Six- and Seven-co-ordinate Complexes of Molybdenum(II) and Tungsten(II) with Thioether Ligands. Crystal Structures of $[WI_2(CO)_3\{4\text{-}MeC_6H_4S(CH_2)_2SC_6H_4Me\text{-}4\}]$ and $[WI_2(CO)_2\{MeS(CH_2)_2S(CH_2)_2SMe\text{-}S,S',S''\}]$†

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Reaction of $[MI_2(CO)_3(NCMe)_2]$ (M = Mo or W) with a slight excess of $RS(CH_2)_2SR$ (R = Ph, 4-MeC_6H_4 or 4-FC_6H_4) in CH_2Cl_2 at room temperature gave $[MI_2(CO)_3\{RS(CH_2)_2SR\}]$. The molecular structure of $[WI_2(CO)_3\{4\text{-}MeC_6H_4S(CH_2)_2SC_6H_4Me\text{-}4\}]$ has been determined by X-ray crystallography. It shows that the tungsten has essentially capped-octahedral geometry with a carbonyl ligand in the unique capping position. Low-temperature ^{13}C NMR studies on the tungsten complexes suggest that their structures in solution are similar to the solid-state structure found. Reaction of $[WI_2(CO)_3(NCMe)_2]$ with 2 equivalents of $PhS(CH_2)_2SPh$ in CH_2Cl_2 afforded $[WI(CO)_3\{PhS(CH_2)_2SPh\text{-}S\}\{PhS(CH_2)_2SPh\text{-}S,S'\}]I$ which was reduced by $LiBu^n$ to *cis*-$[W(CO)_2\{PhS(CH_2)_2SPh\text{-}S,S'\}_2]$. Equimolar quantities of $[MI_2(CO)_3(NCMe)_2]$ (M = Mo or W) and $MeS(CH_2)_2S(CH_2)_2SMe$ reacted in CH_2Cl_2 to give $[MoI_2(CO)_2\{MeS(CH_2)_2S(CH_2)_2SMe\text{-}S,S',S''\}]$ and $[WI_2(CO)_3\{MeS(CH_2)_2S(CH_2)_2SMe\text{-}S,S'\}]$. The latter was converted in $CHCl_3$ into $[WI_2(CO)_2\{MeS(CH_2)_2S(CH_2)_2SMe\text{-}S,S',S''\}]$, the molecular structure of which is essentially a capped octahedron with a carbonyl ligand in the unique capping position.

The importance of molybdenum complexes containing thiolate, thioether or sulfide co-ligands as models for the molybdenum site in nitrogenase has been highlighted by the very recently reported [1–3] crystal structure of the active site of this enzyme. It is our purpose to examine the behaviour of sulfur-ligated molybdenum (and tungsten) complexes as models for the molybdenum site in nitrogenase, which among others has three sulfur-donor ligands and appears to be in a non-zero oxidation state. Sulfur-ligated complexes of molybdenum in the zero oxidation state bind dinitrogen[4,5] but such binding has not yet been observed for sulfur-ligated centres in the more desirable higher oxidation states of the metal. Herein we describe chemistry which relates to binding of nitrogenase substrates and inhibitors at such molybdenum sites in that the nitrogenase inhibitor CO is bound to thioether-ligated molybdenum(II).

Although a wide range of seven-co-ordinate complexes of molybdenum(II) containing nitrogen- and phosphorus-donor ligands has been described,[6–15] there are very few examples containing neutral sulfur-donor ligands. We have previously reported the reactions of $[MI_2(CO)_3(NCMe)_2]$ (M = Mo or W) with $SC(NH_2)_2$ and related ligands[16] and with $SPPh_3$.[17] As far as we are aware the only simple example of a seven-co-ordinate complex containing a neutral bidentate sulfur-donor ligand is $[MoI_2(CO)_3(dth)]$ (dth = 2,5-dithiahexane) described by Mannerskantz and Wilkinson[18] in 1962. In this paper we describe the reactions of $[MI_2(CO)_3(NCMe)_2]$ (M = Mo or W) with the dithioethers $RS(CH_2)_2SR$ (R = Ph, 4-MeC_6H_4 or 4-FC_6H_4) and the trithioether $MeS(CH_2)_2S(CH_2)_2SMe$.

Results and Discussion

Dithioether Complexes.—The starting materials used, $[MI_2(CO)_3(NCMe)_2]$ (M = Mo or W),[19] were prepared as described previously.[19,20] Their reactions with a slight excess of $RS(CH_2)_2SR$ (R = Ph, 4-MeC_6H_4 or 4-FC_6H_4) in CH_2Cl_2 at room temperature gave the seven-co-ordinate complexes $[MI_2(CO)_3\{RS(CH_2)_2SR\}]$ **1–6** in high yield. All the complexes have been characterised by elemental analysis (Table 1), infrared spectroscopy (Table 2), ^1H and, in selected cases, ^{13}C and ^{19}F NMR and UV spectroscopies (Tables 3–6). Conductivity measurements show the complexes to be non-electrolytes. Complexes **1–6** are soluble to varying degrees in chlorinated solvents, acetone and acetonitrile, but insoluble in diethyl ether. Complexes **1–6** are fairly air-sensitive both in the solid state and in solution. They can be stored under nitrogen in the dark for several days without significant decomposition. The tungsten complexes are, as expected, more stable than their molybdenum analogues. The infrared spectra all show three carbonyl stretching bands; this suggests a single isomer for these complexes in $CHCl_3$ solution. Their ^1H NMR spectra (Table 3) all show the expected features for the co-ordinated dithioether ligands with these resonances shifted slightly downfield relative to the free thioethers. The ^{19}F NMR spectrum of **6** shows an unsymmetrical multiplet at δ −116.50 which is slightly shifted from that of the free dithioether (δ −116.36, symmetrical multiplet).

The molecular structure of compound **4** is shown in Fig. 1, with the atom numbering scheme. Atomic coordinates are in Table 7 and selected bond lengths in Table 8. The co-ordination geometry about the tungsten atom may be described as distorted capped octahedral, with the carbonyl ligand of C(4) in the unique capping position.

