# **862.** *Some Sulphide Carbonyl Complexes of Chromium, Molybdenum, Tungsten, and Manganese.*

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Reaction of 2,5-dithiahexane and 3,6,9-trithiaundecane with hexacarbonyl-chromium, -molybdenum, and -tungsten and the bromopentacarbonylmanganese have been studied and the products described. Reaction of the tetracarbonyl-2,5-dithiahexane-molybdenum and -tungsten with iodine and bromine affords seven-co-ordinate dihalogenotricarbonyl complexes.

REPLACEMENT of carbon monoxide groups of the hexacarbonyl-chromium, -molybdenum, or tungsten[1,2] and of bromopentacarbonylmanganese[2] by ligands containing donor nitrogen, phosphorus, etc., atoms is well known. A few complexes of Group VI elements with donor sulphur ligands have been reported[3] which were of the type $L_3Me(CO)_3$, where $L = Me_2S$, $Et_2S$, $[CH_2]_4{>}S$, or thiourea; these compounds were obtained by displacement of the hydrocarbon ligand from tricarbonylcycloheptatrienemolybdenum by the method of Abel *et al.*[2b] No similar manganese compounds appear to exist, although a sulphur-bridged dimer $[C_6H_5SMn(CO)_4]_2$ has been reported;[4] similar, presumably bridged, polymeric materials $[C_6H_5SMo(CO)_2py]_n$ have also been made.[5]

We have now prepared a number of air-stable, well-crystallised compounds by direct reaction of 2,5-dithiahexane and of 3,6,9-trithiaundecane with hexacarbonyl-chromium, -molybdenum, and -tungsten and with bromopentacarbonylmanganese.

A comparison of the infrared spectra in the metal–carbonyl stretching region of the sulphur donor complexes with the spectra of corresponding complexes with other ligands[2] shows that the frequencies lie at slightly lower wave numbers than those of triphenylphosphine compounds. However, comparison with the more closely related carbonyl complexes with the ligand $Et_2P{\cdot}CH_2{\cdot}CH_2{\cdot}PEt_2$[6] shows a partially reversed trend, while other studies[7] on the infrared carbonyl frequencies of phosphorus, arsenic, and sulphur donor complexes have shown no systematic differences except that the sulphur complexes often have carbonyl frequencies slightly lower than those of the arsenic ones. The only conclusion that can be drawn, which is also that drawn by Cotton and Zingales,[3] is that the $\pi$-bonding ability of alkyl sulphides is similar to that of related phosphine or arsine donor ligands.

(*A*) *Group* VI *Complexes*.—(*a*) 2,5-*Dithiahexane*. The carbonyls react at *ca.* 160° with

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[1] For references see Nigam, Nyholm, and Stiddard, *J.*, 1960, 1806.

[2] (*a*) Abel and Wilkinson, *J.*, 1959, 1501; (*b*) Abel, Bennett, and Wilkinson, *J.*, 1959, 2323.

[3] Cotton and Zingales, *Inorg. Chem.*, 1962, **1**, 145.

[4] Hieber and Schropp, *Z. Naturforsch.*, 1959, **14**b, 460.

[5] Hieber and Scharfenberg, *Ber.*, 1940, **73**, 1021.

[6] Chatt and Watson, *J.*, 1961, 4980.

[7] Bouquet and Bigorgne, *Bull. Soc. chim. France*, 1962, 433.

this ligand, and yellow crystalline products $LM(CO)_4$ can be isolated. The infrared spectra of the compounds have bands typical of octahedral *cis*-tetracarbonyls. They also have peaks characteristic of the gauche form of 2,5-dithiahexane, which is found in the pure liquid ligand together with the extended form, although the latter occurs exclusively in the solid state.[8] The sulphur ligand in the chromium compound can be replaced in light petroleum at *ca.* 110° by norbornadiene (2 hr.) and in the chromium, molybdenum, and tungsten compounds by triphenylphosphine, giving products identical with those described previously.[2b,9]

