SULPHUR COMPLEXES OF METAL CARBONYLS, HALIDES AND CARBONYL HALIDES

A Thesis submitted

by

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ABSTRACT.

A series of bi- and tridentate sulphur complexes with the Group VI metal hexacarbonyls has been prepared. Carbonyl halide derivatives of these sulphur carbonyl complexes have been obtained. The tricarbonyl dihalides of molybdenum and tungsten are most probably seven-coordinated. With the exception of two tricarbonyls of tungsten, which could possibly be five-coordinated, all the carbonyls isolated were six-coordinated. A complex of uranium tetrachloride and 2,5-dithiahexane seems to be the first oxygen-free sulphur complex of uranium reported so far.

The following sulphur ligands were used successfully : 2,5-dithiahexane, 1,4-dithian and 3,6,9-trithiaundecane. The bidentate 2,5-dithiahexane, which is known to be present in its gauche form in metal halide complexes prepared earlier, was found to form mononuclear chelated complexes with the metal carbonyls also, and the ligand was present in its gauche form judging from infra red spectra. The bidentate 1,4-dithian was found to give dinuclear, non-chelated complexes. Geometric calculations showed that the ligand is much more likely to be present in a slightly distorted asymmetric boat form in these complexes than in the chair form, a conformation preferred by this ligand in its solid and gaseous state. 3,6,9-trithiaundecane acted as a tri- and bi-dentate ligand,

forming mononuclear tricarbonyls with the Group VI metal hexacarbonyls.

Manganese pentacarbonyl formed unstable complexes with the ligands mentioned. However, air stable six-coordinated tricarbonyl bromide complexes could be obtained from the reaction of 2,5-dithiahexane or 1,4-dithian with either manganese pentacarbonyl bromide or the tetracarbonyl dibromide. 3,6,9-trithiaundecane acted as a bidentate ligand with manganese pentacarbonyl bromide and the reaction product formed an adduct with B_2H_6 corresponding to one uncoordinated sulphur atom.

Infra red spectra of all and nuclear magnetic resonance spectra of many of the complexes are given and discussed.

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INTRODUCTION.

General.

Many metal complexes containing sulphur are known. For instance, compounds with the sulphur in the form of sulphide, thiocyanate, mercaptan, di- and poly-sulphide, or trithiocarbonate have been used as ligands. Sulphur atoms linked by two carbon atoms and present in a suitable configuration have been shown to be good chelating agents.[1,2,3]

Most sulphur complexes known so far are derived from metal halides. A great number of mercuric chloride complexes with sulphur compounds have been prepared as characterising derivatives. Sulphur complexes with platinum metal halides have also been suggested for identification purposes, as they have well-defined melting points.[4] Among the work with transition metals it is also worth mentioning the publications by Livingstone concerning sulphur complexes of nickel, palladium, and platinum.[5]

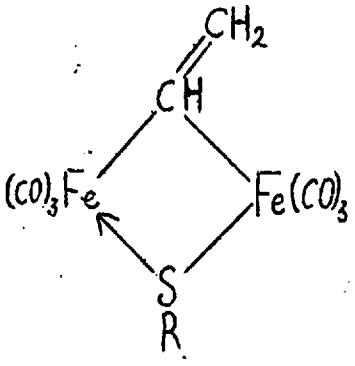
Fewer complexes of metal carbonyls with sulphur ligands have been prepared. Most of the work on metal carbonyls concerns ligands such as As, N, Sb, P, and CNR and a review of the field has been presented by Nigam

et al.[6a] Most of the earliest work on sulphur containing metal carbonyls or carbonyl halides was done by Hieber and his coworkers, who prepared a number of iron carbonyl complexes with the ligands thiophenol, mercaptobenzothiazole, thiosemicarbazide, thionaphtol, and methyl- and ethyl sulphide.[7,8,9] A thiophenol complex of cobalt carbonyl was also obtained. The only compound reported with a group VI metal carbonyl was $C_6H_5S\ Mo(CO)_2\ py$, a brown powder of unknown molecular weight, which formed by reaction between tris-pyridine molybdenum tricarbonyl and thiophenol.[9]

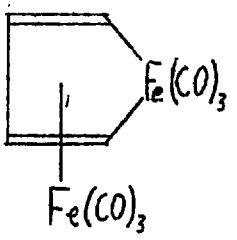
More recently Hieber and Schropp[10] have prepared the sulphur bridged complex $(CO)_4Mn(PhS)Mn\ (CO)_4$ and Hieber and Beck[11] obtained compounds with the general formula $(M(CO)_3X)_2$, where M = Fe or Co and X = S, Se, SC_2H_5 , or SC_6H_5. Cotton and Zingales[12] prepared three molybdenum complexes L Mo $(CO)_3$, where L = $(CH_3)_2S$, $(CH_2)_4S$, or $(NH_2)_2CS$ by allowing tropylidine molybdenum tricarbonyl to react with these sulphur ligands according to the method of Abel, Bennett, and Wilkinson.[13] These complexes and the thiophenol compound reported by Hieber[9] seem to be the only group VI metal carbonyls with sulphur ligands known prior to this work.

During the reaction of metal carbonyls with sulphur ligands rupture of the C-S bond sometimes takes place. Morgan and Ledbury[1] noticed very early that

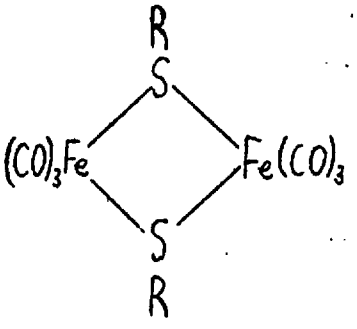
the reaction between thallium hydroxide and thiophene produced Tl_2S and $OH(CH=CH)_2OH$. The work by King et al.[14] with vinyl sulphides and iron dodecacarbonyl often gave volatile complexes of the type $(RSCH=CH)Fe_2(CO)_6$ (I) and (II), and Hieber and Scharfenberg[9] obtained complexes like (III) from dialkyl sulphides.



(I)



(II)

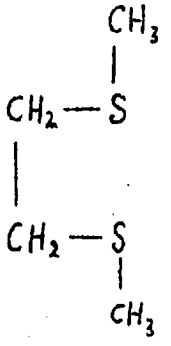


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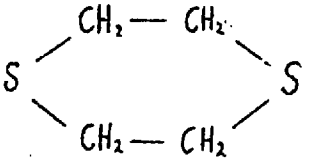
It has also been shown by Kaesz et al.[15] that the main product after reaction of iron carbonyls and thiophene is (II). The desulphurisatiom has not been found to take place during reactions with the group VI metal carbonyls, or with manganese carbonyl bromides during the work presented in this thesis. The work dome here with irom carbonyls gave unsatisfactory results, so that nothing definite can be said about the desulphurisation effect on the ligands used. In all reaction products sulphur was present, but the method of quantitative sulphur analysis used was not satisfactory and the sulphur contents was found by difference.

In this thesis stable bi- and tridentate sulphur complexes with the group VI metal carbonyls, manganese carbonyl bromides and uranium tetrachloride are described. The ligands were of different types. The bidentate ligand 2,5-dithiahexane (IV) occurs in its extended and in its gauche form in the liquid state,[16] but as the S-S distance in the gauche form is suitable for chelation in octahedral complexes of the metals used, it was found to give mononuclear complexes only and with the ligand in the gauche form judging from infra red spectra. The bidentate ligand 1,4-dithian (V) formed dinuclear non-chelated complexes. Although it is known from X-ray and electron diffraction studies that this compound exists in its chair form in its solid and gaseous states,[17a,b] calculations of the geometry of the possible complexes makes the slightly distorted asymmetric boat form seem much more likely to be present after coordination. In models and from calculations it is seen that the 1,4-dithian molecule in these complexes is unlikely to adopt a chair conformation, as this involves very close approach of certain protons of the sulphur ligand molecules on opposite sides of the complex. The potentially tridentate ligand 3,6,9-trithiaundecane (VI) has been found to function as such, although there is infra red indication of bicoordinated complexes being present probably as inter-

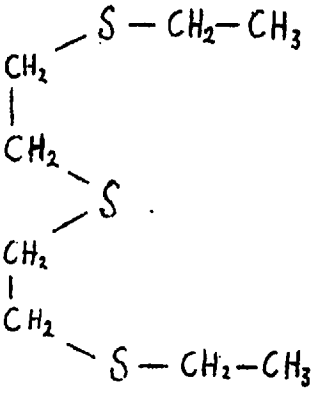
mediates.