In order to compare the solid-state and solution structures of complexes **1–6**, the low-temperature ^{13}C NMR spectra [CD_2Cl_2, −65 °C; or $(CD_3)_2CO$, −60 °C] of the tungsten complexes **2**, **4** and **6** were obtained (Table 5). The spectrum of **4** showed three carbonyl resonances; in view of Colton and Kevekordes' work,[21] it is likely that the very low-field resonance at δ 235.2 is due to the capping carbonyl [C(4), O(4) in the

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

Table 1 Physical and analytical data * for six- and seven-co-ordinate thioether complexes of molybdenum and tungsten

Complex	Colour	Yield (%)	Analysis (%) C	H	S	Mo or W
1 $[MoI_2(CO)_3\{PhS(CH_2)_2SPh\}]$	Brown	73	30.4	2.4	9.8	14.6
			(30.0)	(2.1)	(9.4)	(14.1)
2 $[WI_2(CO)_3\{PhS(CH_2)_2SPh\}]$	Orange	52	26.9	1.8	8.7	24.7
			(26.6)	(1.8)	(8.4)	(23.9)
3 $[MoI_2(CO)_3\{4\text{-}MeC_6H_4S(CH_2)_2SC_6H_4Me\text{-}4\}]$	Brown	70	32.5	2.9	8.7	—
			(32.2)	(2.6)	(9.1)	
4 $[WI_2(CO)_3\{4\text{-}MeC_6H_4S(CH_2)_2SC_6H_4Me\text{-}4\}]$	Orange	52	28.8	2.4	7.8	24.0
			(28.7)	(2.3)	(8.1)	(23.1)
5 $[MoI_2(CO)_3\{4\text{-}FC_6H_4S(CH_2)_2SC_6H_4F\text{-}4\}]\cdot CH_2Cl_2$	Orange	60	26.7	1.6	—	—
			(27.0)	(1.8)		
6 $[WI_2(CO)_3\{4\text{-}FC_6H_4S(CH_2)_2SC_6H_4F\text{-}4\}]$	Orange	58	25.3	1.5	8.5	23.6
			(25.4)	(1.5)	(8.0)	(22.9)
7 $[WI(CO)_3\{PhS(CH_2)_2SPh\text{-}S\}\{PhS(CH_2)_2SPh\text{-}S,S'\}]I$	Light brown	60	36.8	2.7	12.4	18.7
			(36.7)	(2.8)	(12.6)	(18.1)
8 *cis*-$[W(CO)_2\{PhS(CH_2)_2SPh\text{-}S,S'\}_2]$	Yellow	15	48.8	3.7	—	—
			(49.2)	(3.9)		
9 $[MoI_2(CO)_2\{MeS(CH_2)_2S(CH_2)_2SMe\text{-}S,S',S''\}]$	Brown	55	16.0	2.4	16.1	—
			(16.3)	(2.4)	(16.3)	
10 $[WI_2(CO)_3\{MeS(CH_2)_2S(CH_2)_2SMe\text{-}S,S'\}]$	Yellow	60	15.6	2.0	13.4	—
			(15.4)	(2.0)	(13.7)	
11 $[WI_2(CO)_2\{MeS(CH_2)_2S(CH_2)_2SMe\text{-}S,S',S''\}]$	Orange	70	14.4	2.1	—	—
			(14.2)	(2.1)		

* Calculated values in parentheses.

Table 2 Infrared data[a,b] for the complexes

Complex	$\tilde{\nu}(CO)/cm^{-1}$ *a*	*b*
1	2070s, 2015 (br), 1943 (br)	—
2	2028s, 1952s, 1910s	2027s, 1954s, 1911s
3	2069s, 1977s, 1935s	—
4	2026s, 1959 (br), 1920 (br)	2025s, 1952 (br), 1930w (sh), 1908 (br)
5	2072s, 2012s, 1956 (br)	2068m (sh), 2034m, 1974s, 1921 (br)
6	2024s, 1939s, 1901s	2033s, 1961s, 1901s
7	2035s, 1960s, 1930s	
8	1872 (br), 1748 (br)	
9		1944s, 1874s
10		2026s, 1954s, 1910s
11		1931s, 1855s

s = Strong, m = medium, w = weak, sh = shoulder, br = broad.

[a] Spectra recorded in $CHCl_3$ as thin films between NaCl plates. [b] Spectra recorded as KBr discs.

Table 3 Proton NMR data for the complexes at 25 °C, referenced to $SiMe_4$

Complex	δ(*J*/Hz)
1[a]	7.62 (m, 10 H, Ph), 3.70 (s, 4 H, CH_2)
2[a]	7.61 (m, 10 H, Ph), 3.65 (s, 4 H, CH_2)
3[a]	7.53 (d, J_{HH} = 8.1, 4 H, C_6H_4), 7.35 (d, J_{HH} = 8.1, 4 H, C_6H_4), 3.6 (s, 4 H, CH_2), 2.45 (s, 6 H, CH_3)
4[a]	7.55 (d, J_{HH} = 8.1, 4 H, C_6H_4), 7.4 (d, J_{HH} = 8.1, 4 H, C_6H_4), 3.55 (s, 4 H, CH_2), 2.5 (s, 6 H, CH_3)
5[b]	7.52 (m, 4 H, C_6H_4), 7.2 (m, 4 H, C_6H_4), 5.7 (s, 2 H, CH_2Cl_2), 3.2 (s, 4 H, CH_2)
6[b]	7.50 (m, 4 H, C_6H_4), 7.1 (m, 4 H, C_6H_4), 3.15 (s, 4 H, CH_2)
7[a]	7.61 (m, 10 H, Ph, co-ordinated ligand), 7.24 (m, 10 H, Ph, free ligand), 3.6 (s, 4 H, CH_2, co-ordinated ligand), 3.1 (s, 4 H, CH_2, free ligand)
9[c]	2.9 (m, 8 H, CH_2), 2.2 (s, 6 H, CH_3)
10[d]	3.56 [m, 4 H, CH_2SCH_2, (co-ordinated)], 3.46 [br m, 2 H, CH_2SCH_3 (co-ordinated)], 2.9 [s, 3 H, SCH_3 (co-ordinated)], 2.46 [m, 2 H, CH_2SCH_3 (unco-ordinated)], 2.2 [s, 3 H, SCH_3 (unco-ordinated)]
11[c]	2.95 (m, 8 H, CH_2), 2.25 (s, 6 H, CH_3)

s = Singlet, d = doublet, m = multiplet, br = broad.