The tetracarbonyls react readily at room temperature with bromine and iodine, and with the molybdenum and tungsten compounds air-stable orange products are formed, *e.g.*:

$$LW(CO)_4 + I_2 = LW(CO)_3I_2 + CO$$

These compounds are non-conducting in nitrobenzene and can be formulated as seven-co-ordinate complexes similar to those characterised with a chelate diarsine ligand.[1] In the reaction of the tetracarbonylchromium compound with iodine, carbon monoxide was lost and the infrared spectra of the brick-red reaction solution (in methylene chloride) in the carbonyl region was similar to that of the molybdenum and tungsten seven-co-ordinate complexes; the chromium solution decomposed within an hour and attempts to isolate a complex failed. Tetracarbonyl-2,5-dithiahexane molybdenum also reacted at once with chlorine in an inert solvent, to yield an intensely emerald-green oil; this too was unstable and could not be purified.

The halogenotricarbonyl-molybdenum and -tungsten compounds, with lithium aluminium hydride in tetrahydrofuran, give pale yellow solutions evidently containing species with metal–hydrogen bonds since the high-resolution nuclear magnetic resonance spectrum of the tungsten solution shows peaks at $\tau$ 15·41 and 19·57; we have failed to isolate pure compound from these air-sensitive solutions. When the residual products of these reactions are worked up after exposure to air, by chromatography on alumina, in addition to the original tetracarbonyl (which must be formed through carbon monoxide transfer) there appear to be small amounts of a second product. This has proved very difficult to characterise with certainty; analytical data suggest a tricarbonyl $LM(CO)_3$, but such a formulation seems doubtful as no five-co-ordinate zerovalent Group VI compound is known as yet.

Di-iodotricarbonyl 2,5-dithiahexanetungsten decomposes completely above 135° or, in 2,2′-dimethoxydiethyl ether (diglyme) in a sealed tube, above 180°. However, the molybdenum analogue partially decomposes in solution at temperatures as low as 40°, to give a binuclear complex $[LMo(CO)_2I]_2$ which can be obtained by extraction of the evaporated reaction mixture with chloroform. Although this dimer has an infrared band at 1865 $cm.^{-1}$ it is probably an iodide-bridged complex and it readily undergoes cleavage with, for example, *p*-toluidine. The products of these reactions are complex and could not be characterised; similar trouble with sulphur ligands has been noted.[10]

(*b*) 3,6,9-*Trithiaundecane.* No complex of this sulphur ligand appears to have been made previously. This potentially tridentate ligand can also act as a bidentate one, and such behaviour can readily be detected by the interaction of the non-co-ordinated sulphur atom and methyl iodide to form the sulphonium salt (cf. the manganese compound below).

The ligand does not react with hexacarbonyltungsten below 170° and above this temperature complete decomposition occurs. With hexacarbonyl-chromium or -molybdenum crystalline products $LM(CO)_3$, where the ligand functions as tridentate, are obtained. The infrared spectra of these compounds are consistent with the three carbon monoxide groups in mutually *cis*-positions,[1,2] since there are two intense peaks in the carbonyl region. Although these tricarbonyls react with iodine and new peaks then appear in the

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[8] Sweeney, Mizoshima, and Quagliano, *J. Amer. Chem. Soc.*, 1955, **77**, 6521.
[9] Hieber and Peterhaus, *Z. Naturforsch.*, 1959, **14b**, 462.
[10] Cf. Chatt and Venanzi, *J.*, 1957, 2445.

carbonyl stretching region of the spectra, we have been unable to isolate any stable carbonyl iodide complex.

(*B*) *Manganese Complexes*.—Well-defined, air-stable complexes are obtained by reaction of both sulphides with bromopentacarbonylmanganese; the same products are obtained if the tetracarbonyl dimer $[Mn(CO)_4Br]_2$ is used. Decacarbonyldimanganese itself also reacts with the ligands, but rather slowly and only at 120°; the products are unstable and we have been unable to characterise them. The pentacarbonyl bromide also reacts with thiourea but the rose-red product is obtained only in low yield and could be characterised only by its infrared spectrum; the bromide does not react with the compound $(Me_2P{\cdot}S{\cdot})_2$ at temperatures up to 150°.