(IV)

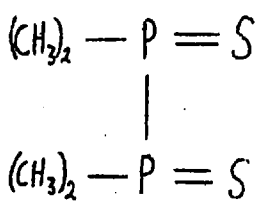


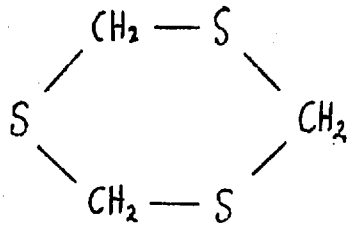
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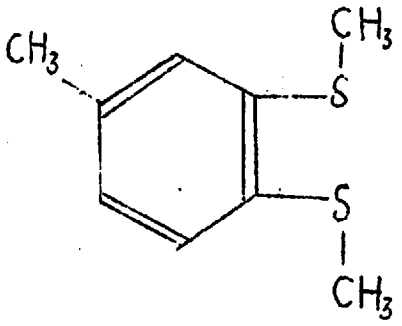


(VI)

Among other sulphur ligands tried with less or no success were tetramethyl biphosphine disulphide (VII) and trithioformaldehyde(VIII), but in the case of the former the S-S distance is rather larger than that needed to form octahedral complexes of chromium, molybdenum, tungsten, or manganese. Possibly further work with uranium or other larger metal atoms would be more satisfactory. Trithioformaldehyde, which gives complexes with some of the platinum metals, reacted with molybdenum hexacarbonyl, but the reaction product could not be purified. An iron complex with toluene 3,4-dimethyl thioether (IX) was obtained, but the reaction products of this ligand and the carbonyls of nickel or molybdenum were obtained in very small yields. As this ligand was more expensive than other suitable ligands available, the work was not pursued further.







(VII) (VIII) (IX)

It is well known from the results of preparative chemistry that complexes containing chelate rings are more stable than similar non-chelated compounds, the stabilising effect being greatest when a five-membered ring is formed. It is thus to be expected that the complexes of 2,5-dithiahexane and 3,6,9-trithiaundecane should be more stable than those of 1,4-dithian, which acted as a bidentate non-chelating ligand. This has indeed been found for the complexes prepared as far as chemical stability is concerned, the difference in the thermostability being less pronounced.

The chelate effect is known to be an entropy phenomenon. When a bidentate chelating ligand replaces a monodentate ligand, there will be a change in the number of freely moving bodies and thus a change in the translational entropy. The chelate effect should thus be

independent of the bond strength between metal and ligand and this has been found to be the case. Schwarzenbach[18] has derived equations for some specially chosen complexes in order to establish the approximate magnitude of this entropy effect, which is very difficult to determine by direct measurements of the quantities ΔH and $T\Delta S$ required in the equation $\Delta G = -RT \ln k = \Delta H - T\Delta S$. Direct measurement of the equilibrium constants has turned out to be more satisfactory, as can be seen from table 1 taken from Bjerrum's work with nitrogen ligands. The table also shows that the chelate effect is greater for a five-membered than for a six-membered ring.

Table 1.

Chelate effect for some metal ions with nitrogen ligands.[19]

log k for complex formation	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}	Cd^{2+}
log k M A	2.08	2.77	4.17	2.31	2.62
log k M A_2	1.60	2.22	3.51	2.38	2.07
log k M en	5.99	7.77	10.73	5.92	5.63
log k M pen	-	6.38	9.80	-	-
Chelate effect					
of en :	2.31	2.78	3.05	1.23	0.94
of pen :		1.39	2.10		

A = monodentate ligand, en = ethylenediamine, pen = propylenediamine.

An explanation of the stability of a chelated complex is the simple one that if one of the two

coordinating linkages is broken, the other can keep the coordinating atom near the central atom until the broken bond is reformed. This explanation has been supported by experiments using radioactive tracers.

In the dinuclear 1,4-dithian complexes it is also possible that a small amount of stabilisation could be derived from the slightly increased ease of reformation of the fourth metal-sulphur bond, although this effect must be much smaller than the corresponding one for a 2,5-dithiahexane metal carbonyl complex.

Generally speaking there is no uniform pattern of coordinating affinities of all ligand atoms for all acceptor molecules and ions, or even for simple alkyls of ligands like PR_3 or R_2S. Rather, their relative affinities depend on the acceptor concerned.[20] For instance, the alkyls of the group VI ligands have the following tendencies towards trimethyl gallium : $O > S < Se > Te$, with platinum II the order is changed to be : $O \ll S < Se < Te$. Schwarzenbach et al.[21] have studied the relative stabilities of multidentate complexes of N, O, and S in the molecule $(HO_2C\ CH_2)_2N(CH_2)_2\ X\ (CH_2)_2\ N(CH_2CO_2H)_2$ where X = N, O, or S. In the case of the alkaline earth metal ions the order of stability was found to be : $O > N > S$. With Cu, Cd, and transition metal ions with nearly filled orbitals the order changed to : $N > S > O$.

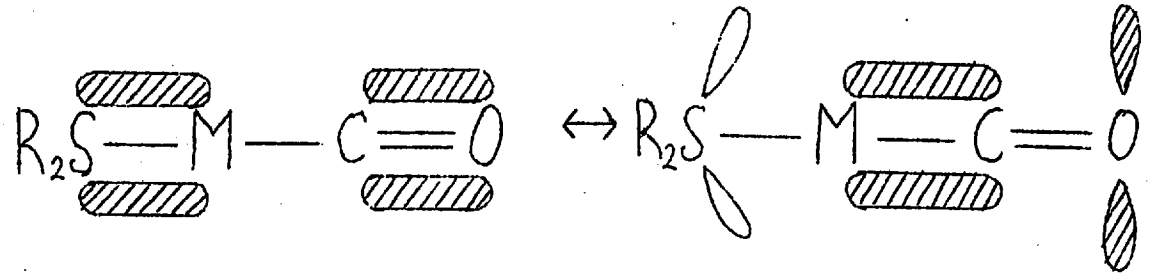
However, there are two regular features concerning ligand affinities. The metals and metal ions can be divided into two classes of ligand acceptors :
a) those which form their most stable complexes with the first ligand atom of each Group, i.e. with N, O, and F.
b) those which form their most stable complexes with the second or a subsequent ligand atom.

Most metals in their common valency states belong to class a). The acceptors of class b), which are less numerous, are almost all found among a number of neighbouring elements occupying an area of more or less triangular shape in the Periodic Table. The base of this triangle stretches in the sixth period from about tungsten to polonium with its apex at Cu. (Cf. Plate 1, p 11).

As can be seen most of the metals investigated in this thesis belong to the border region between class a) and class b) acceptors. Chromium, which is a class a) acceptor with less affinity for sulphur than for oxygen, gave stable carbonyl complexes with the chelating ligands, but no carbonyl iodide complexes containing sulphur could be isolated. The reaction between chromium carbonyl complexes and fluorine has not been investigated.

When sulphur acts as a ligand with a class b) acceptor metal, the σ-bond formed by donation of a pair of electrons from the sulphur to the metal is strengthened

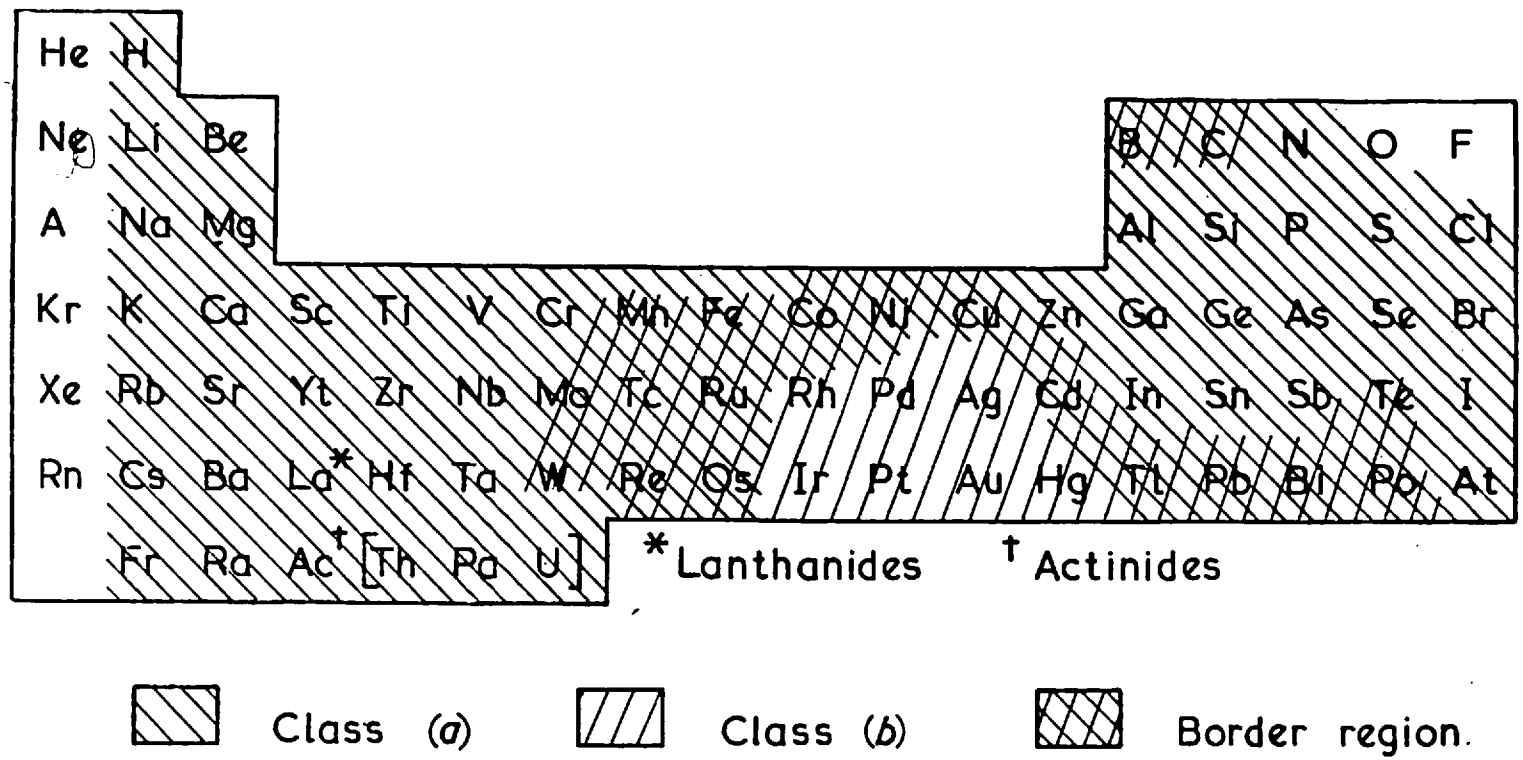
by dative π-bonding from filled d-orbitals on the metal to unfilled d-orbitals on the sulphur. In a metal carbonyl complex there can be competition between the unfilled 3 d-orbitals on the sulphur and the 2 p-orbitals on the carbon atoms belonging to the carbonyl groups for the d-electroms on the metal, which are used for π-bonding. The two possible extreme structures are shown in fig. X, where shaded orbitals are filled, unshaded are unfilled.