[a] Spectra recorded in $CDCl_3$. [b] Spectra recorded in $(CD_3)_2CO$. [c] Spectra recorded in $(CD_3)_2SO$. [d] Spectrum recorded in CD_3NO_2.

solid-state structure shown in Fig. 1]. The other two carbonyls are in slightly different co-ordination sites and so give individual resonances. Ganscow and Vernon[22] have suggested that the shift to low field of resonances for carbonyl ligands in the capping position is due to increased π-back donation. At room temperature (CD_2Cl_2, 25 °C) **4** shows a single resonance at δ 218.6, which suggests the complex is fluxional with a rapid exchange of carbonyl ligands. These observations are consistent with the variable-temperature ^{13}C NMR spectra and molecular structures of the complexes $[PPh_2(C_6H_{11})H][WI_3(CO)_3(SbPh_3)]$[23] and $[WI_2(CO)_3(NCMe)_2]$[24] which some of us have described previously. The low-temperature ^{13}C NMR spectra for **2** and **6** also show three carbonyl resonances in similar positions to those of **4** indicating that these complexes have similar structures.

Reaction of $[WI_2(CO)_3(NCMe)_2]$ with 2 equivalents of $PhS(CH_2)_2SPh$, or of $[WI_2(CO)_3\{PhS(CH_2)_2SPh\}]$ **2**, with 1 equivalent of $PhS(CH_2)_2SPh$, in CH_2Cl_2 at room temperature, gave the cationic complex $[WI(CO)_3\{PhS(CH_2)_2SPh\text{-}S\}\{PhS(CH_2)_2SPh\text{-}S,S'\}]I$ **7** in good yield. This formulation is based on elemental analysis, infrared and ^1H NMR spectroscopy and its conductivity, which is typical of a 1:1 electrolyte (Experimental section). The infrared spectrum ($CHCl_3$) shows three carbonyl bands in a similar position to those of **4**. Since **7** is most likely to be seven-co-ordinate and such complexes are generally capped octahedral,[25,26] it is proposed that the structure is capped octahedral, with one of the sulfur atoms of the $PhS(CH_2)_2SPh$ ligand replacing the least crowded of the iodides as shown in Fig. 2. Complex **7** is very unstable in solution since its ^1H NMR spectrum (Table 3) shows free dithioether to be present. This is in accord with the proposed structure (Fig. 2), where the monodentate ligand would be expected to be substitution labile in solution.

Table 4 Carbon-13 NMR data for selected complexes at 25 °C referenced to $SiMe_4$

Complex	δ(*J*/Hz)
2[a]	218.2 (s, C≡O), 131.8, 130.4, 130.2 (3s, Ph), 41.8 (s, SCH_2)
4[a]	218.6 (s, C≡O), 142.7 (s, SC), 131.8, 130.9 (2s, C_6H_4), 126.8 (s, CH_3C), 42.1 (s, SCH_2), 21.2 (s, CH_3)
6[b]	210 (s, C≡O), 162.8 (d, $^1J_{CF}$ = 250, FC), 133.6 (d, J_{CF} = 10, C_6H_4), 131.5 (d, J_{CF} = 10, C_6H_4), 116.9 (d, J_{CF} = 10, C_6H_4), 34.8 (s, SCH_2)
10[c]	222, 214, 203 (3s, C≡O), 41.7, 41.2, 40.3 [3s, CH_2S (co-ordinated)], 34.1 [s, CH_2S (unco-ordinated)], 23.7 [s, CH_3S (co-ordinated)], 22.6 [s, CH_3S (unco-ordinated)]

[a] Spectra recorded in CD_2Cl_2 on a Bruker WH 400 MHz instrument. [b] Spectrum recorded in $(CD_3)_2CO$. [c] Spectrum recorded in CD_3NO_2.

Table 5 Low-temperature ^{13}C NMR data[a,b] for selected complexes

Complex	δ(*J*/Hz)
2[a]	234.8, 210.6, 208.6 (3s, C≡O), 131.7, 131.1, 130.8, 130.1, 129.2, 128.5, 128.3 (m, Ph), 43.8, 38.6 (2s, SCH_2)
4[a]	235.2, 210.8, 208.9 (3s, C≡O), 142.5, 141.9 (2s, SC), 131.4, 130.7, 129.8, 128.7 (m, C_6H_4), 125.9, 123.9 (2s, CH_3C), 43.8, 38.9 (2s, SCH_2), 20.8 (s, CH_3C)
6[b]	230.2, 210.1, 201.8 (3s, C≡O), 162.1 (d, $^1J_{CF}$ = 240, FC), 132.7 (d, J_{CF} = 10, C_6H_4), 130.8 (d, J_{CF} = 10, C_6H_4), 116.8 (d, J_{CF} = 10, C_6H_4), 33.3 (s, SCH_2)

[a] Spectra recorded in CD_2Cl_2 (−65 °C) on a Bruker WH 400 MHz instrument. [b] Spectrum recorded in $(CD_3)_2CO$ (−60 °C).

Table 6 Ultraviolet spectroscopic data for selected complexes

Complex	λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})
2	423[a] (1 245), 358[b] (13 320), 288[b] (19 700), 249[b] (44 500)
4	423[a] (1 280), 288[b] (19 500), 248[b] (44 700)
6	424[c] (1 420), 295[b] (8 600), 240[b] (30 300)

[a] Recorded in $CHCl_3$ (UV cut-off value = 245 nm). [b] Recorded in NCMe (UV cut-off value = 210 nm). [c] Recorded in Me_2CO (UV cut-off value = 330 nm).

Reduction of complex **7** with LiBu^n in tetrahydrofuran (thf) gave, in low yield, the zerovalent complex **8** formulated as $[W(CO)_2\{PhS(CH_2)_2SPh\}_2]$ as discussed below. It should be noted that the tetracarbonyl dithioether complexes $[M(CO)_4\{RS(CH_2)_2SR\}]$ (M = Mo or W) have been previously reported by Hunter and Massey.[27,28] However, the very electron-rich dicarbonyl complex **8** is the first bis(dithioether) complex of this type to be described. It is an analogue of the macrocyclic thioether complex *trans*-$[Mo(CO)_2(Me_8[16]aneS_4)]$ ($Me_8[16]aneS_4$ = 3,3,7,7,11,11,15,15-octamethyl-1,5,9,13-tetrathiacyclohexadecane) prepared by Yoshida *et al.*[4] and was characterised by elemental analysis and infrared spectroscopy. Its infrared spectrum shows two carbonyl bands of essentially equal intensity which absorb in the expected region for terminal CO bound to a very electron-rich site (1872 and 1748 cm^{-1}) and close to the values observed for *cis*-$[Mo(CO)_2(Ph_2PCH_2CH_2PPh_2)_2]$ (1855 and 1780 cm^{-1}).[29] Thus **8** is very likely to have *cis*-carbonyl ligands.

