Synthesis and Characterization of Bis(xanthate) Complexes of Mo^{II} and W^{II}. Crystal Structure of $[W(S_2COPr^i\text{-}S)(S_2COPr^i\text{-}SS')(CO)_2(PMe_3)_2]$ †

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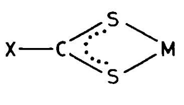
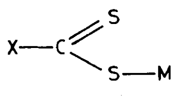
The reactions of $[MoCl_2(CO)_2(PMe_3)_3]$ with potassium xanthates, $K(S_2COR)$, give the red crystalline compounds $[Mo(S_2COR)_2(CO)(PMe_3)_2]$ [R = Me (**1**), Et (**2**), Pr^i (**3**), or Bu^t (**4**)] in which the xanthate groups seem to act as η^3-(*S,S′,C*) pseudo-allylic ligands. Formation of the dicarbonyl species $[Mo(S_2COR)_2(CO)_2(PMe_3)]$ is not detected, but the isopropyl derivative $[Mo(S_2COPr^i)_2(CO)_2(PMe_3)]$ (**5**) can be obtained by carbonylation of (**3**) under relatively forcing conditions. The tungsten complex $[WCl_2(CO)_2(PMe_3)_3]$ reacts similarly with $K(S_2COR)$ but gives mixtures of $[W(S_2COR)_2(CO)_2(PMe_3)_n]$ (*n* = 1 or 2). The monophosphine derivatives [R = Et (**6**) or Pr^i (**7**)] exhibit n.m.r. spectroscopic features similar to those of (**1**)—(**5**), but for the bis(phosphine) species a formulation containing uni- and bi-dentate xanthate groups, $[W(S_2COR\text{-}S)(S_2COR\text{-}SS')(CO)_2(PMe_3)_2]$ [R = Et (**8**) or Pr^i (**9**)] is proposed, and this has been confirmed by an *X*-ray crystal structure determination of complex (**9**). Formation of the dithiocarbonate complexes, $[M(S_2CO)(CO)_2(PMe_3)_3]$ [M = Mo (**11**) or W (**12**)] during the reactions leading to the above xanthates has also been observed. Complex (**9**) is triclinic, space group $P\bar{1}$, with unit-cell constants *a* = 8.775(2), *b* = 14.027(5), *c* = 11.806(5) Å, α = 106.09(2), β = 75.74(3), γ = 109.06(4)°, and *Z* = 2. The structure was refined to an *R* value of 0.032 by using 2 878 independent observed reflections.

Transition metals and dithioacid ligands such as dithiocarbamates and xanthates, share a very rich chemistry.[1] In particular, the implication of Mo–S bonding in the active site of the iron–molybdenum protein of nitrogenase[2] has induced numerous studies on molybdenum and other Group 6A metal complexes of these ligands, which are known to stabilize a wide range of oxidation states.[3] In most cases reported, the dithioacid ligand bonds to the metal centre in a dihapto fashion, (**A**), through both sulphur atoms, although a few complexes of transition metals containing unidentate dithiocarbamate, xanthate, or related ligands, (**B**), are also known.[4] With a few exceptions, the unidentate co-ordination is restricted to the late transition metals, and for dithiocarbamates; the first examples of unidentate complexes of Mo and W are the recently reported $[Mo\{HB(dmpz)_3\}(S_2CNEt_2\text{-}SS')(S_2CNEt_2\text{-}S)]$[5] (dmpz = 3,5-dimethylpyrazol-1-yl and $[W(cp)(S_2CNMe_2\text{-}S)(CO)_3]$ (cp = $\eta\text{-}C_5H_5$).[6]

Recently, the trihapto *S,S′,C* co-ordination mode, (**C**), has been demonstrated in some xanthate,[7,8] thioxanthate,[9,10] and phosphonium dithiocarboxylate[11] complexes. Observation of this type of structure in xanthate and thioxanthate complexes is possibly a reflection of the large contribution of structure (**IV**) to the total structure of the dithioacid ligand, and indeed, nucleophilic attack of phosphines on the CS_2 carbon of xanthate and thioxanthate ligands has been demonstrated recently.[7,9]



(A)



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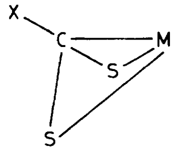
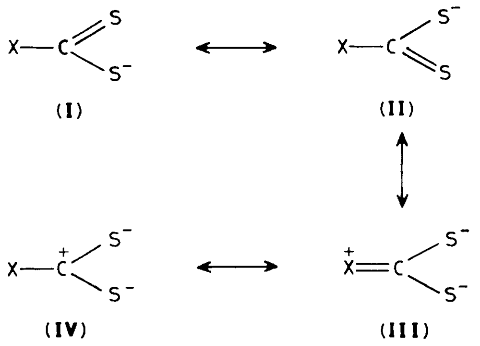


(C)



Following previous work from our laboratories on the chemistry of molybdenum and tungsten complexes with dithioacid ligands,[7,9,12] we have now studied the interaction of $[MCl_2(CO)_2(PMe_3)_3]$ complexes with various xanthate salts. The results of this study, which includes an *X*-ray structural determination of the complex $[W(S_2COPr^i\text{-}S)(S_2COPr^i\text{-}SS')(CO)_2(PMe_3)_2]$ (**9**), are reported in this paper. The reactions leading to the new compounds are shown in the Scheme, analytical and spectroscopic data are collected in Tables 1 and 2.

Results and Discussion

While transition-metal compounds of dithiocarbamate and xanthate ligands display, in general, many similarities, in some

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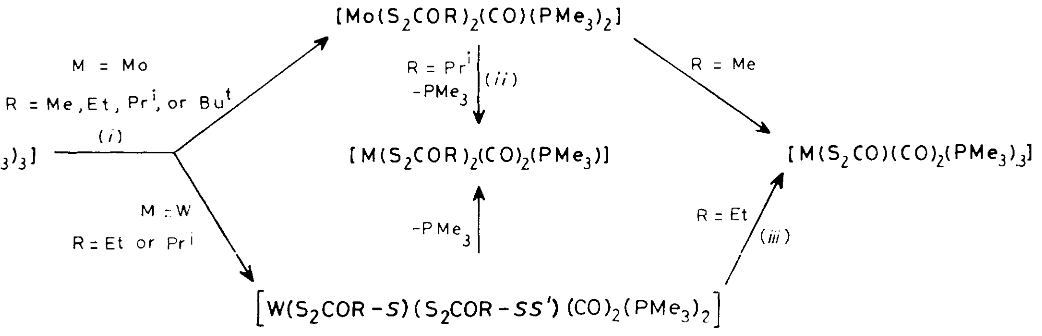
† Dicarbonyl(*O*-isopropyl dithiocarbonato-*SS′*)(*O*-isopropyl dithiocarbonato-*S*)bis(trimethylphosphine)tungsten.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1989, Issue 1, pp. xvii—xx.