X.

It would then be expected that a ligand with strong π-bonding ability would impart more triple bond character to the C-O bond and cause an increase in the carbonyl frequencies in the infra red spectrum. Judging from the results of Cotton and Zingales[12] and comparing the results obtained in this thesis to those of Nigam et al. [6a] sulphur should have a somewhat smaller π-bonding ability than phosphorous, arsenic, and antimon when coordinated to Group VI metal carbonyls. On the other hand, a comparison of the carbonyl frequencies of

Plate 1. *Classification of acceptor atoms in their normal-valent states*[20]



the 2,5-dithiahexane group VI metal carbonyls with those found for phosphorous complexes derived from the very similar ligand $CH_3CH_2P(CH_2)_2PCH_2CH_3$[25] shows little difference or even a reversed trend. Bouquet and Bigorgne[60] found little difference in the carbonyl frequencies of diethyl sulphide molybdenum carbonyls when comparing them to those of similar arsine and phosphine complexes. A close study of their results reveals, however, that the carbonyl frequencies of the sulphur carbonyl complexes are on the whole a little lower than those of the arsine analogues.

The π-bonding ability of a ligand is related to its capacity of directing a second substituent into its trans-position.[22,23] In the case of platinum metals monodentate ligands have been arranged in the order of increasing trans effect and double bonding in the following way :

$H_2O < OH < NH_3 \sim RNH_2 <$ pyridine $< Cl < Br < CNS < I \sim NO_2 \sim SO_3H \sim PR_3 \sim R_2S \sim SCNH_2 < NO \sim CO \sim C_2H_4 \sim CN$.[22]

According to Chatt et al.[23] the trans effect does not always bring about weakening of the bond opposite to a trans directing ligand. If this bond does not depend on dative π-bonding from the metal, the metal-ligand bond may actually become strengthened. As an example the two following reactions can be cited :

$$K(NH_3,PtCl_3) + C_2H_4 \longrightarrow \underline{cis}\ (NH_3,C_2H_4,PtCl_2) + KCl$$

$$K(C_2H_4,PtCl_3) + NH_3 \longrightarrow \underline{trans}\ (NH_3,C_2H_4,PtCl_2) + KCl$$

Since the nitrogen has no suitable orbitals to receive electrons from the metal it will be more strongly bound to the metal through the σ-bond electrons, as the electron affinity of the metal is increased by the π-bonding to the trans directing ligand. The electron withdrawal occurs mainly from the antinodes of the d-orbital most remote from the trans directing ligand; thus the Pt-N bond is most strengthoned, and the ethylene group enters into the cis-position. When the ethylene group directs the NH_3 group into the trans-position, the nucleophilic attack of the nitrogen atom will take place at the antinodes most remote from the ethylene group, that is where the electron density is most lowered.

Different metals transmit the trans effect to different degrees : platinum is a very good transmitter as there is a small energy difference between its 5 d and 6 s or 6 p orbitals; palladium is found to be less effective As most of the research has been done on the platinum metals, little is known about other metals. It would be expected by analogy with the research done that tungsten should transmit better than molybdenum or chromium. As most of this work deals with complexes where cis- or trans-positions are determined by geometric reasons not related to the trans effect, little can be said about the group VI metals or manganese as transmitters. However, when com-

plexes of the type $L_3M(CO)_3$ were formed from chromium and molybdenum with the tridentate ligand 3,6,9-trithiaundecane, the configuration most likely to arise considering the great trans directing effect of the carbonyl groups[24] seems to have been achieved, judging from the infra red carbonyl spectrum and considerations of symmetry properties. Complexes of the type $L_3Mo(CO)_3$ with similar infra red carbonyl spectra were obtained from monodentate phosphine, arsine, and stibine ligands by Abel et al.[13] As these complexes arose by replacement of cycloheptatriene, the geometry of the starting material may have been of importance. It is however, not possible to be sure of configurations adopted on the basis of infra red spectra alone. Dipole moment measurements and X-ray work would be needed for certainty.

When a bidentate sulphur ligand has replaced carbonyl groups, the remaining groups trans to the sulphur atoms should be more inert to nucleophilic attack, as they face less competition for the d-electrons of the metal. The entry of a second bidentate chelating ligand is thus made more difficult, for its second sulphur atom is trying to attach itself in a now deactivated position. As it is indicated by the infra red carbonyl frequencies that sulphur has a somewhat smaller π-bonding ability than arsenic, it is to be expected that the carbonyl groups trans to sulphur atoms are more inactivated than carbonyl groups trans to

arsenic. Thus it is not altogether surprising that no dicarbonyl derivatives analogous to the ones obtained from the Group VI hexacarbonyls with arsines by Nigam et al.[6a] could be obtained with 2,5-dithiahexane in similar conditions. Only tetracarbonyls and some tricarbonyl material possibly containing 5-coordinated complexes, which could not be fully characterised, were obtained.

The replacement of the last two carbonyls in a hexacarbonyl is even more difficult. Chatt and Watson[25] succeeded in making the complex Mo L_3, where L = ditertiary phosphine, but the replacement could not be made to take place directly as in the case of nickel carbonyl, where aromatic tertiary diphosphines replaced all carbonyl groups at 150°.[26] In order to get Mo L_3 dibenzene molybdenum was heated with the tertiary diphosphine in a sealed tube at 140° for 50 hours. Dibenzene chromium could not be made to react at all. It is possible that complexes with two or three bidentate chelating sulphur ligands attached to molybdenum could be obtained from dibenzene molybdenum in these conditions or at higher temperatures, but this approach has not been tried yet.

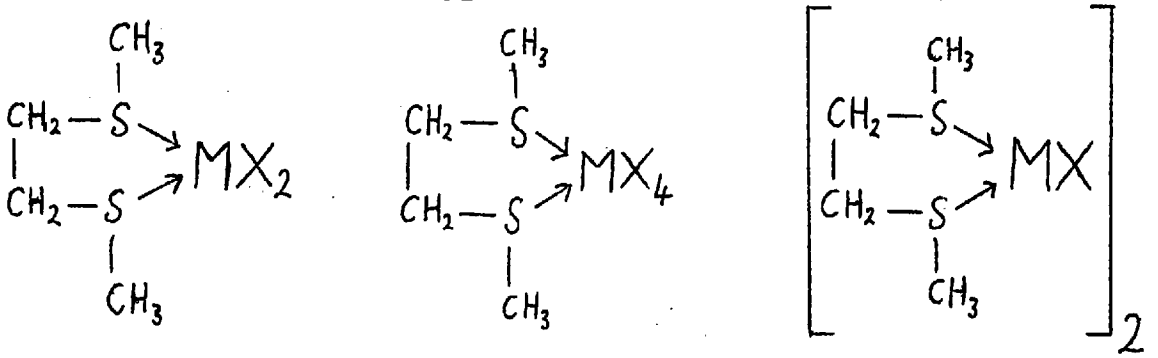
Stability and the course of replacement reactions do, however, not depend only on the degree of double bonding and steric strain. The fact that there is no universal pattern for complex formation shows that many

variables must be involved. The stabilisation energy of the crystal field of the ligands may make an important contribution, especially if a change in coordination number and configuration occurs in a replacement reaction. As is well known, the presence of different ligands affects the energy levels of the d-orbitals of a metal, causing energy differencies characteristic of the configuration of the complex. These energy levels have been determined spectrometrically. From maximum frequencies of symmetric complexes of Cu II, Co III, and Ni II the order of decreasing ligand effect has been found for these metal ions, and ligands have been arranged in the so called Fajans-Tsuchida series : $CN^{-1} > 1,10\text{-phenantroline} > NO_2 >$ ethylenediamine $> NH_3 > SCN^{-1} > H_2O > F^- > RCO_2^- > OH^- > Cl^- > Br^-$. The comparisons of complexes containing F^-, Br^-, NO_2^-, and CN^- depend both on interpretation of optical spectra and on lattice energy calculations. Not much has been done to determine thermodynamic values of complexes with these ligands from solution data and even less is known about complexes with ligands containing sulphur, phosphorous, and arsenic. Thus not much can be said quantitatively about the field strength of sulphur ligands until further work on spectra, lattice energies, and thermodynamics of sulphur complexes has been carried out.