Trithioether Complexes.—Reaction of $[MoI_2(CO)_3(NCMe)_2]$ with an equimolar amount of $MeS(CH_2)_2S(CH_2)_2SMe$ in CH_2Cl_2 at room temperature for 2 h gave the complex $[MoI_2(CO)_2\{MeS(CH_2)_2S(CH_2)_2SMe\text{-}S,S',S''\}]$ **9** in 55% yield, whereas treatment of $[WI_2(CO)_3(NCMe)_2]$ with 1 equivalent of $MeS(CH_2)_2S(CH_2)_2SMe$ in CH_2Cl_2 under the same conditions afforded $[WI_2(CO)_3\{MeS(CH_2)_2S(CH_2)_2SMe\text{-}S,S'\}]$ **10** in 60% yield. Upon stirring in $CHCl_3$ solution for 1 week **10** was converted into the dicarbonyl complex $[WI_2(CO)_2\{MeS(CH_2)_2S(CH_2)_2SMe\text{-}S,S',S''\}]$ **11** in 70% yield. The non-conducting complexes **9**–**11** have been characterised by elemental analysis, infrared and ^1H NMR spectroscopy and by a crystal structure determination of **11**. All three complexes are insoluble in diethyl ether but slightly soluble in acetone and acetonitrile; in addition, **9** is insoluble in chlorinated solvents but soluble in dimethyl sulfoxide, **10** is moderately soluble in chlorinated solvents and nitromethane, but very soluble in tetrahydrofuran, and **11** is insoluble in chlorinated solvents, slightly soluble in nitromethane, and very soluble in tetrahydrofuran. Complexes **9** and **11** are reasonably air-stable in the solid state, however they are much more air-sensitive in solution.

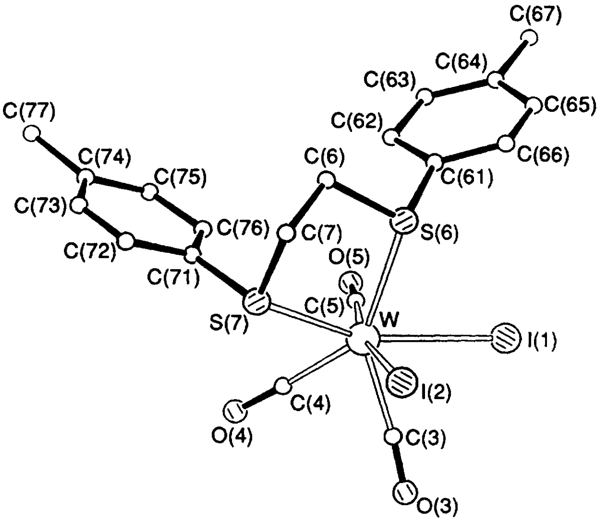

Fig. 1 Molecular structure of $[WI_2(CO)_3\{4\text{-}MeC_6H_4S(CH_2)_2SC_6H_4\text{-}Me\text{-}4\}]$ **4** showing the atom numbering scheme

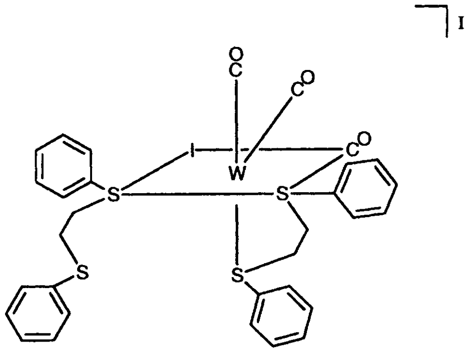

Fig. 2 Proposed structure of $[WI(CO)_3\{PhS(CH_2)_2SPh\text{-}S\}\{PhS(CH_2)_2SPh\text{-}S,S'\}]I$ **7**

The two carbonyl stretching bands of complexes **9** and **11** and their ^1H NMR spectra (Table 3) are as expected. The ^1H NMR spectrum of the tricarbonyltungsten complex **10** shows methyl groups in distinctly different environments, and the CH_3 group next to the unco-ordinated sulfur is at considerably higher field (δ 2.2) compared to the methyl groups on the co-ordinated sulfur atom (δ 2.9). The ^{13}C NMR spectrum (CD_3NO_2, 25 °C) shows three carbonyl resonances at δ 203, 214 and 222 (Table 4). The last is typical of a carbonyl in a capping position in a capped octahedral geometry.[21] In view of this and since the vast majority of seven-co-ordinate complexes have this geometry,[25,26] it is likely that **10** has capped octahedral geometry, possibly as shown in Fig. 3.

Table 7 Final atomic coordinates (fractional × 10^4) for $[WI_2(CO)_3\{4\text{-}MeC_6H_4S(CH_2)_2SC_6H_4Me\text{-}4\}]$ **4** with estimated standard deviations (e.s.d.s) in parentheses

Atom	*x*	*y*	*z*
W	1833.3(4)	121.6(4)	1402.1(2)
I(1)	4823.8(8)	925.7(8)	1116.8(3)
I(2)	588(1)	2564.5(9)	822.4(3)
C(3)	2456(16)	1923(15)	1724(5)
O(3)	2711(13)	2919(11)	1907(4)
C(4)	1040(14)	−201(15)	2040(4)
O(4)	607(12)	−463(13)	2420(3)
C(5)	2996(11)	−1509(12)	1702(5)
O(5)	3676(10)	−2406(10)	1901(4)
S(6)	1915(3)	−1034(3)	611(1)
C(61)	3303(14)	−2372(12)	564(4)
C(62)	3321(14)	−3713(12)	851(5)
C(63)	4594(14)	−4603(14)	811(5)
C(64)	5705(13)	−4212(13)	484(5)
C(65)	5576(15)	−2890(14)	203(5)
C(66)	4422(14)	−2007(13)	222(5)
C(67)	7073(17)	−5204(18)	467(7)
C(6)	151(12)	−2067(14)	560(4)
C(7)	−1084(11)	−1120(15)	721(5)
S(7)	−876(3)	−767(3)	1320(1)
C(71)	−1248(12)	−2630(13)	1584(4)
C(72)	−2758(13)	−3137(19)	1622(5)
C(73)	−3102(15)	−4482(17)	1781(5)
C(74)	−2097(17)	−5526(15)	1940(5)
C(75)	−615(16)	−5029(16)	1922(7)
C(76)	−174(13)	−3603(15)	1744(6)
C(77)	−2483(20)	−7110(15)	2114(7)