Bromotricarbonyl-2,5-dithiahexanemanganese appears to be a normal stable octahedral complex, is a non-conductor in nitrobenzene, and is monomeric.

Bromotricarbonyl-3,6,9-trithiaundecanemanganese, which is formed from the reactants essentially quantitatively, is a deep-red viscous oil and a non-conductor in nitrobenzene. Since a seven-co-ordinate manganese(I) complex is improbable, the ligand must be here bidentate, and indeed the compound forms a sulphonium salt with methyl iodide and (in diglyme) also absorbs diborane to give an adduct; the latter adduct is air-sensitive and the red oil can be recovered from the hydrolysed product.

## EXPERIMENTAL

Microanalyses and molecular weights (ebullioscopic in benzene) were made by the Microanalytical Laboratory, Imperial College.

2,5-Dithiahexane (L. Light and Co.) was used without special purification. 3,6,9-Trithiaundecane was obtained by the method of Helferich and Reid [11] and was distilled twice under reduced pressure, the fraction of b. p. 152—155°/10 mm. being collected.

The reactions were carried out under nitrogen.

Some properties of the *compounds* prepared and their analyses are given in the Table.

Sulphur ligand complexes.

| | | Found (%) | | | | | | Required (%) | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Compound | M. p. | C | H | O | Hal | M | *M* | C | H | O | Hal | M | *M* |
| L = 2,5-*Dithiahexane* | | | | | | | | | | | | | |
| $LCr(CO)_4$ [a] | 130° † | 33·8 | 3·8 | 22·4 | — | 18·2 | 285 | 33·5 | 3·5 | 22·3 | — | 18·2 | 286 |
| $LMo(CO)_4$ [b] | 148 † | 29·5 | 3·3 | 29·2 | — | 19·5 | 339 | 29·1 | 3·2 | 29·1 | — | 19·4 | 330 |
| $LW(CO)_4$ [c] | 160 † | 23·5 | 2·7 | 15·8 | — | 43·5 | — | 23·0 | 2·4 | 15·3 | — | 43·9 | — |
| $LMo(CO)_3I_2$ [d] | 40 † | 15·3 | 1·9 | 8·8 | 43·5 | 17·5 | 506 * | 15·1 | 1·8 | 8·6 | 45·5 | 17·2 | 556 |
| $LMo(CO)_3Br_2$ [e] | 125 † | 17·7 | 2·2 | 10·4 | 34·5 | 21·0 | 478 | 18·2 | 2·2 | 10·4 | 34·6 | 20·8 | 462 |
| $LW(CO)_3I_2$ [f] | 135 † | 13·3 | 1·8 | 7·2 | 39·7 | — | 631 | 13·1 | 1·6 | 7·5 | 39·4 | — | 644 |
| $LW(CO)_3Br_2$ [e] | 145 † | 15·5 | 2·0 | 8·9 | 28·5 | — | — | 15·3 | 1·8 | 8·7 | 29·1 | — | — |
| $[LMo(CO)_2I]_2$ [g] | 85 † | 17·6 | 2·5 | 8·2 | 31·7 | 24·3 | 795 | 18·0 | 2·5 | 8·0 | 31·6 | 23·9 | 802 |
| $LMn(CO)_3Br$ [e] | 135—136 | 24·6 | 3·1 | 13·7 | 23·5 | — | 345 | 24·7 | 3·0 | 14·1 | 23·4 | — | 341 |
| L = 3,6,9-*Trithiaundecane* | | | | | | | | | | | | | |
| $LCr(CO)_3$ [b] | 130 † | 38·1 | 5·2 | 14·0 | — | — | 345 | 38·1 | 5·2 | 13·8 | — | — | 347 |
| $LMo(CO)_3$ [h] | 145 † | 33·4 | 4·6 | 12·2 | — | 24·3 | 378 | 33·8 | 4·6 | 12·3 | — | 24·5 | 390 |
| $LMn(CO)_3Br$ [i] | Oil | 31·7 | 4·3 | 11·3 | 19·0 | 12·6 | 442 | 31·6 | 4·2 | 11·2 | 18·6 | 12·8 | 429 |

* Isopiestic, in tetrahydrofuran. † With decomp.