Scheme. (*i*) $2K(S_2COR)$; (*ii*) CO; (*iii*) PMe_3

Table 1. Physical, analytical, and i.r. spectroscopic data (cm^{-1} in Nujol mulls) for the new compounds

		Analysis (%)[a]		I.r.	
Complex	Colour	C	H	ν(CO)	S_2COR
(**1**) $[Mo(S_2COMe)_2(CO)(PMe_3)_2]$	Red	26.9 (26.9)	4.8 (4.9)	1 795s	1 220vs, 1 160s, 1 055s
(**2**) $[Mo(S_2COEt)_2(CO)(PMe_3)_2]$	Red	30.5 (30.1)	5.3 (5.4)	1 800s	1 220vs, 1 130s, 1 050s
(**3**) $[Mo(S_2COPr^i)_2(CO)(PMe_3)_2]$	Red	33.0 (33.0)	5.9 (5.9)	1 780s	1 235vs, 1 100s, 1 050s
(**4**) $[Mo(S_2COBu^t)_2(CO)(PMe_3)_2]$	Red	35.6 (35.5)	6.3 (6.3)	1 785s	1 235vs, 1 130s, 1 050s
(**5**) $[Mo(S_2COPr^i)_2(CO)_2(PMe_3)]$	Red	31.5 (31.3)	4.6 (4.6)	1 950s, 1 860s	1 235vs, 1 090s, 1 050s
(**6**) $[W(S_2COEt)_2(CO)_2(PMe_3)]$	Red	24.2 (23.7)	3.5 (3.4)	1 930s, 1 840s	1 245vs, 1 125s, 1 040s
(**7**) $[W(S_2COPr^i)_2(CO)_2(PMe_3)]$	Red	26.8 (26.6)	3.8 (3.9)	1 930s, 1 840s	1 245vs, 1 090s, 1 040s
(**8**) $[W(S_2COEt\text{-}S)(S_2COEt\text{-}SS')(CO)_2(PMe_3)_2]$	Yellow	26.2 (26.5)	4.4 (4.4)	1 915s, 1 830s	1 230s, 1 175s, 1 115s, 1 040s
(**9**) $[W(S_2COPr^i\text{-}S)(S_2COPr^i\text{-}SS')(CO)_2(PMe_3)_2]$	Yellow	29.2 (29.0)	4.8 (4.8)	1 920s, 1 830s	1 245vs, 1 200s, 1 100s, 1 040s
(**10**) $[W(S_2COPr^i)_2(CO)(PMe_3)_2]$	Red	29.1 (28.4)	5.2 (5.1)	1 750s	1 230s, 1 090s, 1 045s
(**12**) $[W(S_2CO)(CO)_2(PMe_3)_3]$	Yellow	25.8 (25.7)	4.8 (4.8)	1 915s, 1 820s	*b*

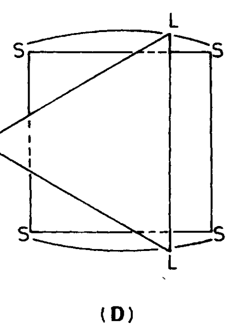
[a] Calculated values are given in parentheses. [b] S_2CO i.r. bands at 1 710m and 1 585s cm^{-1}.

Table 2. N.m.r. data for complexes (**1**)—(**12**)

	^1H		$^{31}P\text{-}\{^1H\}$		$^{13}C\text{-}\{^1H\}$			
Complex	MeP ($^2J_{HP}$)	R	PMe_3	($^1J_{PW}$)	MeP ($^2J_{CP}$)	R	S_2C (J_{CP})	CO ($^2J_{CP}$)
(**1**)	1.50 (d, 9.1)	3.43 (s, CH_3)	15.55 (s)		12.65 (m)	56.48 (s, CH_3)	218.18 (t, 9.0)	242.91 (t, 28)
(**2**)	1.38 (d, 8.4)	4.17 (q, CH_2) 0.91 (t, CH_3)	20.01 (s)		15.24 (dc, 28.2)	66.25 (s, CH_2) 13.65 (s, CH_3)	217.78 (t, 10.0)	242.91 (t, 28)
(**3**)	1.39 (d, 8.4)	5.41 (spt, CH) 1.04 (d, CH_3)	20.10 (s)		15.30 (dc, 27.5)	74.25 (s, CH) 21.37 (s, CH_3)	217.52 (t, 11.0)	242.48 (t, 28)
(**4**)	1.42 (d, 7.6)	1.47 (s, CH_3)	19.68 (s)		15.31 (m)	87.92 (s, *C*Me_3) 28.26 (s, CH_3)	217.37 (t, 10.0)	241.16 (t, 28)
(**5**)	1.14 (d, 9.4)	5.36 (spt, CH) 0.97 (d, CH_3)	17.40 (s)		16.38 (d, 31.1)	76.01 (s, CH) 21.11 (s, CH_3)	224.86 (d, 8.3)	251.74 (d, 26)
(**6**)	1.20 (d, 9.6)	4.04 (q, CH_2) 0.78 (t, CH_3)	−15.63 (s)	213.3	16.37 (d, 34.2)	67.10 (s, CH_2) 13.05 (s, CH_3)	227.22 (d, 7.0)	245.89 (d, 19)
(**7**)	1.19 (d, 9.2)	5.27 (spt, CH) 0.94 (d, CH_3)	−15.50 (s)	213.0	16.35 (d, 33.9)	76.01 (s, CH) 20.96 (s, CH_3)	226.84 (d, 8.0)	—
(**8**)[a]	1.74 (d, 9.8)	4.46 (q, CH_2) 1.36 (t, CH_3)	−8.79 (s)	142.5	17.27 (m)	68.62 (s, CH_2) 13.76 (s, CH_3)	226.21 (s)	234.72 (t, 26)
(**9**)	1.74 (d, 9.2)	5.47 (spt, CH) 1.33 (d, CH_3)	−8.71 (s)	143.3	17.40 (m)	76.95 (s, CH) 21.51 (s, CH_3)	225.67 (s)	235.20 (t, 25)
(**10**)	1.51 (d, 8.5)	5.33 (spt, CH) 1.03 (d, CH_3)	−8.02 (s)	203.4	15.35 (m)	74.03 (s, CH) 21.24 (s, CH_3)	—	—
(**11**)	1.38 (d, 8.5)		16.90 (br) −18.00 (br)		17.41 (br)[a]		200.61 (s)[a]	240.94 (br)[a]
(**12**)	1.56 (br)		−14.53 (br) −38.57 (br)		18.83 (m) 13.05 (d, 25.4)[b]		200.95 (br)[a]	235.62 (br)[a]