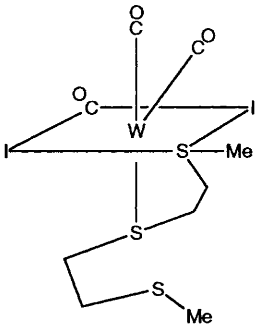

Fig. 3 Proposed structure of $[WI_2(CO)_3\{MeS(CH_2)_2S(CH_2)_2SMe\text{-}S,S'\}]$ **10**

Table 8 Selected dimensions (bond lengths in Å, angles in °) in $[WI_2(CO)_3\{4\text{-}MeC_6H_4S(CH_2)_2SC_6H_4Me\text{-}4\}]$ **4** with e.s.d.s in parentheses

(*a*) About the tungsten			
W–I(1)	2.836(1)	W–C(5)	1.954(11)
W–I(2)	2.875(1)	W–S(6)	2.593(3)
W–C(3)	2.017(13)	W–S(7)	2.536(3)
W–C(4)	1.948(12)		
I(1)–W–I(2)	93.1*	I(2)–W–S(6)	82.4(1)
I(1)–W–C(3)	72.7(4)	C(3)–W–S(6)	143.7(4)
I(2)–W–C(3)	75.9(4)	C(4)–W–S(6)	142.9(4)
I(1)–W–C(4)	127.8(4)	C(5)–W–S(6)	90.4(4)
I(2)–W–C(4)	115.3(4)	I(1)–W–S(7)	157.4(1)
C(3)–W–C(4)	73.3(6)	I(2)–W–S(7)	78.2(1)
I(1)–W–C(5)	76.9(3)	C(3)–W–S(7)	123.8(4)
I(2)–W–C(5)	168.6(4)	C(4)–W–S(7)	74.4(4)
C(3)–W–C(5)	105.7(5)	C(5)–W–S(7)	109.1(3)
C(4)–W–C(5)	75.7(5)	S(6)–W–S(7)	78.3(1)
I(1)–W–S(6)	80.0(1)		
(*b*) In the carbonyl ligands			
C(3)–O(3)	1.106(15)	W–C(3)–O(3)	175.8(13)
C(4)–O(4)	1.154(15)	W–C(4)–O(4)	176.4(11)
C(5)–O(5)	1.133(13)	W–C(5)–O(5)	175.5(12)
(*c*) In the thioether ligand			
S(6)–C(6)	1.816(11)	C(7)–S(7)	1.785(14)
S(6)–C(61)	1.770(12)	S(7)–C(71)	1.798(12)
C(6)–C(7)	1.514(19)		
W–S(6)–C(6)	107.0(4)	W–S(7)–C(7)	105.8(4)
W–S(6)–C(61)	115.8(4)	W–S(7)–C(71)	113.6(4)
C(6)–S(6)–C(61)	104.0(6)	C(7)–S(7)–C(71)	97.8(6)
S(6)–C(6)–C(7)	107.1(8)	C(6)–C(7)–S(7)	112.4(8)
(*d*) Torsion angles in the thioether ligand			
C(6)–S(6)–C(61)–C(62)	−54.3(11)		
C(6)–S(6)–C(61)–C(66)	126.7(10)		
C(61)–S(6)–C(6)–C(7)	165.6(8)		
S(6)–C(6)–C(7)–S(7)	−61.8(10)		
C(6)–C(7)–S(7)–C(71)	−68.0(9)		
C(7)–S(7)–C(71)–C(72)	−78.7(11)		
C(7)–S(7)–C(71)–C(76)	100.2(12)		

* E.s.d. is less than 0.05°.

Table 9 Final atomic coordinates (fractional × 10^4) for $[WI_2(CO)_2\{MeS(CH_2)_2S(CH_2)_2SMe\}]$ **11** with e.s.d.s in parentheses

Atom	*x*	*y*	*z*
W	3445.2(4)	2740.1(3)	251.4(2)
I(1)	4487.2(8)	2962.3(5)	−1426.4(4)
I(2)	1078.6(7)	1237.3(5)	−644.6(4)
C(3)	1662(11)	3648(8)	−400(6)
O(3)	665(8)	4200(5)	−762(5)
C(4)	2928(11)	3802(8)	1063(6)
O(4)	2606(9)	4462(6)	1523(5)
C(5)	6758(13)	4050(9)	1748(7)
S(5)	6150(3)	3781(2)	586(2)
C(56)	7850(11)	2859(8)	474(6)
C(65)	7684(10)	1833(7)	914(6)
S(6)	5627(2)	1247(2)	503(1)
C(67)	5293(10)	483(7)	1446(6)
C(76)	3413(11)	429(7)	1477(6)
S(7)	2458(3)	1718(2)	1463(1)
C(7)	3497(14)	2155(10)	2548(6)

The molecular structure of $[WI_2(CO)_2\{MeS(CH_2)_2S(CH_2)_2SMe\text{-}S,S',S''\}]$ **11** has been determined by X-ray crystallography, and is shown in Fig. 4; atomic coordinates are in Table 9 and bond dimensions in Table 10. The co-ordination pattern is very similar to that of **4**; the carbonyl group of C(4) is again the capping group in the distorted capped-octahedral arrangement. The views in Figs. 1 and 4 are of a similar perspective and the atoms of the two molecules have been labelled correspondingly. The principal difference in the co-ordination geometry results from the replacement of the carbonyl C(5) group in **4** by the sterically constrained third sulfur atom S(5) in **11**.

