{\cdot}12$ mm^{-1}, $F(000) = 1776$, $T = 295$ K, $R = 0{\cdot}0438$ for 7302 unique observed reflections. There are three crystallographically independent, but pratically identical, molecules. In each molecule the gold atom is linearly coordinated by the P atom from PPh_3 and by a C atom from the organic ligand. The intermolecular Au···Au distances are very long so that no metal–metal interaction is observed.

Introduction. By the reaction of an isocyanide, *R*NC, with a metal complex dissolved in an alcohol, *R'*OH, in the presence of an alkali, various species having the general formula $L_nM[-C(OR')=NR]_m$ were obtained, where *M* includes Hg, Ag, Au or Pt, *L* may be a phosphine or an isocyanide, *m* is equal to the oxidation number of the metal *M*, and *n* = 0, 1 or 2 (Minghetti & Bonati, 1972, 1974; Minghetti, Bonati & Massobrio, 1973, 1975; Minghetti, Bonati & Banditelli, 1973, 1976; Bonati, Minghetti & Banditelli, 1976; Banditelli, Bonati & Minghetti, 1977, 1980; Bonati & Clark, 1979; Banditelli, Bandini, Minghetti & Bonati, 1979; Banditelli, Bandini, Bonati, Goel & Minghetti, 1982).

Formally these species can be considered in several ways, *i.e.* either as substituted metal alkyls, or as *C*-metallated derivatives of an ester of formimidic acid, H—C(O*R'*)=N*R* (Minghetti, Banditelli & Bonati, 1975), or even as carbeniates, which are compounds obtained by deprotonation of a carbene complex of a metal, *M*←C(O*R'*)(NH*R*) (Schmidbauer, 1980). Accordingly they were indicated as (alkoxy)(*N*-alkylimino)-methylmetal, or *C*-metallated alkyl formimidate, or, more recently, metal (alkoxy)(*N*-alkylimino)carbeniate.

Although these complexes are generally stable, they have been characterized simply by analytical and spectroscopic techniques and among them only one X-ray crystal structure has been determined, namely that of [Au—C(OEt)=N(*p*-tolyl)]$_3$, (1), (Tiripicchio, Tiripicchio Camellini & Minghetti, 1979), a homoleptic gold alkyl, where an ennea-atomic ring is present, to be compared with the recently reported [Au(mesityl)]$_5$ (Gambarotta, Floriani, Chiesi Villa & Guastini, 1983). Since the structure determination of (1) revealed certain peculiar characteristics, such as both *intra*- and *inter*molecular interactions, it was decided to extend our investigations to a related complex, namely [Ph$_3$PAu—C(OEt)=N(*p*-tolyl)], (2).



(1)

Here the results of the X-ray crystal structure determination are reported and their significance is discussed.

Experimental. D_m by flotation, prismatic crystal 0·35 × 0·25 × 0·12 mm, Siemens AED diffractometer, Nb-filtered Mo $K\alpha$, lattice parameters refined by least squares of 18 reflections ($8 < \theta < 14°$), 12 853 independent reflections ($3 \leq \theta \leq 25°$, $\theta/2\theta$ scan), $-25 \leq h \leq 24$, $-19 \leq k \leq 20$, $0 \leq l \leq 12$, 7302 reflections with $I \geq 2\sigma(I)$ considered observed (1 standard

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