Recorded in C_6D_6 unless otherwise specified: s = singlet, d = doublet, dc = doublet with some central intensity, t = triplet, q = quartet, spt = septet, m = multiplet, and br = broad signal. Coupling constants in Hz. [a] Recorded in $CDCl_3$. [b] Recorded in $CDCl_3$ at −55 °C.

cases important differences in their structural and chemical behaviour, which can probably be related to the lower electron-donor ability of the OR group compared with the NR_2 group, can be noted. Dithiocarbamate ligands are strongly electron-releasing groups which can stabilize high oxidation states of the metals,[3] yielding compounds in which C–N bond rotation is frequently hindered, due to the multiple bond character of the $C\overset{...}{-}N$ bond.[13] In the analogous xanthates, however, restricted rotation around the C–O bond can seldom be observed, and on the other hand, η^3-pseudo-allylic structures, so far unobserved



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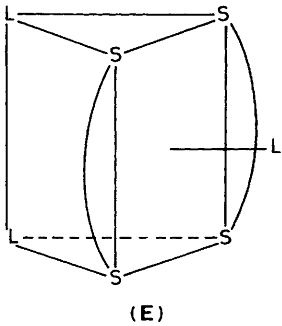


(E)

for dithiocarbamate complexes, are starting to become familiar[7,8] in xanthate chemistry. In addition, the xanthate ligand is prone to undergo nucleophilic attack at the CS_2 carbon atom, with or without rupture of the CO–R bond.[7,14,15] As an example illustrating some of the differences in the behaviour of these two types of dithioacid ligands the reaction of the oxo compounds $[MOCl_2(PMe_3)_3]$ (M = Mo or W) with the sodium or potassium salts of various dithiocarbamates and xanthates can be mentioned. This provides normal dithiocarbamate complexes $[MO(S_2CNR_2)_2(PMe_3)]$[16,17] but the unusual xanthates $[MO\{S_2C(PMe_3)OR\text{-}SS'\}(S_2COR\text{-}SS'C)]$.[7]

The interaction of the seven-co-ordinate compounds $[MCl_2(CO)_2(PMe_3)_3]$ (M = Mo or W) with $Na(S_2CNR_2)$ has been reported[12] to provide mainly the dicarbonyl complexes $[M(S_2CNR_2)_2(CO)_2(PMe_3)]$. In contrast, the analogous reactions with xanthate salts, $K(S_2COR)$, takes place as shown in equations (1) and (2). For the molybdenum system only

$$[MoCl_2(CO)_2(PMe_3)_3] + 2K(S_2COR) \longrightarrow [Mo(S_2COR)_2(CO)(PMe_3)_2] + CO + PMe_3 + 2KCl \quad (1)$$

$$[WCl_2(CO)_2(PMe_3)_3] + 2K(S_2COR) \longrightarrow [W(S_2COR)_2(CO)_2(PMe_3)_2] + PMe_3 + 2KCl \quad (2)$$

the monocarbonyl compounds $[Mo(S_2COR)_2(CO)(PMe_3)_2]$ [R = Me (**1**), Et (**2**), Pr^i (**3**), or Bu^t (**4**)] are obtained. Formation of the dicarbonyls $[Mo(S_2COR)_2(CO)_2(PMe_3)]$ is not detected under normal conditions, but if the reaction with $K(S_2COPr^i)$ is performed under CO pressure (2—3 atm; atm = 101 325 Pa), the i.r., ^1H and $^{31}P\text{-}\{^1H\}$ n.m.r. spectra of the extracted reaction mixture reveal the existence of minor amounts of the dicarbonyl complex $[Mo(S_2COPr^i)_2(CO)_2(PMe_3)]$ (**5**). For preparative purposes (see Experimental section), the latter compound can be obtained by carbonylation of pure $[Mo(S_2COPr^i)_2(CO)(PMe_3)_2]$ (**3**), under rather forcing conditions (8 h in boiling tetrahydrofuran, thf), as shown in equation 3. This process can be readily reversed, addition of a

$$[Mo(S_2COPr^i)_2(CO)(PMe_3)_2] \underset{PMe_3\,(fast)}{\overset{CO\,(slow)}{\rightleftharpoons}} [Mo(S_2COPr^i)_2(CO)_2(PMe_3)] \quad (3)$$

stoicheiometric amount of PMe_3 to this reaction mixture rapidly results in the complete transformation into the parent complex (**3**). This is at variance with the results found for the analogous complexes of the dithiocarbamate ligands, for which formation of the dicarbonyls is favoured on electronic grounds.[12] As already mentioned, this different behaviour probably reflects corresponding differences in the electron-releasing ability of the $RCOS_2^-$ and $R_2NCS_2^-$ ligands.

The new compounds (**1**)—(**5**) are red, diamagnetic crystalline solids, readily soluble in common organic solvents with the exception of light petroleum, in which they are only sparingly soluble. Although moderately stable in the solid state they decompose in solution in the presence of air. The monocarbonyls (**1**)—(**4**) exhibit i.r. spectra (measured in Nujol mulls or in thf solution) that are characterized by a strong ν(C–O) band in the proximity of 1 800 cm^{-1} (see Table 1), while the dicarbonyl (**5**) shows two carbonyl bands at 1 950 and 1 860 cm^{-1}. These absorptions are systematically at higher wavenumbers than those found for the analogous dithiocarbamate complexes {*e.g.* 1 760 cm^{-1} for $[Mo(S_2CNR_2)_2(CO)(PMe_3)_2]$, 1 915 and 1 830 cm^{-1} for $[Mo(S_2CNPr^i)_2(CO)_2(PMe_3)]$[12]}, in agreement with the lower ability of the xanthate ligand, as compared with the dithiocarbamate, to effect the transfer of electron density to the metal centre. In addition to these bands, all of the compounds show three xanthate absorptions in the region 1 250—1 000 cm^{-1}, which are consistent with the presence of chelating xanthate ligands.