The bond dimensions in the two complexes are also very similar. The mean W–I distances at 2.86(2) and 2.867(1) Å in the two complexes are typical of such bonds in seven-co-ordinate tungsten(II) species, whether cationic, neutral or anionic, *e.g.* $[WI(CO)_3(\eta^6\text{-}C_6H_3Me_3\text{-}1,3,5)][W_2I_5(CO)_6]$,[30] $[WI_2(CO)_2(Bu^tNC)_3]$[31] and $[PBu^t{}_3I][WI_3(CO)_4]$.[32]

The W–S distances in both our complexes vary according to the ligand in the *trans* position (in the approximately octahedral arrangement); the thioether S atom opposite an iodide ligand has a rather shorter W–S length than that opposite a carbonyl group. There are few tungsten thioether complexes with which to make comparisons, but $[(dth)(OC)_3W(\mu\text{-}Cl)(SnMeCl_2)]$,[33] $[W(CO)_4L]$[34] (L = a cyclic [15]aneS_5–thiophene derivative) and $[W(CO)_4\{Bu^tS(CH_2)_nSBu^t\}]$, for n = 2 or 3,[35] all have chelating thioether groups and show W–S distances within the range 2.537(8)–2.586(5) Å; in these complexes the tungsten is W^0 or W^{II} and either six- or seven-co-ordinate. Our values

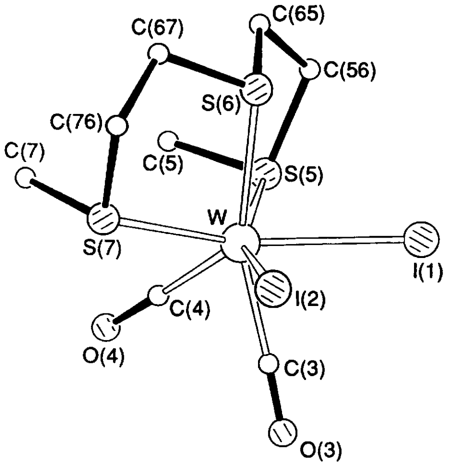

Fig. 4 Molecular structure of $[WI_2(CO)_2\{MeS(CH_2)_2S(CH_2)_2SMe$-*S*,*S′*,*S″*$\}]$ **11**. The view is similar to that of **4** in Fig. 1, and the atoms are numbered correspondingly

Table 10 Molecular dimensions (bond lengths in Å, angles in °) in $[WI_2(CO)_2\{MeS(CH_2)_2S(CH_2)_2SMe$-*S*,*S′*,*S″*$\}]$ **11** with e.s.d.s in parentheses

(*a*) About the tungsten

W–I(1)	2.866(1)	W–S(5)	2.519(2)
W–I(2)	2.867(1)	W–S(6)	2.566(2)
W–C(3)	1.968(9)	W–S(7)	2.514(2)
W–C(4)	1.933(9)		
I(1)–W–I(2)	84.8*	I(2)–W–S(6)	87.5*
I(1)–W–C(3)	77.8(3)	C(3)–W–S(6)	157.8(3)
I(2)–W–C(3)	77.7(3)	C(4)–W–S(6)	129.8(3)
I(1)–W–C(4)	130.1(3)	S(5)–W–S(6)	79.4(1)
I(2)–W–C(4)	125.0(3)	I(1)–W–S(7)	154.2(1)
C(3)–W–C(4)	72.4(4)	I(2)–W–S(7)	75.0(1)
I(1)–W–S(5)	75.5(1)	C(3)–W–S(7)	112.4(3)
I(2)–W–S(5)	157.2(1)	C(4)–W–S(7)	75.5(3)
C(3)–W–S(5)	108.6(3)	S(5)–W–S(7)	119.8(1)
C(4)–W–S(5)	77.3(3)	S(6)–W–S(7)	78.8(1)
I(1)–W–S(6)	84.6*		

(*b*) In the carbonyl ligands

C(3)–O(3)	1.134(10)	W–C(3)–O(3)	177.7(8)
C(4)–O(4)	1.155(11)	W–C(4)–O(4)	177.5(8)

(*c*) In the trithianonane ligand

C(5)–S(5)	1.798(10)	S(6)–C(67)	1.805(8)
S(5)–C(56)	1.832(9)	C(67)–C(76)	1.523(12)
C(56)–C(65)	1.486(13)	C(76)–S(7)	1.808(9)
C(65)–S(6)	1.819(8)	S(7)–C(7)	1.812(10)
W–S(5)–C(5)	111.9(4)	C(65)–S(6)–C(67)	101.5(4)
W–S(5)–C(56)	106.0(3)	S(6)–C(67)–C(76)	110.0(6)
C(5)–S(5)–C(56)	98.1(5)	C(67)–C(76)–S(7)	112.4(6)
S(5)–C(56)–C(65)	112.8(6)	W–S(7)–C(76)	106.7(3)
C(56)–C(65)–S(6)	110.6(6)	W–S(7)–C(7)	111.6(4)
W–S(6)–C(65)	107.7(3)	C(76)–S(7)–C(7)	98.2(5)
W–S(6)–C(67)	108.8(3)		

(*d*) Torsion angles in the trithianonane ligand

C(5)–S(5)–C(56)–C(65)	70.1(7)
S(5)–C(56)–C(65)–S(6)	55.5(8)
C(56)–C(65)–S(6)–C(67)	−151.6(6)
C(65)–S(6)–C(67)–C(76)	148.5(6)
S(6)–C(67)–C(76)–S(7)	−54.7(7)
C(67)–C(76)–S(7)–C(7)	−68.5(7)

* E.s.d. is less than 0.05°.

extend slightly outside that range, probably as a result of the *trans* influences in our complexes.

Similarly, the W–C distances in complex **4** appear to depend on the ligand opposite: that to C(5), opposite the iodide, is rather shorter than that to C(13), *trans* to the thioether; the W–C(4) distances, involving the capping carbonyl groups, are marginally the shortest in both our structures.

It is also interesting to compare the structure of complex **11** with that of the only other crystallographically characterised complex of $MeS(CH_2)_2S(CH_2)_2SMe$, $[Mo(CO)_3\{MeS(CH_2)_2S(CH_2)_2SMe\}]$.[36] Whereas the latter complex crystallised as the *syn*(*endo*) regioisomer, in which the two methyl groups of the thioether ligand are arranged so as to give the maximum mutual separation, **11** crystallises as the *syn*(*exo*) isomer, where the methyl groups are approximately parallel (see Fig. 4). The fact that our seven-co-ordinate complex can achieve this geometry suggests that the *syn*(*exo*) geometry is not so sterically demanding as was originally thought.[36]

Since the carbonyl stretching bands for complexes **9** and **11** are in similar positions it is likely that these two complexes are isostructural.