2,5-DITHIAHEXANE COMPLEXES.

Earlier work on 2,5-dithiahexane.

The bidentate chelating sulphur ligand 2,5-dithiahexane, 1,2-dimethylthioethane, has been shown to form complexes of the type :



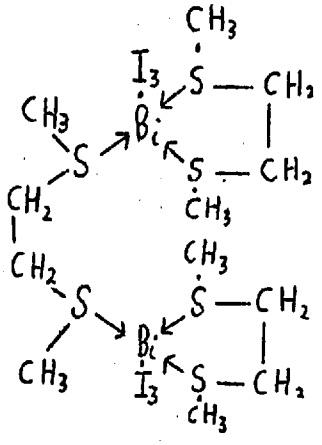
a b c

XII.

where X = Cl, Br, and I.[1] Since no molecular weights were reported, the possibility of di- or polymer formation can not be excluded. Different types of complexes were obtained depending on the metal halide. With M = Pd II, Zn II Cd II, and Hg II type a was formed, with Sn IV, type b. The halides of Cu II and Au I were believed to change their valencies to Cu I and Au III and give the suggested dimers of type c.

This ligand could also act as a bidentate, non-chelating ligand. With bismuth iodide Morgan and Ledbury[1] obtained a bright red crystalline solid, which analysed for a ligand to metal ratio of 3 : 2. They suggested structure d (cf. fig. XII) for the red crystals, which on

exposure to light or moisture relinquished two molecules of 2,5-dithiahexane to give a compound for which structure e (cf. fig. XII) was proposed. Determination of the molecular weight has not been done.



d. XII e.

The work by Backhouse et al.[3] on Ni II halides and 2,5-dithiahexane led to the formation of complexes like $Ni(chelate)_2(hal.)_2$. These compounds decomposed in water, ethanol, or acetone. Conductivity and magnetic susceptibility determinations indicated an octahedral configuration. Attempts to make complexes from higher valency states were unsuccessful. The 2,5-dithiahexane complexes were, however, more stable than those of the similar aromatic ligand toluene 3,4-dimethylthioether, which on reaction with nickel halides gave minute amounts of unstable complexes.

Some of the work by Morgan and Ledbury[1] was repeated by Bennett et al.[28], who prepared the two most stable 2,5-dithiahexane complexes from Pd Cl_2 and Hg I_2 in order to establish the presence of isomers with methyl groups cis or trans to the chelate ring. As it can be estimated from thermodynamic data that the energy required to move a methyl group from the cis to trans position is about 5 kcal./mole it is not surprising that only one compound could be isolated.

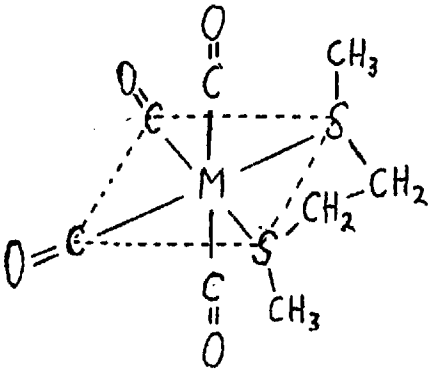
The complex $RS(CH_2)_2SR$ Pd Cl_2, where R = $CH_3C_6H_4$, had the special feature of adding one molecule of acetone or chloroform per metal atom on contact with these solvents. In this thesis recrystallisation of 2,5-dithiahexane complexes from these solvents never seemed to lead to this type of addition.

2,5-dithiahexane is known to exist in its gauche form in complexes judging from infra red spectra. Sweeney et al.[16] assigned two strong peaks at 735 and 728 cm^{-1} to the extended or trans form of the ligand, which showed these peaks in its liquid form together with peaks at 840, 900, 1010, and 1272 cm^{-1} attributed to the gauche form. In the solid state the ligand did not have this four last peaks. No infra red evidence of the eclipsed cis-form was reported. The cis-form is somewhat less stable because of proton interaction, which makes its presence less likely. The spectra are shown in Table 2.

Group VI metal complexes.

2,5-dithiahexane carbonyl complexes of chromium, molybdenum, and tungsten.

When 2,5-dithiahexane reacted with the hexacarbonyls of chromium, molybdenum, and tungsten in nitrogen atmosphere, carbon monoxide was evolved readily at 150° and only one type of complex was found in these reaction conditions. These yellow compounds are tetracarbonyls, which are most probably octahedral, as they are hexacoordinate monomers. The tungsten complex was too insoluble for molecular weight determination in benzene, but is assumed to be monomeric in analogy with the chromium and molybdenum complexes. Their proposed structure is shown in fig. XIII:



XIII.

This structure has C_{2v} symmetry and should give rise to four carbonyl stretching bands in the infra red, as was in fact observed for the complexes. (cf. table 2.)

The rest of the infra red spectra are shown in table 2. By comparison with the liquid and solid spectra of the ligand it is evident that the complexes are typical of the gauche form just as in the case of other metal halide complexes of this ligand.[16] The weak band at 900 cm^{-1} is not always visible, the 1010 cm^{-1} band is shifted about 15 cm^{-1} upwards and the 1272 cm^{-1} band is shifted as much downwards. The peaks in the region around 730 cm^{-1} are missing.

The distance between the two sulphur atoms of 2,5-dithiahexane in its gauche form has been calculated to be about 3.35 A, a distance which is suitable for a cis-configuration in an octahedral sulphur complex of chromium, molybdenum, or tungsten, where the distance between cis-positions ranges from about 3.1 to 3.3 A. The distance in the eclipsed cis-form of 2,5-dithiahexane is 2.88 A.

The complexes are similar in type to the tetracarbonyls prepared by Nigam et al.[6a] from ditertiary arsine. Their thermostabilities were found to be slightly lower than those of the arsine complexes. The chromium compound darkened in a closed tube around 130° , the molybdenum one at 150° with subsequent melting at 160-3°, and the tungsten one at 160°. The tetracarbonyls could be recrystallised in air without decomposition, from benzene, chloroform, or acetone, which last is to be preferred in the case of tungsten. They chromatograph well on alumina in

TABLE 2.

NON-CARBONYL IR-SPECTRA OF 2,5-DITHIAHEXANE AND ITS COMPLEXES.

Ligand[16] Liquid	Ligand[16] Solid	Ligand $M(CO)_4$ Mulls with CaF_2 and NaCl optics of chromium	molybdenum	tungsten
2925s 2825vw	2910s	2929m	2923w	2928w
-	-	cf. table 8.		
1430vs	1430vs	1433w 1421w 1412w	1433w 1421w 1412w	1433w 1420w 1411w
1323m	1320m	1317w 1299w	1325w 1301w	1321m 1300w
1272s*	-	1254m*	1259m*	1257w* 1)
1203vs	1210vs	1160w		1169w
1136s	1137s			1137w
1010m sh*	-	1024w*	1027w*	1026s* 2)
958vs	964vs	967w	967w	969m* 3)
900w	-			895w
840m*	-	833w*	838w*	832m* 3)
736vs	735vs+ 728vs sh+			3) 4)
682vs	678vs	681w 643m	662w	662w 4) 4)

The bands marked * are attributed to the gauche form.
The bands marked + are attributed to the trans form.

1) probably CH_2 wagging
2) probably C-C stretch
3) CH_2 rocking
4) C-S stretch

These assignations are given by Sweeney et al.[16]

benzene or chloroform and can be kept for months in a sample tube. The nuclear magnetic resonance spectra, which have been obtained from the chromium and molybdenum tetracarbonyls will be discussed in a later chapter. (cf. table 7) They show the complexes to be diamagnetic.

Attempted preparation of bis-2,5-dithiahexane metal dicarbonyl.

Nigam et al.[6a] succeeded in making $L_2 M(CO)_2$ when reacting a ditertiary arsine ligand with the group VI hexacarbonyls in a bomb at 250° with periodical release of the carbon monoxide formed. However, when 2,5-dithiahexane was kept at 255° for three hours in a bomb with the hexacarbonyls of molybdenum and tungsten, the anticipated reaction did not take place at all. Instead a mixture of tetracarbonyl and a yellow material, which after recrystallisation analysed for tricarbonyl, was obtained.