The ^1H, $^{13}C\text{-}\{^1H\}$, and $^{31}P\text{-}\{^1H\}$ n.m.r. spectra of compounds (**1**)—(**4**) (Table 2) show resonances corresponding to two equivalent xanthate ligands and to two, also equivalent, *cis*-PMe_3 groups. For the dicarbonyl complex (**5**), a doublet at 252 p.p.m. [$^2J(P\text{–}C) = 26$ Hz] can be assigned to the CO ligands. Although the geometry of these seven-co-ordinate complexes cannot be unequivocally assigned on the basis of the spectroscopic data already discussed, the above considerations are in accord with a symmetrical distribution of the four sulphur atoms, which could be located on the quadrilateral face in a 4:3 'piano-stool' or capped prismatic geometry as shown in (**D**) and (**E**). An additional, and otherwise interesting, feature in the $^{13}C\text{-}\{^1H\}$ n.m.r. spectra of compounds (**1**)—(**5**) is the splitting of the ^{13}C resonance of the $ROCS_2$ carbon atom, due to coupling to the adjacent ^{31}P nuclei [$J(P\text{–}C) \approx 8$—11 Hz]. Although the scarcity of information on ^{13}C n.m.r. data of xanthate ligands does not allow any definite conclusions to be drawn, the observation of such a coupling seems to suggest the existence of a direct interaction between the CS_2 carbon and the molybdenum atom, *i.e.* that the xanthate ligands are bonded to the metal centre in a trihapto fashion, as shown in (**C**). This hypothesis seems plausible since: (*a*) in the recently described[11] $[MoCl(NO)(S_2CPMe_3)(PMe_3)_2]$ a similar proposal based on the observation of coupling (5.2 Hz) between the ^{13}C nucleus of the S_2CPMe_3 ligand and the ^{31}P nuclei of the molybdenum-bonded PMe_3 groups was confirmed by an *X*-ray analysis, which showed a direct and fairly strong bonding interaction [Mo–C 2.14(3) Å] between these two atoms; (*b*) η^3-xanthate (or thioxanthate) structures are more common than previously thought, in particular in molybdenum chemistry, and have convincingly been demonstrated at least in $[Mo_2(S_2COEt)_4]$,[8] $[MoO(S_2CSPr^i)_2]$,[10] $[MoO(S_2COPr^i)\{S_2C(PMe_3)OPr^i\}]$,[7] and $[MoO(S_2CSPr^i)\{S_2C(PMe_3)SPr^i\}]$.[9]

In contrast with the behaviour found for the molybdenum complexes already discussed, the main products of the reactions of $[WCl_2(CO)_2(PMe_3)_3]$ with 2 equivalents of $K(S_2COR)$ (R = Et or Pr^i), in thf, are always the dicarbonyls $[W(S_2COR)_2(CO)_2(PMe_3)_n]$ (*n* = 1 or 2). Both mono- and bisphosphine complexes, $[W(S_2COR)_2(CO)_2(PMe_3)]$ [R = Et (**6**) or Pr^i (**7**)] and $[W(S_2COR)_2(CO)_2(PMe_3)_2]$ [R = Et (**8**) or Pr^i (**9**)], can be isolated. Performing the reaction under carbon monoxide pressure introduces no significant changes but addition of PMe_3 to the reaction mixture (less than 1 equivalent) causes quantitative formation (n.m.r. spectroscopy, >80% yield of isolated products) of the bis(phosphine) complexes (**8**) and (**9**). Interconversion of the two types of complex can be readily achieved as shown in equation 4. Moderate heating of solutions of $[W(S_2COR)_2(CO)_2(PMe_3)_2]$ in thf, with occasional pumping of the solution, effects loss of PMe_3 and formation of the monophosphine derivatives (**6**) and

$$[W(S_2COR)_2(CO)_2(PMe_3)_2] \underset{+PMe_3\,(fast)}{\overset{-PMe_3\,(slow)}{\rightleftharpoons}} [W(S_2COR)_2(CO)_2(PMe_3)] \quad (4)$$

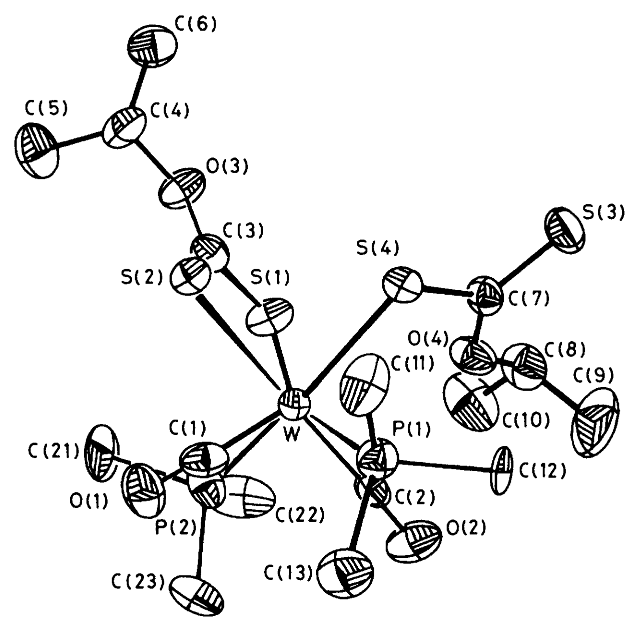
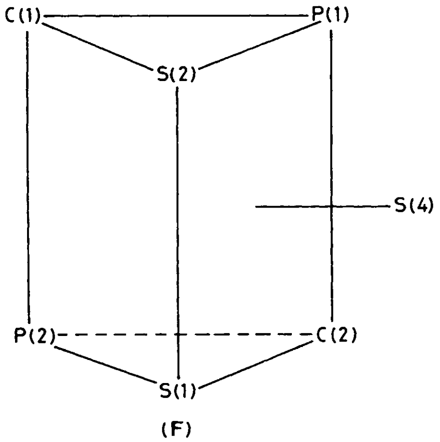


Figure. Structure of the complex [$W(S_2COPr^i$-*S*)(S_2COPr^i-*SS′*)$(CO)_2(PMe_3)_2$] (**9**)

Table 3. Experimental data for the crystallographic analysis of compound (**9**)

Formula	$C_{16}H_{32}O_4P_2S_4W$
M	662.2
Crystal system	Triclinic
a/Å	8.775(2)
b/Å	14.027(5)
c/Å	11.806(5)
α/°	106.09(2)
β/°	75.74(3)
γ/°	109.06(4)
U/Å^3	1 300.1(8)
Space group	*P*1
Z	2
D_c/g cm^{-3}	1.69
F(000)	656
μ/cm^{-1}	49.8



(F)

(**7**), while addition of 1 equivalent of PMe_3 to solutions of the latter compounds rapidly results in the formation of (**8**) or (**9**). In some instances, the prolonged heating of thf solutions of (**9**), under reduced pressure, gives, in addition to (**7**), small amounts of a monocarbonyl species, whose i.r. and n.m.r. spectroscopic properties are very similar to those found for the molybdenum complex (**3**), and suggest therefore its formulation as [$W(S_2COPr^i)_2(CO)(PMe_3)_2$] (**10**). Due to similar solubility, separation of this complex from the main reaction product, (**7**), is tedious, but analytically pure dark red crystals of (**10**) can be obtained after several recrystallizations from light petroleum at 0 °C. With respect to the reactivity of compounds (**8**) and (**9**) towards ligand dissociation or substitution, it seems that the preferred reaction involves loss of a PMe_3 ligand rather than of a CO group, in agreement with the previous suggestion that the presence of two carbonyl ligands in this type of complex represents the optimum situation[18] for d^4 ions.