Conclusion

We have prepared and structurally characterised a series of new sulfur-ligated carbonyl complexes of M^{II} (M = Mo or W). They will provide useful synthons for other complexes of this type by metathetical and CO-displacement reactions.

Experimental

All the reactions were carried out under an atmosphere of dry nitrogen using standard Schlenk techniques. Solvents were dried and degassed before use. The complexes $[MI_2(CO)_3(NCMe)_2]$ (M = Mo or W) and thioethers $PhS(CH_2)_2SPh$, $4\text{-}MeC_6H_4S(CH_2)_2SC_6H_4Me\text{-}4$ and $4\text{-}FC_6H_4S(CH_2)_2SC_6H_4F\text{-}4$ were prepared by literature methods,[19,37] but $MeS(CH_2)_2S(CH_2)_2SMe$ was prepared by a different method from that given in ref. 36, as described below. All other chemicals used were obtained from commercial sources.

Proton NMR spectra were recorded on Bruker AC/250 or JEOL GSX 270 spectrometers, ^{13}C NMR spectra on a Bruker WH 400 MHz spectrometer and ^{19}F NMR spectra on a JEOL GSX 270 spectrometer. The ^1H and ^{13}C NMR spectra were referenced to tetramethylsilane and ^{19}F NMR spectra to $Et_2O{\cdot}BF_3$. Infrared spectra were recorded on a Perkin-Elmer 1600 series FTIR spectrophotometer and atomic absorption readings on a Video IIE aa/ae spectrophotometer. Elemental analyses were determined using a Carlo Erba MOD 1106 instrument (helium carrier gas): C, H, N by Mr. K. Jones (Bangor), S by Mr. C. J. Macdonald (Nitrogen Fixation Laboratory, Sussex). Conductivities were measured using a Portland Electronics conductivity bridge.

Preparations.—*2,5,8-Trithianonane.* Sodium (7.2 g, 313 mmol) was dissolved in ethanol (220 cm^3) and 2-mercaptoethyl sulfide (20 cm^3, 154 mmol) was added dropwise over 15 min. The solution was stirred at 60 °C for 30 min and iodomethane (19.5 cm^3, 313 mmol) was added dropwise over 10 min. The mixture was boiled under reflux for 2 h and a small amount of precipitate formed on cooling. The solvent was removed *in vacuo* and the residue was shaken with water (100 cm^3) plus ether (100 cm^3). The water layer was extracted once with ether (100 cm^3) and the combined organic extract was dried over Na_2SO_4. Concentration *in vacuo* gave the product in high yield as a clear colourless oil, which was used without further purification. Yield 21.9 g (78%). NMR (CD_3NO_2): ^1H, δ 2.76 (m, 8 H, CH_2CH_2) and 1.2 (s, 6 H, CH_3); ^{13}C-{H}, δ 15.7 (s, CH_3), 32.5 and 35.1 (2s, CH_2).

$[WI_2(CO)_3\{4\text{-}MeC_6H_4S(CH_2)_2SC_6H_4Me\text{-}4\}]$ **4**. To a stirred solution of $[WI_2(CO)_3(NCMe)_2]$ (0.3 g, 0.497 mmol) in CH_2Cl_2 (15 cm^3) under a stream of dry nitrogen was added $4\text{-}MeC_6H_4S(CH_2)_2SC_6H_4Me\text{-}4$ (0.19 g, 0.696 mmol). The mixture was stirred for 2 h. The solvent was removed *in vacuo* to produce a green powder (yield = 0.21 g, 52%) which was redissolved in CH_2Cl_2 and filtered to produce an orange solution. This solution was reduced to minimum volume and cooled to −17 °C for 24 h to give orange single crystals of $[WI_2(CO)_3\{4\text{-}MeC_6H_4S(CH_2)_2SC_6H_4Me\text{-}4\}]$ **4** which were suitable for X-ray crystallography.

Similar reactions of $[MI_2(CO)_3(NCMe)_2]$ (M = Mo or W) with a slight excess of L $[PhS(CH_2)_2SPh$, $4\text{-}MeC_6H_4S(CH_2)_2SC_6H_4Me\text{-}4$ or $4\text{-}FC_6H_4S(CH_2)_2SC_6H_4F\text{-}4]$, followed by recrystallisation from CH_2Cl_2–Et_2O at −17 °C, gave complexes **1–3**, **5** and **6** (see Table 1 for physical and analytical data).

$[WI(CO)_3\{PhS(CH_2)_2SPh\text{-}S\}\{PhS(CH_2)_2SPh\text{-}S,S'\}]I$ **7**. To $[WI_2(CO)_3(NCMe)_2]$ (0.30 g, 0.497 mmol) dissolved in CH_2Cl_2 (15 cm^3) with stirring under nitrogen was added $PhS(CH_2)_2SPh$ (0.26 g, 1.06 mmol). After the mixture had been stirred for 3 h the solvent was removed *in vacuo* to produce a brown powder, which was redissolved in CH_2Cl_2 and filtered. The solvent was again removed *in vacuo* to produce a light brown product, which was washed with Et_2O to remove excess of thioether and to give analytically pure $[WI(CO)_3\{PhS(CH_2)_2SPh\text{-}S\}\{PhS(CH_2)_2SPh\text{-}S,S'\}]I$ **7** as brown crystals (0.30 g, 60%). Molar conductance in $MeNO_2$ 80 (expected for a 1:1 electrolyte 75–95 S cm^2 mol^{-1}).

cis-$[W(CO)_2\{PhS(CH_2)_2SPh\text{-}S,S'\}_2]$ **8**. To complex **7** (0.2 g, 0.197 mmol) dissolved in thf (20 cm^3) with stirring under a stream of dry nitrogen was added an excess of $LiBu^n$ (0.16 cm^3, 0.414 mmol in hexane). The mixture was stirred for 24 h and the solvent removed *in vacuo* to produce a dark yellow oily product. This was washed with hexane and subsequently recrystallised from toluene–hexane to produce a yellow solid, *cis*-$[W(CO)_2\{PhS(CH_2)_2SPh\text{-}S,S'\}_2]$ which was analytically pure (0.02 g, 15%).