In the case of molybdenum the tricarbonyl material, which always analysed for one more carbon atom than required for 2,5-dithiahexane molybdenum tricarbonyl and was monomeric, was possibly impure tetracarbonyl, as it had the same infra red carbonyl spectrum. Unlike the tetracarbonyl it could, however, not be successfully chromatographed on alumina. This material, which was also obtained by reduction of carbonyl halide derivatives of the 2,5-dithiahexane tetracarbonyls (cf. p.37), could not

be satisfactorily characterised, although made in fair yield repeatedly with constant analysis.

After the bomb experiment with tungsten hexacarbonyl at 250° decomposition took place, at 220°, however, a mixture of two carbonyls formed and was separated on alumina in benzene-petrol mixture 1 : 1. The first yellow band, which contained a small amount of material, had a new spectrum (cf. type B, on plate 8.) almost identical to those of tricarbonyls isolated from 1,4-dithian (cf. table 10). The analysis of C and H corresponded to those required for 2,5-dithiahexane tungsten tricarbonyl. As there was insufficient material for further analysis 5-coordinated tungsten can not be stated to be present. The second band off the column had a spectrum identical to that of the tetracarbonyl and analysed accordingly. No other carbonyl compounds could be isolated.

Ligand replacement reactions of 2,5-dithiahexane group VI metal carbonyls.

Reaction with dienes and cycloheptatriene.

Norbornadiene, C_7H_8, bicyclo-(2,2,1)-hepta-2,5-diene, is known to react directly with the hexacarbonyls of chromium, molybdenum, and tungsten to give complexes of the type $C_7H_8\ Mo(CO)_4$.[29,30] These reactions are complicated by diene polymerisation, which takes place readily in the case of molybdenum and tungsten. In the case of chromium, however, there is little or no polymerisation. Several days are needed for the reactions with the hexacarbonyls.

When norbornadiene reacted with 2,5-dithiahexane chromium tetracarbonyl at 110° in petrol, it replaced the sulphur ligand in an hour. No polymerisation occurred and the yellow solid subliming in vacuo at 100° was identical with the norbornadiene chromium tetracarbonyl obtained by Abel et al.[29] and by Pettit[30] judging from analysis, infra red spectrum, and melting point. With molybdenum this reaction proceeded less satisfactorily because of the diene polymerisation. There was infra red evidence of the formation of the molybdenum analogue, but the compound was not isolated.

As the reaction with norbornadiene took place readily, replacement reactions with other dienes were attempted. 1,4-cyclohexadiene and 1,4-diphenyl-1,3-buta-

diene did , however, not replace 2,5-dithiahexane at 110°in petrol. Even when the 1,4-cyclohexadiene reaction was allowed to run for four days, only the starting materials were recovered.

Cycloheptatriene in the complex $C_7H_8Mo(CO)_3$ has been replaced by monodentate sulphur ligands.[12] It is thus not surprising that when cycloheptatriene was allowed to react with 2,5-dithiahexane molybdenum tetracarbonyl at 120° for 1.5 hours no replacement occurred. Instead a new orange carbonyl compound with an infra red band at 1960 cm^{-1} formed, but it was not isolated.

Reactions with triphenylphosphine and its oxide.

2,5-dithiahexane chromium tetracarbonyl was heated with triphenylphosphine oxide for one hour at 110°, but afterwards only the starting materials could be recovered. Under these conditions triphenylphosphine will replace 2,5-dithiahexane in the group VI tetracarbonyls. In replacement reactions there is not always retention of configuration and it is not surprising that the more stable trans-isomers were the only carbonyl products in the case of chromium and tungsten, while with molybdenum there was a mixture of the cis- and trans-isomers and also possibly some formation of triphenylphosphine metal tri- and pentacarbonyl judging from infra red spectra. The analyses of the

complexes isolated from the first band off the column on chromatography on alumina in benzene were approximately correct for bis-triphenylphosphine metal tetracarbonyl, but some impurities seemed to accompany the complexes. The decomposition temperatures were lower than those found for the pure compounds.

These results are in accordance with the results of other workers. When Hieber and Peterhans[31] let the group VI hexacarbonyls react with two equivalents of triphenylphosphine in a sealed tube at 140-60°, they obtained the trans-isomers of all three metal carbonyls. Poilblanc and Bigorgne[32] found that by heating either isomer of bis-triphenylphosphine molybdenum tetracarbonyl for an extended period, a cis : trans equilibrium ratio of 1 : 4 was established. Bennett[27] also prepared a mixture of these isomers by replacing norbornadiene in norbornadiene molybdenum tetracarbonyl by two molecules of triphenylphosphine. The cis-isomer could not be isolated, as it was contaminated with triphenylphosphine. The main reaction product was the trans-isomer.

Replacement by pyridine.

Pyridine replaced 2,5-dithiahexane with ease on molybdenum giving rise to bis-pyridine molybdenum tetracarbonyl identical to that obtained by Strohmeier and Gerlach[33].

In the unrecrystallised reaction product there was a small amount of tris-pyridine tricarbonyl present judging from a typical strong infra red carbonyl peak at 1715 cm^{-1}, which was also present in the compound made by Hieber and Mühlbauer[34]. This tris-pyridine molybdenum tricarbonyl was the main product when the 2,5-dithiahexane molybdenum carbonyl material obtained in several ways (cf. pp. 23, 38) was allowed to react with pyridine, although a considerable amount of tetracarbonyl was also isolated.

Attempted replacement by 3,6,9-trithiaundecane.

The tridentate ligand did not replace the bidentate one on heating of 2,5-dithiahexane chromium tetracarbonyl with 3,6,9-trithiaundecane at 110° or at 155°.

2,5-dithiahexane carbonyl halides of chromium, molybdenum, and tungsten.

Orange tricarbonyl diiodides and dibromides were obtained from the 2,5-dithiahexane group VI metal tetracarbonyls by reaction with iodine or bromine at room temperature. It was important that no excess of the halide was present, as decomposition set in and with bromine other complexes formed.

The complexes were found to be diamagnetic and monomolecular, and only the tungsten tricarbonyl dibromide was too insoluble for molecular weight determination in boiling benzene or for nuclear magnetic resonance examination. The reaction of the tetracarbonyls with iodine and bromine gives high yield and probably corresponds to the equation :

$$CH_3S(CH_2)_2SCH_3\ M(CO)_4 + Hal._2 = CH_3S(CH_2)_2SCH_3\ M^{II}(CO)_3Hal._2 + CO$$

showing the formation of seven-coordinate complexes analogous to the arsine complexes reported by Nigam et al.[6b] The sulphur carbonyl halides were non-conductors in nitrobenzene. The possibility of halogen being attached directly to sulphur was considered unlikely, because benzene solutions of the tricarbonyl diiodides were not decolourised by sodium thiosulphate, whereas the ligand halogen adducts are.

The amount of carbon monoxide evolved was not determined.

The diiodides could be recrystallised in air and best from benzene, although they did not decompose much in chloroform, dichloromethane, or acetone. The dibromides decomposed more and were best obtained directly from the filtered benzene reaction solution by evaporation of part of the solvent in vacuo. However, the thermostability of the dibromides was greater than that of the diiodides. It was also found that the tungsten diiodide complex was much more stable thermally than the molybdenum one. The molybdenum carbonyl halides also started to decompose when dissolved in nitrobenzene as could be seen from the value of the conductivity, which rose with time much faster than expected from the hygroscopic properties of dry nitrobenzene. The tungsten complexes showed no such effect when left in nitrobenzene for ten minutes after the conductivity determination.

When 2,5-dithiahexane chromium tetracarbonyl was allowed to react with iodine under nitrogen, the reaction solution at once turned orange as in the case of molybdenum and tungsten. However, the reaction product could not be isolated. The infra red spectrum of the carbonyl region of the reaction mixture showed two new carbonyl peaks at 2083 and 1970 cm^{-1}, which disappeared in one hour. Under the same conditions the molybdenum analogue showed two peaks at 2046 and 1966 cm^{-1}, so it is probable that the chromium

complex is analogous. As chromium is a smaller atom, the seven-coordinate complex should form with difficulty and be unstable. The infra red carbonyl spectra of the carbonyl halides are shown in table 9 . The non-carbonyl infra red spectra appear in table 3 together with spectra of the tetraiodide adduct of the sulphur ligand. Judging from the spectra the adduct also occurs in the extended or trans form in the solid state and as a mixture of the trans and gauche forms in the liquid state. In the carbonyl halides the ligand is again present in its gauche form. A band at about 750 cm^{-1} was seen in the case of the diiodides after some runs, but as some decomposition may have taken place and some of the ligand or its tetraiodide adduct may have been formed, this band is not to be considered as evidence for the presence of the trans-form.