Complexes (**6**) and (**7**) and the monocarbonyl (**10**) display physical and spectroscopic properties very similar to those observed for the analogous molybdenum complexes, and are therefore assigned structures of type (**D**) or (**E**). As for the molybdenum derivatives, coupling between the xanthate CS_2 carbon atom and the tungsten-bound PMe_3 ligands is detected [J(P–C) $\approx$ 7—8 Hz] and hence co-ordination mode (**C**) is suggested for the xanthate groups in these compounds.

Some additional comments are needed on the spectroscopic and structural properties of compounds (**8**) and (**9**), for which both electron-counting rules and the co-ordination numbers commonly observed in compounds of this type suggest the presence of unidentate and chelating xanthate groups. The i.r. spectra display *four* xanthate bands in the region 1 250—1 000 cm^{-1}, in accord with the above proposal. The n.m.r. spectra are however very simple and exhibit only one set of resonances for the two xanthate groups. Cooling at −70 °C does not cause splitting of the single phosphorus resonance and, on the other hand, the coupling between the ^{31}P and the ^{183}W nuclei is preserved in the temperature range −70 to 30 °C. Thus, the fluxional process responsible for the equilibration of the xanthate groups is very rapid, even at low temperatures, and does not involve phosphine dissociation. On the other hand, and at variance with the situation found for compounds (**1**)—(**7**), no coupling between the CS_2 carbon and the tungsten-bound ^{31}P nuclei is observed. Xanthate dissociation[15] may be invoked to explain the lack of such a coupling, but an alternative explanation, which does not require xanthate dissociation although is compatible with it, is to assume the absence of S_2C–W bonding interaction in these compounds, that is to propose that one of the $ROCS_2^-$ groups is *S,S′*-bonded to the tungsten centre, while the other is unidentate, and that there is a rapid process which interchanges these groups. As discussed below, the proposed formulation, [$W(S_2COR$-*S*)(S_2COR-*SS′*)$(CO)_2(PMe_3)_2$], has been confirmed by *X*-ray studies.

In order unequivocally to ascertain the structural characteristics of these compounds, an *X*-ray crystal structure determination of the isopropyl derivative, (**9**), has been undertaken. The molecular structure and atom-labelling scheme are shown in the Figure; crystal and other relevant structural data are compiled in Table 3. The structure consists of monomeric molecules of [$W(S_2COPr^i)_2(CO)_2(PMe_3)_2$], in which the tungsten atom is seven-co-ordinated to the two sulphur atoms of one of the xanthate groups, to one of the sulphur atoms of the second xanthate ligand, and to two carbonyls and two phosphines. The structural parameters in Table 4 allow the description[18] of the geometry of the co-ordination polyhedron in (**9**) as a 4:3 'piano-stool', with the atoms C(1), C(2), P(1), and P(2) lying in the quadrilateral face and the three co-ordinated sulphur atoms in the triangular face. Both planes are essentially parallel [angle between planes of 1.9(2)°]. In an alternative description the co-ordination geometry can be approximately described as a capped trigonal prism (**F**), with S(4) capping the quadrangular face formed by S(1), S(2), P(1), and C(2). The two triangular

Table 4. Bond distances (Å) and angles (°) for complex (**9**)

W–S(1)	2.556(3)	W–S(2)	2.590(3)	P(2)–C(21)	1.81(1)	P(2)–C(22)	1.82(1)
W–S(4)	2.573(3)	W–P(1)	2.495(3)	P(2)–C(23)	1.82(1)	C(1)–O(1)	1.16(2)
W–P(2)	2.473(3)	W–C(1)	1.942(12)	C(2)–O(2)	1.17(1)	O(3)–C(3)	1.32(1)
W–C(2)	1.957(9)	S(1)–C(3)	1.697(9)	O(3)–C(4)	1.47(1)	O(4)–C(7)	1.34(1)
S(2)–C(3)	1.672(9)	S(3)–C(7)	1.653(13)	O(4)–C(8)	1.45(1)	C(4)–C(5)	1.47(2)
S(4)–C(7)	1.714(10)	P(1)–C(11)	1.83(1)	C(4)–C(6)	1.50(2)	C(8)–C(9)	1.49(2)
P(1)–C(12)	1.82(1)	P(1)–C(13)	1.83(1)	C(8)–C(10)	1.50(2)		
S(1)–W–S(2)	67.9(1)	S(1)–W–S(4)	80.0(1)	W–C(1)–O(1)	175.0(9)	W–C(2)–O(2)	176.3(9)
S(1)–W–P(1)	155.6(1)	S(1)–W–P(2)	77.1(1)	S(1)–C(3)–S(2)	117.0(6)	S(1)–C(3)–O(3)	116.9(7)
S(1)–W–C(1)	127.9(3)	S(1)–W–C(2)	103.8(3)	S(2)–C(3)–O(3)	126.2(8)	C(3)–O(3)–C(4)	120.1(7)
S(2)–W–S(4)	77.0(1)	S(2)–W–P(1)	111.1(1)	O(3)–C(4)–C(5)	108(1)	O(3)–C(4)–C(6)	104.6(8)
S(2)–W–P(2)	103.4(1)	S(2)–W–C(1)	79.7(3)	C(5)–C(4)–C(6)	115.1(1)	S(3)–C(7)–S(4)	122.0(6)
S(2)–W–C(2)	171.5(3)	S(4)–W–P(1)	76.1(1)	S(3)–C(7)–O(4)	124.4(6)	S(4)–C(7)–O(4)	113.5(7)
S(4)–W–P(2)	154.9(1)	S(4)–W–C(1)	131.5(3)	C(7)–O(4)–C(8)	122.1(8)	O(4)–C(8)–C(9)	109(1)
S(4)–W–C(2)	100.3(3)	P(1)–W–P(2)	125.1(1)	O(4)–C(8)–C(10)	105(1)	C(9)–C(8)–C(10)	113(1)
P(1)–W–C(1)	73.7(3)	P(1)–W–C(2)	75.7(3)	C(11)–P(1)–C(12)	103.8(5)	C(11)–P(1)–C(13)	102.8(5)
P(2)–W–C(1)	72.1(3)	P(2)–W–C(2)	75.6(3)	C(12)–P(1)–C(13)	100.2(5)	C(21)–P(2)–C(22)	103.1(6)
C(1)–W–C(2)	107.7(4)	W–S(1)–C(3)	87.9(3)	C(21)–P(2)–C(23)	103.6(6)	C(22)–P(2)–C(23)	100.7(6)
W–S(2)–C(3)	87.3(4)	W–S(4)–C(7)	109.9(4)				

faces are almost parallel [7.8(2)°] but of the quadrilateral faces only that containing the atoms C(1), P(2), C(2), and P(1) is planar. In the capped face, for instance, the atom C(2) deviates by −0.7 Å from the mean-square plane.