$[MoI_2(CO)_2\{MeS(CH_2)_2S(CH_2)_2SMe\text{-}S,S',S''\}]$ **9**. The complex $[MoI_2(CO)_3(NCMe)_2]$ (1.20 g, 2.33 mmol) was dissolved in CH_2Cl_2 (20 cm^3) and $MeS(CH_2)_2S(CH_2)_2SMe$ (0.45 cm^3, 2.64 mmol) added. The mixture was stirred for 2 h and the solvent removed *in vacuo* to produce a dark brown powder. This was washed with ether and recrystallised from acetonitrile to produce a brown crystalline solid (0.75 g, 55%). Molar conductance in dimethylformamide (dmf) 20 (expected for a 1:1 electrolyte in dmf 65–95 S cm^2 mol^{-1}).

$[WI_2(CO)_3\{MeS(CH_2)_2S(CH_2)_2SMe\text{-}S,S'\}]$ **10**. The complex $[WI_2(CO)_3(NCMe)_2]$ (0.3 g, 0.497 mmol) was dissolved in CH_2Cl_2 (20 cm^3) and $MeS(CH_2)_2S(CH_2)_2SMe$ (0.1 cm^3, 0.587 mmol) added. The mixture was stirred for 2 h and the solvent removed *in vacuo* to produce a light brown oily material. This was washed with ether and recrystallised from acetonitrile to produce a yellow crystalline solid. Yield (0.21 g, 60%). Molar conductance in CH_3NO_2 35 (expected for 1:1 electrolyte in $MeNO_2$ 75–95 S cm^2 mol^{-1}).

$[WI_2(CO)_2\{MeS(CH_2)_2S(CH_2)_2SMe\text{-}S,S',S''\}]$ **11**. Complex **10** (0.15 g, 0.213 mmol) was dissolved in $CHCl_3$ (20 cm^3) and stirred under N_2 for 1 week. The solvent was removed *in vacuo* and the product recrystallised from acetonitrile followed by nitromethane at −18 °C to give orange crystals of $[WI_2(CO)_2\{MeS(CH_2)_2S(CH_2)_2SMe\text{-}S,S',S''\}]$ **11** which were suitable for X-ray crystallographic analysis (0.1 g, 70%).

Crystal Structure Analysis of Complex **4**, $[WI_2(CO)_3\{4\text{-}MeC_6H_4S(CH_2)_2SC_6H_4Me\text{-}4\}]$.—*Crystal data.* $C_{19}H_{18}I_2O_3S_2W$, $M = 796.1$, triclinic, space group $B\bar{1}$ (equivalent to no. 2), $a = 8.897(3)$, $b = 9.052(4)$, $c = 28.628(16)$ Å, $\alpha = 84.14(4)$, $\beta = 90.01(4)$, $\gamma = 91.70(3)°$, $U = 2292.4$ Å^3, $Z = 4$, $D_c = 2.306$ g cm^{-3}, $F(000) = 1472$, μ(Mo-Kα) = 80.1 cm^{-1}, λ(Mo-Kα) = 0.710 69 Å.

Several large, red, rectangular plates were mounted on glass fibres and the one (*ca.* 0.07 × 0.50 × 0.70 mm) showing least streakiness in photographic examination was transferred to an Enraf-Nonius CAD4 diffractometer (with monochromated radiation) for determination of accurate cell dimensions (from the settings of 25 reflections with θ *ca.* 10.25°, each centred in four orientations) and measurement of diffraction intensities to $\theta_{max} = 26°$. The intensities were corrected for Lorentz-polarisation effects and absorption (by analytical methods); no correction for crystal deterioration was required. 4494 Unique reflections were input to the SHELX system[38] for structure determination by the heavy-atom method and refinement by full-matrix least-squares methods to $R = 0.082$ and $R_g = 0.101$[38] for 4189 reflections (those with $I > \sigma_I$) weighted $w = (\sigma_F^2 + 0.005F^2)^{-1}$. All non-hydrogen atoms were refined anisotropically, but some of the U_{ii} values were not wholly satisfactory. Hydrogen atoms were included in calculated positions and geometrically constrained in the refinement.

There were several large peaks (to 4.8 e Å^{-3}) outstanding in the final difference map, but these were all close to the W and I atoms.

Crystal Structure Analysis of Complex **11**, $[WI_2(CO)_2\{MeS(CH_2)_2S(CH_2)_2SMe\text{-}S,S',S''\}]$.—*Crystal data.* $C_8H_{14}I_2O_2S_3W$, $M = 676.0$, monoclinic, space group $P2_1/n$ (equivalent to no. 14), $a = 8.0426(6)$, $b = 12.7087(8)$, $c = 15.369(2)$ Å, $\beta = 100.395(7)°$, $U = 1545.1$ Å^3, $Z = 4$, $D_c = 2.906$ g cm^{-3}, $F(000) = 1224$, μ(Mo-Kα) = 119.7 cm^{-1}.

One red-brown plate *ca.* 0.06 × 0.12 × 0.37 mm was mounted on a glass fibre in air. A similar procedure of examination, diffractometry and analysis was followed as for compound **4**. Accurate cell dimensions were refined using reflections having θ = 8–10°. Intensities of 2712 independent reflections (2279 with $I > 2\sigma_I$) with $\theta_{max} = 25°$ were recorded and corrected for Lorentz-polarisation effects, absorption (by ψ-scan methods) and to eliminate negative net intensities; a correction for slight crystal deterioration (3.3% overall) was also applied.

In the refinement all non-hydrogen atoms were allowed anisotropic thermal parameters. Hydrogen atoms of methylene groups were included in calculated positions; those in methyl groups were refined with geometrical restraints; the U_{iso} thermal parameters of all were refined freely. At convergence, $R = 0.038$ and $R_g = 0.039$[38] for 2708 reflections (all but four low-angle planes) weighted $w = (\sigma_F^2 + 0.000\,26F^2)^{-1}$. There was nothing above the noise level (*ca.* 1.0 e Å^{-3}) in the final difference map.

For both analyses, scattering factor curves for neutral atoms were taken from ref. 39. Computer programs used in the analyses have been noted above and in Table 4 of ref. 40, and were run on the MicroVAX II computer in the Nitrogen Fixation Laboratory.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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