None of the 2,5-dithiahexane metal carbonyl halides could be chromatographed on alumina. Although the 2,5-dithiahexane tungsten tricarbonyl diiodide darkened at 135° in a closed tube, the molybdenum analogue started to change at 40° in a closed tube or when heated in a solvent above this temperature. The molecular weight obtained in boiling benzene was abnormally high, but did not correspond to that of the dimer. As it was suspected that a new complex had formed, the tricarbonyl diiodide was heated at a bath temperature of 115° in benzene and the red brown solid

residue was extracted with much chloroform until a new portion of the solvent did not turn dark red and opaque at once. If the last part of the residue consisted of well formed crystals 2,5-dithiahexane molybdenum dicarbonyl monoiodide dimer could then be obtained pure by recrystallisation from chloroform, in which solvent it was slowly soluble to give a red transparent solution. The molecular weight of this new complex is in very close agreement with the molecular weight obtained on attempting to determine the value by the ebullioscopic method in benzene. Attempts to confirm the molecular weight by the isopiestic method in dry tetrahydrofuran failed. Unfortunately, it was impossible to prepare sufficient pure material for determination of the magnetic susceptibility. Paramagnetic impurities accompanied the complex and caused too high values, so that no information about the number of unpaired electrons could be obtained.

The reaction taking place should thus correspond to the following equation :

$$2\ CH_3S(CH_2)_2SCH_3\ Mo(CO)_3I_2 \xrightarrow[\text{benzene}]{\text{rflx in}} [CH_3S(CH_2)_2SCH_3\ Mo(CO)_2I_2]_2 + 2\ CO + I_2$$

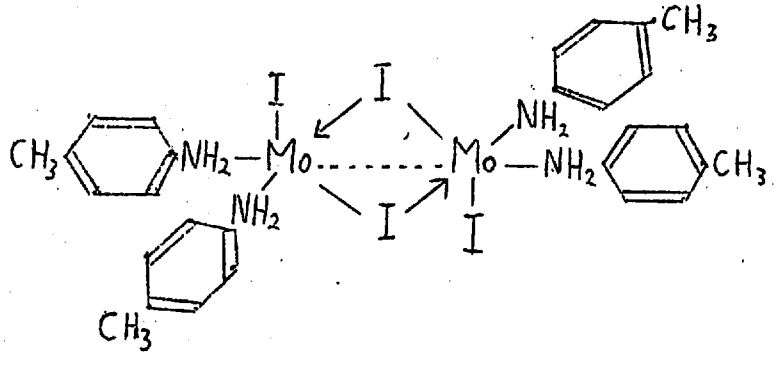
However, it was not clear if the dimer contained halogen or carbonyl bridges. The infra red spectrum in chloroform, in which solvent the compound is somewhat soluble, showed three bands at 2000, 1945, and 1866 cm^{-1}. It is well known that

the triple bonded carbon monoxide molecule absorbs in the infra red at 2143 cm^{-1} and the double bonded ketones around 1700 cm^{-1}. Bridging carbonyl groups have been found to absorb in the region between 1700 and 1850 cm^{-1}, as can be seen, for instance, from the spectra of cobalt octacarbonyl or iron enneacarbonyl.[35,36] This assumption has been found valid for metal carbonyls and carbonyl halides in general, although it must be borne in mind that not all carbonyl peaks in this low region are derived from bridging carbonyls.[13, 34, 37] The 2,5-dithiahexane molybdenum dicarbonyl iodide dimer has the lowest band a little above 1850 cm^{-1}, perhaps too near to the bridging carbonyl region to rule out the possibility of a carbonyl bridge altogether.

Chatt, Duncanson, and Venanzi[23] working with palladium complexes with halogen bridges found that amines such as p-toluidine, piperidine, or n-octylamine reacted with the bridge halogen to give mononuclear compounds like L am Pd Hal_2. However, these new complexes could not always be isolated depending on the nature of L. When L = PR_3 or As R_3, no difficulties arose, but if L = R_2S, R_2Se, or R_2Te, the amine complexes decomposed. It was also found that the stability of the amine complex decreased with increasing molecular weight of the halogen.

If there were halogen bridges present in the dimeric molybdenum carbonyl halide, the complex would be

expected to react with p-toluidine and this was found to be the case on warming in benzene. It is not surprising that the amine complex could not be characterised considering the results of Chatt and his coworkers[23]. However, when in one experiment the benzene solution was refluxed in a bath at 100° , there was formation of a compound of very intense violet colour. This very insoluble material could be freed from dark brown reaction products by many times repeated centrifugation in benzene. The violet solid was concentrated on top. The analysis of this product corresponded to $[(p\text{-toluidine})_2 \text{ molybdenum diiodide}]_x$ and this result was corroborated by the qualitative analysis, which was positive for Mo, I, and N, but negative for S. The infra red spectrum showed no carbonyl bands. The complex decomposed at 150° in a closed tube. As not much work was done on this compound and as no molecular weight could be obtained, no definite statement could be made concerning its structure, although the one shown in fig. XIV could be possible.



XIV.

TABLE 3.

INFRA RED SPECTRA OF 2,5-DITHIAHEXANE TETRAIODIDE AND 2,5-DITHIAHEXANE CARBONYL HALIDES OF MOLYBDENUM AND TUNGSTEN.

L I_4 NaCl optics CS_2 or CH_2Cl_2	L I_4 Mulls	L $M(CO)_3I_2$ Mulls, NaCl or CaF_2 optics.	L $M(CO)_3Br_2$	$[L\ Mo(CO)_2I]_2$
2973w		2980w	2980w	
		2958w	2945w	
2920m		2910w		2922w
–	–	cf. table 9.		
		1440w	1440m	1431m
	1433m	1432w	1425m	1424m
		1417m	1413m	1411m
	1405m	1400w	1405m	
		1331w		
1320s	1315m	1324w	1323m	1317w
1263s*		1250w*	1248w*	
1203s	1215m	1231w		
		1172w		
1126m		1124w	1124w	
1040m*		1022w*	1032m	1018w*
996w		981m	980sh	
		970s	975m	
957s*	950m	963s	967sh	968m
916w sh		914w*	959sh	
	894w*	909w	917w*	
			905sh	
840w*		842m*	849m*	
			838m	856w*
728w+	732m+	(756m)1		
	725m+			
	675w			

*The bands marked * are attributed to the gauche form.
The bands marked + are attributed to the trans form.
For assignations cf. table 2.
1) band presemt after some runs in solvents containing Cl.

From table 3 it can be seen that the tetraiodide adduct of 2,5-dithiahexane has the same configurations in the liquid and solid state as the sulphur ligand. In the carbonyl halide complexes the bands typical of the gauche form of 2,5-dithiahexane are visible. The diiodides did after some runs show a band at 756 cm^{-1}, which was not to be found when the complexes had been handled in benzene only; in solvents like chloroform, dichloromethane, or acetone some decomposition always took place, even if the complex could be obtained pure enough to give correct analysis after recrystallisation from these solvents. The carbonyl spectra of the tricarbonyl dihalides in dichloromethane were very complex, but the corresponding carbon disulphide spectra were simple, as can be seen in table 9 .

Attempted Grignard reaction with 2,5-dithiahexane molybdenum tricarbonyl diiodide.

When 2,5-dithiahexane molybdenum tricarbonyl diiodide was added to a solution of two equivalents of CH_3MgI, the orange colour of the reaction solution disappeared. The same colour reappeared after a few minutes owing to the formation of the reaction products. The orange solid, which was isolated from the ether extract after hydrolysis in small yield, was probably a mixture of complexes, as the analysis did not fit a definite formula, although the molecular weight fitted exactly with the dimethyl derivative expected.

REDUCTION OF THE 2,5-DITHIAHEXANE TRICARBONYL DIIODIDES OF MOLYBDENUM AND TUNGSTEN.

Reduction with $LiAlH_4$ or $NaBH_4$.

When 2,5-dithiahexane tungsten tricarbonyl diiodide reacted in dry tetrahydrofuran with $LiAlH_4$, there was nuclear magnetic resonance evidence of hydride formation corresponding to two high field bands at τ = 15.41 and τ = 19.57. The hydrides have not been isolated from the solution, which on exposure to the air changed its colour from light yellow to yellow brown. The light yellow colour returned when more $LiAlH_4$ was added. After exposure to air the tetrahydrofuran solution was evaporated in vacuo. A benzene extract of the residue was concentrated, and chromatographed on alumina. As in the case of the bomb reaction with tungsten hexacarbonyl and 2,5-dithiahexane at 220° two yellow bands containing the same reaction products separated. The first band thus contained a small amount of a yellow solid, which analysed for 2,5-dithiahexane tungsten tricarbonyl in the C and H determination, which was the only one done owing to the small yield. The infra red spectrum is shown in plate 8. The second band contained the tetracarbonyl, which had the spectrum shown in plate 7.

When the same reaction was carried out with $NaBH_4$, the reaction solution showed the same colour changes on exposure to air, but no hydride peaks were visible in the

high resolution nuclear magnetic resonance spectrum and only traces of the yellow solid from the first band off the column formed.