[a] Bright yellow. [b] Yellow. [c] Pale yellow. [d] Dark orange. [e] Orange. [f] Pale orange. [g] Red-brown. [h] Off-white. [i] Deep red.

Infrared spectra were taken on a Perkin–Elmer model 21 instrument, and nuclear magnetic resonance measurements on a Varian instrument at 56·45 Mc./sec. The latter, in chloroform solution, show very little difference between 2,5-dithiahexane [$\tau$ 7·85 ($CH_3$), 7·28 ($CH_2$)] and

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[11] Helferich and Reid, *J. Amer. Chem. Soc.*, 1920, **42**, 1224.

the co-ordinated ligand in $LM(CO)_4$ (Cr: $\tau$ 7·65, 7·35; Mo: 7·56, 7·26). 3,6,9-Trithiaundecane (in $CCl_4$) gave $\tau$ 8·65, triplet (end $CH_3$), 7·49, quadruplet (ethyl group $CH_2$), 7·33, complex (bridge $CH_2$): the complexes $LMo(CO)_3$ gave $\tau$ 8·59, asymmetric triplet (separation 7·25 c./sec.), a partly obscured quadruplet, *ca.* 7·45 (separation 7 c./sec.) and 7·30 (unresolved).

*Tetracarbonyl*-2,5-*dithiahexane-chromium, -molybdenum, and -tungsten.*—The hexacarbonyl (*ca.* 1·5 g.) was heated with an excess of the ligand (*ca.* 5 ml.) at 150—165° until gas evolution ceased. After cooling, the solid was removed, unchanged carbonyl sublimed in a vacuum at 70°, and the residue crystallised from chloroform. Yields were *ca.* 65% for Cr, 43% for Mo, 26% for W, based on the hexacarbonyl. The chromium and the molybdenum compound are soluble in chloroform, acetone, and benzene but sparingly soluble in light petroleum. The tungsten compound is less soluble and is best crystallised from acetone. Infrared maxima were: (Cr) 2020m, 1914s, 1898s, 1869s ($CHCl_3$, $CaF_2$); (Mo) 2030s, 1919s, 1905s, 1868s ($CHCl_3$, $CaF_2$); (W) 2023s, 1910s, 1896s, 1867m ($CHCl_3$, $CaF_2$). The remainder of the spectrum is essentially similar in all three compounds; in mulls with sodium chloride and calcium fluoride optics for the chromium compound the bands are at 2929m (2025s, 1906s, 1888ms, 1845s, CO stretches), 1433w, 1421w, 1412w, 1317w, 1160w, 1024w, 967m, 833w, 681w, 643m.

*Di-iodotricarbonyl*-2,5-*dithiahexane-molybdenum and -tungsten.*—To the tetracarbonyls (*ca.* 1 g.) in benzene (50 ml.) was added slowly with stirring a benzene solution (100 ml.) of slightly less than the stoicheiometric amount of iodine. On removal of solvent, deep orange crystals of *di-iodide* separated. These were recrystallised from benzene, chloroform, or acetone. Yields were *ca.* 85%. Infrared maxima were at: (Mo) 2040s, 1988sh, 1960s ($CS_2$, NaCl); (W) 2033m, 1943s, 1906w, ($CS_2$, NaCl), and 2037, 1948, 1910s (hexachlorobutadiene, NaCl).

The *bromides* were prepared similarly. They decompose more readily than the iodides on recrystallisation, but the products obtained directly from the reaction mixtures appear to be quite pure. Infrared maxima were at: (Mo) 2044m, 1990sh, 1955m ($CS_2$, NaCl), and 2060s, 1989, 1930 (Nujol, NaCl); (W) 2054s, 1976s, 1912s (Nujol, NaCl).