The bond lengths from tungsten appear normal, and compare well with those reported in the literature for related complexes. The average carbonyl W–C bond length of 1.95 Å is close to the 1.97 Å found for $[W(S_2CNEt_2)_2(CO)_2(PPh_3)]$,[19] while the W–P bond distance of 2.48 Å (av.), although normal, is in the lower limit of the range usually found in tungsten carbonyl-phosphine complexes. The W–S distances for the bidentate xanthate in (**9**) [2.556(3) and 2.590(3) Å] parallel the tungsten–sulphur bond lengths in the related dithiocarbamate complexes $[W(S_2CNEt_2)_2(CO)_2(PPh_3)]$[19] and $[W(S_2CNEt_2)_2(CO)_3]$,[20] but the W–S separation for the unidentate xanthate of 2.573(3) Å is longer than the corresponding distance of 2.496(1) Å found in the dithiocarbamate complex $[W(cp)(S_2CNMe_2)(CO)_3]$.[6] The absence of interaction between the metal centre and the CS_2 carbon atom of the bidentate xanthate group is demonstrated by the W–C(3) separation of 3.02 Å, which is substantially longer than the sum of covalent radii [1.58(W) + 0.70(C) = 2.28 Å].[21] For comparative purposes, Mo–C separations of 2.274(5) and 2.302(6) Å have been found in the η^3-xanthate linkages of the oxo complexes $[MoO(\eta^3\text{-}S_2COPr^i)\{S_2C(PMe_3)OPr^i\}]$[7] and $[Mo_2(S_2COEt)_4]$,[8] respectively.

The bidentate xanthate ligand has a very short bite, the angle S(1)–W–S(2) having the low value of 67.9(1)°. Bond distances and angles within the OCS_2 unit of this xanthate group are normal, in the range found for other bidentate xanthate ligands.[22] The second xanthate, however, shows the expected asymmetry, with the bond length from C(7) to the unco-ordinated sulphur S(3) of 1.653(13) Å being shorter than that to the other sulphur [1.714(10) Å]. The latter is slightly shorter than a C–S single bond (1.81 Å) and the former longer than a normal carbon–sulphur double bond (1.61 Å).

A final point of interest in connection with the reactions providing compounds (**1**)—(**10**) is the formation, in some cases, of variable amounts of the dithiocarbonate derivatives $[M(S_2CO)(CO)_2(PMe_3)_3]$ [M = Mo (**11**) or W (**12**)]. This result is not unexpected since dithiocarbonate complexes have been reported to form by reaction of xanthate transition-metal compounds with $K(S_2COR)$ salts[1] or by the action of phosphines on xanthate complexes.[14,15,23] It appears that the R group of the $ROCS_2^-$ ligand has an effect on the formation of the S_2CO^{2-} ligand, and indeed, for our molybdenum compounds, the dithiocarbonate derivative $[M(S_2CO)(CO)_2(PMe_3)_3]$ (**11**) is only produced in the reaction of $[MoCl_2(CO)_2(PMe_3)_3]$ with $K(S_2COMe)$. Formation of (**11**) can be monitored by i.r. or $^{31}P\text{-}\{^1H\}$ n.m.r. spectroscopy, following the appearance of i.r. bands at 1 950 and 1 855 cm^{-1}, or that of a ^{31}P resonance at −7.9 p.p.m. Complex (**11**) has been fully characterized by comparison of its i.r., ^1H and $^{31}P\text{-}\{^1H\}$ n.m.r. spectra with those of an authentic sample, previously prepared in our laboratory by a different route.[24]

For the tungsten complexes investigated in this work, the formation of $[W(S_2CO)(CO)_2(PMe_3)_3]$ (**12**), is also strongly dependent on the nature of the R group of the xanthate ligand. Thus, the reaction of $[WCl_2(CO)_2(PMe_3)_3]$ with $K(S_2COPr^i)$ does not produce detectable amounts of complex (**12**), and on the other hand the action of an excess of PMe_3 on a chloroform solution of $[W(S_2COPr^i\text{-}S)(S_2COPr^i\text{-}SS')(CO)_2(PMe_3)_2]$ (**9**) yields only very small amounts of the dithiocarbonate (**12**). In contrast, the analogous reactions of $[WCl_2(CO)_2(PMe_3)_3]$ with $K(S_2COR)$ (R = Me, Et, or Bu^t) afford respectively 80, 50, and 20% of isolated (**12**). Not surprisingly, the reaction of $[W(S_2COEt\text{-}S)(S_2COEt\text{-}SS')(CO)_2(PMe_3)_2]$ (**8**) with PMe_3 is faster than that of the isopropyl analogue (**9**), and produces, after stirring at room temperature for *ca.* 18 h, 80% yields of (**12**). All these observations taken together clearly indicate that the formation of dithiocarbonates (**11**) and (**12**) from the corresponding xanthates is best accomplished for the methyl xanthate derivatives. The fact that the presence of an excess of the $ROCS_2^-$ ligand does not accelerate the reaction is consistent with either an intramolecular process implying nucleophilic attack of the unco-ordinated sulphur of a unidentate xanthate on the alkoxy-group of a dihapto xanthate, or with an analogous intermolecular reaction following prior dissociation of a co-ordinated xanthate ligand.