The reaction of 2,5-dithiahexane molybdenum tricarbonyl diiodide with $LiAlH_4$ or $NaBH_4$ in dry tetrahydrofuran afforded again the same compound as the bomb reaction at 220° between the sulphur ligand and the hexacarbonyl. No evidence of hydride formation could be obtained. The yellow monomer with the $C_8H_{10}S_2MoO_3$ analysis and the tetracarbonyl type spectrum was isolated in 30 % yield by ether extraction of the residue after the evaporation of the solvent. The compound appeared to decompose in benzene on an alumina column, and fractional recrystallisation from benzene, ether, or a mixture of light petrol and dichloromethane did not reveal new compounds. The solid reacted with carbon monoxide at 80° and 100 atm. in a bomb to give the molybdenum hexacarbonyl. Under milder conditions no reaction took place. It reacted with pyridine at 60° to give about 60 % tris-pyridine molybdenum tricarbonyl and about 40 % of the tetracarbonyl in one experiment. The 2,5-dithiahexane molybdenum tetracarbonyl afforded these compounds in yields of 10 and 90 % respectively under the same conditions in another experiment. Because of this contradictory evidence nothing can be said with certainty about this solid, which was obtained in three different

ways and had many times repeated constant analysis. Its nuclear magnetic resonance spectrum was very like that of the tetracarbonyl and contained no hydride bands.

Reaction with KOH in ethanol.

Chatt and Shaw[61] have shown that tertiary phosphine complexes of transition metals undergo both reduction and carbonylation on heating with KOH in ethanol. The 2,5-dithiahexane tricarbonyl diiodides of molybdenum or tungsten reacted at once and at room temperature with these reagents; but only in the case of molybdenum could a reaction product be isolated. This yellow solid was the same compound $C_8H_{10}S_2MoO_3$ although the oxygen analysis tended to be a little too high, perhaps the solvent acted as a ligand in part of the material. The infra red carbonyl spectrum was again the same as that of the tetracarbonyl and there was no hydride evidence.

Reduction with sodium amalgam.

Attempts to reduce 2,5-dithiahexane tungsten tricarbonyl diiodide with sodium amalgam in dry tetrahydrofuran were made. Reaction took place immediately, but no definite products could be isolated.

Bis-2,5-dithiahexane uranium tetrachloride.

Although many uranium complexes with oxygen and nitrogen ligands are known, few have been prepared with phosphorous or sulphur as donor atoms, as is shown in a review of actinide complexes by Comyns.[39] Allison and Mann[40] prepared four trialkylphosphine complexes with the formula $UX_4 \cdot 2PR_3$, where X = Cl or Br and R = C_2H_5 or C_3H_7. Attempts to make the analogues from trialkylarsines or chelating diarsines failed.

Uranyl complexes of a number of thioacids, thiolactic and thioglycocollic, in which sulphur is most probably coordinated to the metal, have been obtained, but no oxygen-free sulphur complex of uranium seems to have been isolated prior to this work. It is known that uranium tetrachloride is soluble in dimethylsulphide, a fact which indicates sulphur coordination to uranium IV, but this system has not been much studied.[41] Also, Albers and Lange[42] have suggested that dialkyl-dithiocarbamates of uranium IV were intermediates in their synthesis of uranyl complexes.

It has been found that sulphur is a weaker donor to uranium and thorium than is oxygen. Wendlandt and Bryant[43] showed that the solubilities of uranyl and thorium nitrates in tributylthiophosphate are twenty times lower than those of the oxygen analogue, notwithstanding the similar dielectric constants of these media (ϵ = 6.82 and 8.05 resp.)

In this work two equivalents of 2,5-dithiahexane were allowed to react with one equivalent of anhydrous uranium tetrachloride under nitrogen at room temperature in dry tetrahydrofuran. The reaction was complete in about twentyfour hours. Bis-2,5-dithiahexane uranium tetrachloride, a grey-green solid, could be obtained pure after evaporation of the solvent in vacuo and washing with light petrol under nitrogen. The low conductivity in nitrobenzene indicates an eight-coordinated complex. This compound is not analogous to the hexa-coordinated compounds reported by Allison and Mann[40] but to the similarly grey-green complex bis-1,2-dimethoxyethane uranium tetrachloride prepared from 1,2-dimethoxyethane and anhydrous uranium tetrachloride by Parshall.[44] As no molecular weights have been determined of these compounds owing to low solubility in benzene or decomposition in tetrahydrofuran, when the isopiestic method was tried, the coordination numbers can not be stated with certainty.

Solid bis-2,5-dithiahexane uranium tetrachloride is very stable in the absence of air and can be kept under nitrogen in a stoppered flask for several months without decomposition. It is not very soluble in organic solvents except tetrahydrofuran or nitrobenzene. On heating in a closed tube the complex decomposed at 150°. The infra red spectrum showed the ligand to be present in the gauche form, so that the monomeric structure seemed most likely.

Attempted reactions between uranium tetrachloride and other sulphur ligands.

When uranium tetrachloride was allowed to react with 1,4-dithian or 3,6,9-trithiaundecane in the same conditions as with 2,5-dithiahexane, reaction took place similarly, as could be seen from the change of colour from yellow-green to blue-green. However, because of much lower stabilities the complexes isolated under nitrogen gave unsatisfactory analyses. They decomposed very quickly in air and also under nitrogen during washing with solvents like dry benzene or petrol, which were tried to minimise the sticky appearance of the reaction products.

The molecular weight of the trithiaundecane reaction product was 770 and indicated a monomer with two sulphur ligands coordinated partly or fully to a molecule of uranium tetrachloride.

REACTION OF 2,5-DITHIAHEXANE WITH TUNGSTEN HEXACHLORIDE.

Whereas tungsten hexacarbonyl reacted with 2,5-dithiahexane at 150° to form a metal organic complex without decomposition of the sulphur ligand, tungsten hexachloride behaved very differently in the same conditions. The mixture of tungsten hexachloride and 2,5-dithiahexane turned violet at 100°; at higher temperature this colour disappeared and the reaction mixture turned brown. The sulphur ligand was attacked and transformed into a number of other sulphur compounds. When the reaction mixture was chromatographed on alumina, about 10 % yield of the white volatile solid 1,4-dithian (MP 110-12°)was isolated from the light petrol eluent. (cf. fig. V). Other sulphur compounds formed were not characterised.

However, as the yield of the 1,4-dithian was low and as this compound was not always formed, the catalytic decomposition of 2,5-dithiahexane is not recommended as an improved method of preparation of 1,4-dithian, which is made in better yield by the method of Meyer[45], Husemann[46], or Masson[47] from sodium sulphide and ethylene dibromide, with subsequent decomposition of a polymer intermediate by heating with phenol at 160°. If pure 1,4-dithian is needed, chromatography on alumina in light petrol is recommended.

1,4-DITHIAN COMPLEXES.

Earlier work on 1,4-dithian.

1,4-dithian (cf. fig. V) in its solid and gaseous form has been shown to have the centrosymmetric chair configuration.[17a,b] It is thus analogous to dioxan.[49] It can be seen from calculations that in the boat form of 1,4-dithian some hydrogen atoms come close together, making this isomer less stable. Furthermore there will be considerable repulsion between lone pairs of electrons on the sulphur atoms. This latter effect will not necessarily be important in the complexed molecule.

Although the configuration of a ligand may be much changed on complex formation, it seemed likely that 1,4-dithian would tend to form di- or polynuclear complexes and act as bidentate non-chelating ligand. This was found to be so in all cases, when the molecular weight could be determined. Most of the complexes were indeed sufficiently soluble in benzene for molecular weight determination. The possible structures of the complexes will be discussed later.

Borknight and Smith[50] have prepared a number of 1,4-dithian complexes of metal salts. Typical complexes obtained include the following compounds, all of which have unknown molecular weights and thus are probably di- or polymeric :

$PtCl_4$ 2 dt	Cu_2I_2 dt
$PtCl_2$ dt	$Cu(CN)_2$ dt
$CuCl_2$ dt	$Hg(ClO_4)$ 2 dt
$CuBr_2$ dt	$Hg(NO_3)_2$ dt
CuF_2 2 dt	$HgCl_2$ dt
Cu_2Cl_2 dt	$Ag(ClO_4)$ dt
Cu_2Br_2 dt	

Group VI metal complexes.

1,4-dithian carbonyls of tungsten and molybdenum.

The bidentate non-chelating ligand 1,4-dithian formed less stable complexes of the hexacarbonyls of the group VI metals than did the bidentate chelating 2,5-dithiahexane. This was to be expected because of the stabilising influence of a five-membered chelate ring in the case of the latter.

When the hexacarbonyls were heated in molten 1,4-dithian at temperatures between 140° and 160°, there was formation of tetra- and tricarbonyls with spectra very similar to those derived from the 2,5-dithiahexane complexes, as far as the infra red carbonyl region was concerned. (cf. tables 8 and 10, and also plates 7 and 8).

With molybdenum both a tri- and a tetracarbonyl were obtained. The yellow tetracarbonyl crystals formed by slow cooling of the reaction mixture, were well washed with much benzene, and big crystals, separated by hand

picking, analysed correctly for 1,4-dithian molybdenum tetracarbonyl. Attempted recrystallisation from benzene, chloroform, or acetone invariably led to complete decomposition. From the benzene extract of the reaction mixture a white tricarbonyl could be isolated in low yield; it analysed approximately for 1,4-dithian molybdenum tricarbonyl dimer. The molecular weight of the tetracarbonyl could not be obtained. Both complexes appeared to decompose slowly in air and the yellow crystals tended to wither to a powder.