The iodides and bromides undergo some decomposition in chloroform, methylene chloride, or acetone, as shown by changes in the infrared spectra over short periods of time. There appears to be no decomposition in carbon disulphide or in benzene (which is the only practicable solvent for the bromides).

*Bis(iododicarbonyl*-2,5-*dithiahexanemolybdenum).*—A benzene solution (15 ml.) of the di-iodotricarbonyl (*ca.* 8 g.) was refluxed for 2 hr. The solution was filtered and the residue extracted with several portions (50 ml. each) of cold chloroform until the filtrate was light red-brown. The residue was crystallised from chloroform (yield *ca.* 25%). Infrared maxima were at 2000m, 1945m, 1866m ($CHCl_3$, NaCl).

*Tricarbonyl*-3,6,9-*trithiaundecanechromium.*—The hexacarbonyl (2·8 g.) and the ligand (3 ml.) were refluxed in light petroleum (b. p. 100—120°; 20 ml.) for 3 hr. The deep yellow crystals which separated on cooling were washed with light petroleum (b. p. 30—40°) and unchanged hexacarbonyl was sublimed from the residue in a vacuum at 60°. Extraction with *cold* benzene (4 × 5 ml.) removed some yellow oily impurity and the residual *complex* was then crystallised from benzene (yield, *ca.* 50% based on hexacarbonyl). Infrared maxima were at 1932s, 1818s ($CH_2Cl_2$, $CaF_2$), and 2954w, 2925w, 1907s, 1790s, 1409m, 1285w, 1248w, 1164m, 1123m, 1050m, 972m, 911m, 830s, 771m, 760m, 688m, 660w (mulls, NaCl).

*Tricarbonyl*-3,6,9-*trithiaundecanemolybdenum.*—The hexacarbonyl (1 g.) and ligand (0·7 ml.) were refluxed in light petroleum (b. p. 100—120°; 5 ml.) for 2 hr. On cooling, two liquid phases separated. The upper layer was removed and the lower oily layer treated with small portions of ether to precipitate off-white crystals of the *complex*. These recrystallised from 1 : 1 chloroform–light petroleum (b. p. 30—40°) and had $\nu_{max.}$ 1932s, 1812s ($CH_2Cl_2$, NaCl).

*Bromotricarbonyl*-2,5-*dithiahexamanganese.*—The pentacarbonyl bromide (1 g.) was heated with an excess of 2,5-dithiahexane (*ca.* 3 ml.) at 75° for 30 min. The orange solid obtained on cooling was collected and washed with light petroleum (b. p. 40—60°); traces of solvent and unchanged starting materials were removed in a vacuum at 90° and the residue crystallised from ether. The yield was *ca.* 90% based on $Mn(CO)_5Br$. The *compound* is very soluble in chloroform and moderately soluble in ether and light petroleum and has $\nu_{max.}$ 2052s, 1970s, 1922s ($CHCl_3$, NaCl), and 2926w, 1430s, 1328m, 1250w, 1122w, 1024w, 972s, 840m, 670m (mulls in Nujol and hexachlorobutadiene, NaCl).

*Bromotricarbonyl*-3,6,9-*trithiaundecanemanganese.*—A mixture of the compound $Mn(CO)_5Br$ (2·5 g.) and the ligand (3 ml.) in light petroleum (b. p. 100—120°; 15 ml.) was heated at 100°

for 1 hr. The heavy red oil that separated was removed and purified by chromatography on alumina with ether as eluant. The solvent was removed under a high vacuum at room temperature [yield, *ca.* 90% based on $Mn(CO)_5Br$]. Infrared maxima were at 2046s, 1965s, 1920s ($CH_2Cl_2$, NaCl). 380 mg. (0·887 mmole) of the *compound* in diglyme (2·5 ml.) absorbed 0·305 mmole of diborane, corresponding to 70% of the theoretical amount required for one unco-ordinated sulphur atom.

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