Experimental

Microanalyses were carried out by the Analytical Service of the University of Seville. Infrared spectra were recorded as Nujol mulls or in an appropriate solvent on Perkin-Elmer model 577 and 684 instruments. The ^1H, $^{13}C\text{-}\{^1H\}$, and $^{31}P\text{-}\{^1H\}$ n.m.r. spectra were run on a Varian XL-200 instrument. All preparations and operations were carried out under oxygen-free nitrogen or argon, following conventional Schlenk techniques. Solvents were dried by standard techniques and degassed before use. The compounds $[\mathrm{MCl_2(CO)_2(PMe_3)_3}]$ (M = Mo or W) were prepared according to the literature procedures.[12] The potassium xanthates, $\mathrm{K(S_2COR)}$, were obtained by slow addition of $\mathrm{CS_2}$ to solutions of KOH in the corresponding alcohols (MeOH, EtOH, $\mathrm{Pr^iOH}$, or $\mathrm{Bu^tOH}$) and used without further purification. The $\mathrm{PMe_3}$ ligand was prepared according to the literature procedure.[25]

Preparation of the Complexes $[\mathrm{Mo(S_2COR)_2(CO)(PMe_3)_2}]$ [R = Me (**1**), Et (**2**), $\mathrm{Pr^i}$ (**3**), *or* $\mathrm{Bu^t}$ (**4**)].—These complexes were synthesized and crystallized in a similar manner. The experimental procedure, using complex (**3**) as a representative example, was as follows: thf (40 $\mathrm{cm^3}$) was syringed into a mixture of $[\mathrm{MoCl_2(CO)_2(PMe_3)_3}]$ (0.45 g, 1 mmol) and anhydrous $\mathrm{K(S_2COPr^i)}$ (0.35 g, 2 mmol). As the reaction mixture was stirred at room temperature for *ca.* 2 h, the colour of the supernatant solution gradually changed from the initial yellow to red, and a white, finely divided, solid resulted. The solvent was then stripped off *in vacuo* and the residue extracted with light petroleum–diethyl ether (1:1, 30 $\mathrm{cm^3}$). Centrifugation and cooling at −35 °C afforded the desired product as red crystals in *ca.* 70% yield.

Starting with the appropriate potassium xanthate salts, the following compounds were obtained by the above procedure as red crystalline solids: $[\mathrm{Mo(S_2COMe)_2(CO)(PMe_3)_2}]$ (**1**), 40% yield; $[\mathrm{Mo(S_2COEt)_2(CO)(PMe_3)_2}]$ (**2**), 60% yield; $[\mathrm{Mo(S_2COBu^t)_2(CO)(PMe_3)_2}]$ (**4**), 50% yield.

Preparation of $[\mathrm{Mo(S_2COPr^i)_2(CO)_2(PMe_3)}]$ (**5**).—Carbon monoxide was bubbled through a solution of $[\mathrm{Mo(S_2COPr^i)_2(CO)(PMe_3)_2}]$ (0.28 g, 0.5 mmol) in thf (60 $\mathrm{cm^3}$), at 70 °C (bath temperature) for 8 h with periodical replacement of the evaporated thf. The solvent was then stripped *in vacuo* and the residue extracted with light petroleum. Centrifugation and cooling at −35 °C afforded the desired product as red crystals in *ca.* 50% yield.

Preparation of the Complexes $[\mathrm{W(S_2COR\text{-}\mathit{S})(S_2COR\text{-}\mathit{SS'})(CO)_2(PMe_3)_2}]$ [R = Et (**8**) *or* $\mathrm{Pr^i}$ (**9**)].—These two complexes were also synthesized in a similar manner. The experimental procedure, using complex (**8**) as a representative example, was as follows: a solution of $[\mathrm{WCl_2(CO)_2(PMe_3)_3}]$ (0.54 g, 1 mmol) in thf (35 $\mathrm{cm^3}$) was treated with $\mathrm{K(S_2COEt)}$ (0.32 g, 2 mmol). To the resulting suspension was added $\mathrm{PMe_3}$ (0.7 mmol), and the reaction mixture was stirred at room temperature for 2—3 h. The supernatant solution was filtered, the solvent removed under reduced pressure, and the resulting residue extracted with light petroleum–diethyl ether (1:1). Centrifugation and cooling at −35 °C afforded $[\mathrm{W(S_2COEt\text{-}\mathit{S})(S_2COEt\text{-}\mathit{SS'})(CO)_2(PMe_3)_2}]$ as yellow crystals in *ca.* 90- yield.

The complex $[\mathrm{W(S_2COPr^i\text{-}\mathit{S})(S_2COPr^i\text{-}\mathit{SS'})(CO)_2(PMe_3)_2}]$ (**9**) was obtained by the same procedure as yellow crystals from acetone at −35 °C in *ca.* 80% yield.

We have been unable to isolate the complexes $[\mathrm{W(S_2COR\text{-}\mathit{S})(S_2COR\text{-}\mathit{SS'})(CO)_2(PMe_3)_2}]$ (R = Me or $\mathrm{Bu^t}$) by using a similar procedure. The salts $\mathrm{K(S_2COR)}$ (R = Me or $\mathrm{Bu^t}$) react with the dichloride complex $[\mathrm{WCl_2(CO)_2(PMe_3)_3}]$ in $\mathrm{Et_2O}$ or thf, and red oils, displaying spectroscopic properties (i.r. and $^{31}\mathrm{P}\text{-}\{^1\mathrm{H}\}$ n.m.r.) similar to those recorded for complexes (**8**) and (**9**), were obtained. Nevertheless, only the dithiocarbonate $[\mathrm{W(S_2CO)(CO)_2(PMe_3)}]$ could be isolated from these oily materials, in *ca.* 80- yield from the $\mathrm{K(S_2COMe)}$ reaction, and in much lower yields (20%) from the analogous reaction with $\mathrm{K(S_2COBu^t)}$.

Preparation of the Complexes $[\mathrm{W(S_2COR)_2(CO)_2(PMe_3)}]$ [R = Et (**6**) *or* $\mathrm{Pr^i}$ (**7**)] *and* $[\mathrm{W(S_2COPr^i)_2(CO)(PMe_3)_2}]$ (**10**).—The complexes $[\mathrm{W(S_2COR)_2(CO)_2(PMe_3)}]$ (R = Et or $\mathrm{Pr^i}$) were prepared by moderate heating of thf solutions of the corresponding $[\mathrm{W(S_2COR\text{-}\mathit{S})(S_2COR\text{-}\mathit{SS'})(CO)_2(PMe_3)_2}]$ compounds under a slight dynamic vacuum. After 2—4 h at 40 °C the conversion into the products was more than 60% and they were isolated by fractional crystallization from light petroleum–diethyl ether (1:1). Recrystallization from light petroleum at −35 °C afforded the desired complexes as analytically pure red crystals.

In a related preparation, $[\mathrm{WCl_2(CO)_2(PMe_3)_3}]$ (0.27 g, 0.5 mmol) was treated with a suspension of $\mathrm{K(S_2COPr^i)}$ in thf at room temperature for 2 h. I.r. solution studies revealed the formation of complex (**9**). The suspension was heated at 40—50 °C for 4 h with periodical pumping, the solvent was then removed under reduced pressure, and the resulting red oil extracted with light petroleum. Attempted crystallization provided a reddish oil which was separated and the supernatant evaporated under vacuum and extracted again with light petroleum. After repeating this process three or four times, small amounts (20 mg, 6%) of red crystals of the monocarbonyl $[\mathrm{W(S_2COPr^i)_2(CO)(PMe_3)_2}]$ (**10**) were obtained.

Formation of the Dithiocarbonates $[\mathrm{M(S_2CO)(CO)_2(PMe_3)_3}]$ [M = Mo (**11**) *or* W (**12**)].—The molybdenum derivative (**11**) was isolated as a by-product, during the preparation of the xanthate $[\mathrm{Mo(S_2COMe)_2(CO)(PMe_3)_2}]$ (**1**). Fractional crystallization of the extracted reaction mixture provided yellow crystals of (**11**) which were recrystallized from diethyl ether at −35 °C (yield 25%). The compound was identified by comparison of its i.r., ^{1}H and $^{31}\mathrm{P}\text{-}\{^1\mathrm{H}\}$ n.m.r. spectra with those of an authentic sample.[24] Variable, albeit in some cases small, amounts of the tungsten derivative (**12**) were formed in the reactions of $[\mathrm{WCl_2(CO)_2(PMe_3)_3}]$ with the xanthate salts used in this work. The highest yield was however obtained with $\mathrm{K(S_2COMe)}$ as described below: a solution of $[\mathrm{WCl_2(CO)_2(PMe_3)_3}]$ (0.54 g, 1 mmol) in thf (45 $\mathrm{cm^3}$) was treated with $\mathrm{K(S_2COMe)}$ (0.30 g, 2 mmol) at room temperature over a period of 2 h. When the reaction was complete a yellow solution and a white finely divided solid resulted. This suspension was evaporated to dryness and the residue extracted with diethyl ether–acetone (2:1). Centrifugation, partial evaporation of the extracts to *ca.* 20 $\mathrm{cm^3}$, and subsequent cooling at −35 °C overnight produced the desired product as yellow crystals in *ca.* 80% yield.

Complex (**12**) can also be obtained by the reaction of complex (**8**) with $\mathrm{PMe_3}$: to a stirred yellow solution of complex (**8**) (0.33 g, 0.5 mmol) in $\mathrm{CHCl_3}$ (10 $\mathrm{cm^3}$) was added an excess of $\mathrm{PMe_3}$ (0.2 $\mathrm{cm^3}$, 2 mmol) and the resulting solution was stirred at room temperature for *ca.* 18 h. Removal of solvent *in vacuo* and crystallization of the remaining residue afforded $[\mathrm{W(S_2CO)(CO)_2(PMe_3)_3}]$ in *ca.* 80% yield.

When the above reaction was carried out in the presence of added $\mathrm{K(S_2COEt)}$ no significant changes were observed and when $\mathrm{Et_2O}$ was the reaction solvent more than 3 d were needed for complete transformation into complex (**11**).

The complex $[\mathrm{W(S_2COPr^i)_2(CO)_2(PMe_3)_2}]$, dissolved in $\mathrm{CHCl_3}$, was also partially converted (less than 50%) into complex (**12**) after stirring at room temperature for 3 d in the presence of an excess of $\mathrm{PMe_3}$.

Crystallography.—A summary of the crystallographic and other data for complex (**9**) is given in Table 3, the final fractional atomic co-ordinates being listed in Table 5. A yellow prismatic crystal of size 0.2 × 0.2 × 0.3 mm was mounted in an Enraf-Nonius CAD4-F automatic diffractometer. The cell dimensions were refined by least-squares fitting of the values of 25 reflections. The intensities of all 3 701 unique reflections with $1 < \theta < 25$ and ranging from (−10, −16, 0) to (10, 16, 9) were measured at 295 K with monochromatic Mo-K_α radiation

Table 5. Final fractional atomic co-ordinates for complex (**9**)

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
W	0.226 16(4)	0.331 18(3)	0.174 49(4)
S(1)	0.172 91(28)	0.136 85(17)	0.090 16(25)
S(2)	0.445 98(27)	0.288 14(16)	−0.007 57(23)
S(3)	0.419 60(39)	0.194 84(23)	0.461 77(30)
S(4)	0.429 01(27)	0.293 30(18)	0.269 02(24)
P(1)	0.338 45(28)	0.499 35(17)	0.308 82(24)
P(2)	−0.021 46(29)	0.287 00(20)	0.085 01(27)
O(1)	0.275 99(92)	0.498 82(55)	0.033 65(72)
O(2)	−0.058 88(87)	0.350 64(59)	0.390 34(72)
O(3)	0.393 55(80)	0.083 73(46)	−0.083 51(63)
O(4)	0.161 08(78)	0.203 36(51)	0.390 38(66)
C(1)	0.252 20(107)	0.437 97(70)	0.090 35(99)
C(2)	0.049 82(110)	0.341 87(67)	0.311 90(91)
C(3)	0.346 75(108)	0.163 48(66)	−0.011 35(90)
C(4)	0.538 19(115)	0.100 14(73)	−0.177 32(94)
C(5)	0.483 28(174)	0.091 85(127)	−0.288 64(132)
C(6)	0.619 00(144)	0.019 67(85)	−0.181 16(110)
C(7)	0.324 49(114)	0.228 42(66)	0.380 83(88)
C(8)	0.050 99(137)	0.139 02(88)	0.470 59(116)
C(9)	0.015 93(188)	0.205 29(143)	0.591 12(137)
C(10)	−0.097 91(158)	0.084 77(114)	0.413 70(146)
C(11)	0.558 62(125)	0.557 02(78)	0.270 57(96)
C(12)	0.307 68(126)	0.498 89(80)	0.466 72(92)
C(13)	0.253 00(147)	0.604 51(77)	0.317 88(106)
C(21)	0.008 56(140)	0.251 21(104)	−0.076 77 (104)
C(22)	−0.191 62(121)	0.181 35(79)	0.129 64(117)
C(23)	−0.122 51(129)	0.388 70(92)	0.121 23(120)

(λ = 0.710 69 Å) and an ω—2θ scan technique. There was no appreciable change in the periodically monitored standard reflection. The intensities were corrected for Lorentz and polarization effects and 2 878 of these were considered as observed with $I > 2\sigma(I)$.

Scattering factors for neutral atoms and anomalous dispersion corrections for W, P, and S were taken from ref. 26.

The structure was solved by Patterson and Fourier methods. An empirical absorption correction[27] was applied at the end of the isotropic refinement. Anisotropic full-matrix least-squares refinement with unit weights, minimizing $\Sigma w(|F_o| - |F_c|)^2$, led to $R = 0.036$. No trend in ΔF *vs.* F_o or $(\sin\theta)/\lambda$ was observed. Final refinement with fixed isotropic thermal parameters and co-ordinates for H atoms gave $R = 0.032$ and $R' = 0.038$. Maximum and average shifts/error were 0.12 and 0.02 respectively. Most of the calculations were carried out with *X*-RAY 80.[28]

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates and thermal parameters.

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