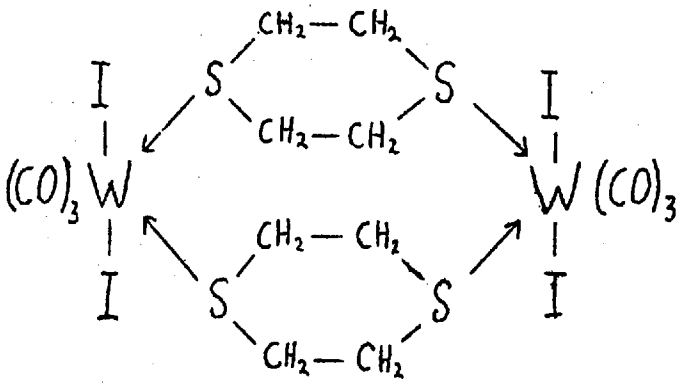
The tungsten hexacarbonyl reaction afforded only one defined product, a yellow 1,4-dithian tungsten tricarbonyl dimer, which was stable in air and had the typical infra red carbonyl spectrum found for the 2,5-dithiahexane tungsten tricarbonyl material and for 1,4-dithian molybdenum tricarbonyl dimer. The 1,4-dithian tungsten tricarbonyl was purified by benzene extraction of soluble impurities and subsequent recrystallisation of the residue from much benzene. The yield was about 5 % and attempts to raise it by performing the reaction in petrol ether (boiling point about 135°) were unsatisfactory. This compound should contain five-coordinated tungsten, and as this coordination number is unusual, the reaction was repeated for confirmation. The first half dozen times it was made it analysed correctly using the same batch of starting material. On changing to another batch of the 1,4-dithian, which had been purified

differently and contained different impurities, the analysis of the 1,4-dithian tungsten tricarbonyl dimer. formed was too high for carbon and oxygen and very discrepant from run to run. The reaction product always retained its carbonyl spectrum with no new peaks visible. Thus, although it seems very probable that the five-coordinated tungsten complex existed, more work would be necessary to establish its existence beyond doubt.

Reaction of the 1,4-dithian carbonyl complexes of tungsten and molybdenum with iodine.

1,4-dithian tungsten tricarbonyl reacted readily with iodine under nitrogen at room temperature. Care was taken to avoid excess of iodine, but the yield of deep orange tricarbonyl diiodide dimer was only about 50 %, so that the small amount of effervescence observed may have been caused by decomposition. The amount of carbon monoxide evolved was not determined, as it was thought to be of doubtful significance, because of the unknown nature of the decomposition products. The tricarbonyl diiodide dimer, contained no uncoordinated sulphur, was non-conducting in nitrobenzene and is certainly analogous to the 2,5-dithiahexane metal tricarbonyl dihalides and thus seven-coordinated. The infra red carbonyl spectra are also similar. (cf. table 9) It was more stable than the 2,5-dithiahexane tungsten tricarbonyl diiodide and gave a simple carbonyl spectrum in

dichloromethane, in which solvent it was very soluble. It decomposed at 85° in a closed tube - that is fifty degrees lower than the 2,5-dithiahexane analogue. The seven-coordinated dimer should thus correspond to the structure shown in fig. XV :



XV

With molybdenum a very similar infra red carbonyl spectrum was observed in the reaction solution, indicating that the analogous complex had formed, but the material isolated and recrystallised from benzene seemed to have decomposed, as no carbonyl peaks remained. (cf. table 9).

Attempted reaction between 1,4-dithian and chromium hexacarbonyl.

With chromium hexacarbonyl a yellow complex with the same type of infra red carbonyl spectrum as the tungsten tricarbonyls was obtained with 1,4-dithian in the same conditions. This chromium complex was rather unstable and a definite analysis could not be obtained, although the

molecular weight and hydrogen values indicated that only one 1,4-dithian molecule connected two chromium atoms. This arrangement seemed likely from geometric considerations because of the smaller size of the chromium.

The 1,4-dithian complexes of tungsten and chromium were chromatographed on alumina in benzene, but there seemed to be decomposition.

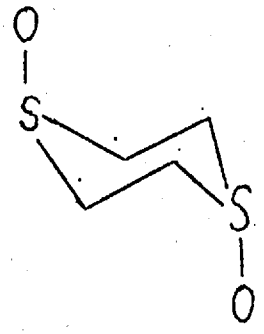
Reactions with cycloheptatriene tungsten tricarbonyl and cycloheptatriene.

It is known from the work by Cotton and Zingales[12] that three monodentate sulphur ligands will replace cycloheptatriene in its molybdenum tricarbonyl on refluxing in petrol at 100-20°. In an attempt to raise the yield of 1,4-dithian tungsten tricarbonyl dimer. C_7H_8 W $(CO)_3$ was allowed to react in the same conditions with 1,4-dithian. The initial red colour of the reaction solution persisted. On examining the infra red carbonyl spectrum of the solution no bands typical of the 1,4-dithian tungsten tricarbonyl. dimer. could be seen.

On the other hand, when the 1,4-dithian tungsten tricarbonyl dimer. was heated with cycloheptatriene for half an hour at 130° in a preliminary experiment, new carbonyl bands were found at 2008, 1987, and 1900 cm^{-1}, indicating formation of new carbonyl compounds or even possibly C_7H_8 W $(CO)_3$.

The stereochemistry of the 1,4-dithian complexes.

The oxygen analogue of 1,4-dithian retains its chair configuration in those complexes, which have been studied by x-ray.[51,52] 1,4-dithian also retains the chair form in its oxygen and iodine compounds shown in fig. XVI and XVII[48,53] :



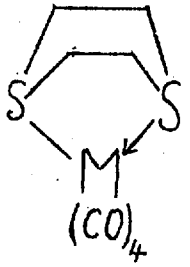
XVI.



XVII.

It is thus to be expected that 1,4-dithian complexes with metal carbonyls should retain the chair configuration also. With the carbonyls of the group VI metals it has been found in this work that dimeric complexes with no bridging carbonyl bands in the infra red spectrum were formed, and structures like those shown in plates 2 and 3, might be expected. However, studies of models and careful calculations[54] show that the distances between the protons labelled a and a' and the protons b and b' are about 1.05 A for plate 2 and 1.15 A for plate 3. These distances are so much less than twice the van der Waals' radius of the hydrogen atom (2 × 1.2 A) that this structure seems improbable.

The interaction of the lone electron pairs of the sulphur atoms, which makes the boat form of 1,4-dithian much less stable than the chair form, is no impediment to its existence in complexes. This conformation will still be destabilised to an extent of about 5 kcal/mole with respect to the chair conformation as a result of non-bonded interactions between the protons of the adjacent methylene groups. The distance between the sulphur atoms in the boat form (2.88 A.) is rather too short for formation of a strainless mononuclear complex of the type shown in fig. XVIII, where the distance between octahedral cis-positions is calculated to be about 3.3 A for tungsten and molybdenum.



XVIII.

In the complexes the conformation of 1,4-dithian which seems most probable from consideration of calculated atomic distances, involves a slightly distorted asymmetric boat form with carbon atoms at bow and stern. It has been pointed out by Hazebroek and Oosterhoff[55], that the boat of cyclohexane is just one member of an infinite class of flexible strainless forms, and that some of these

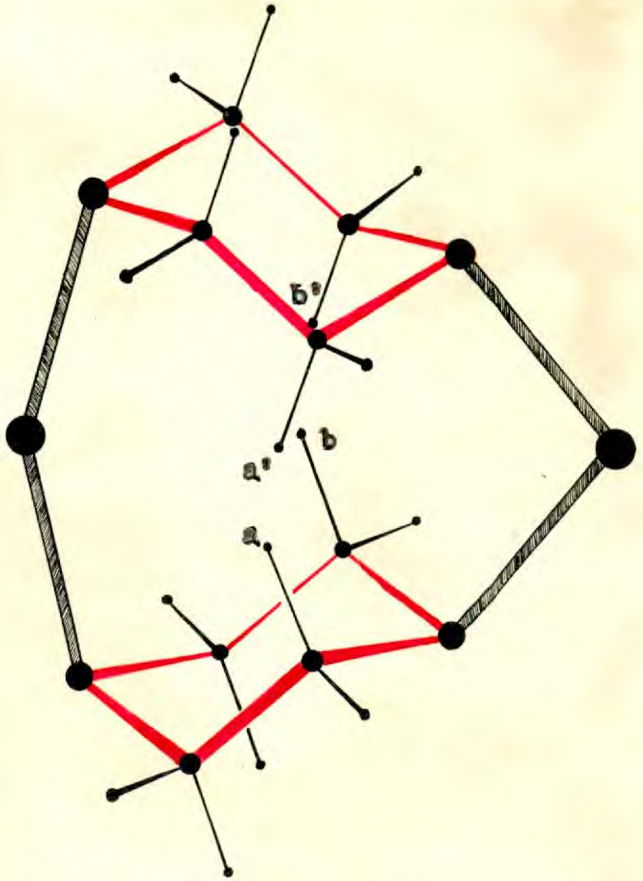


Plate 2.

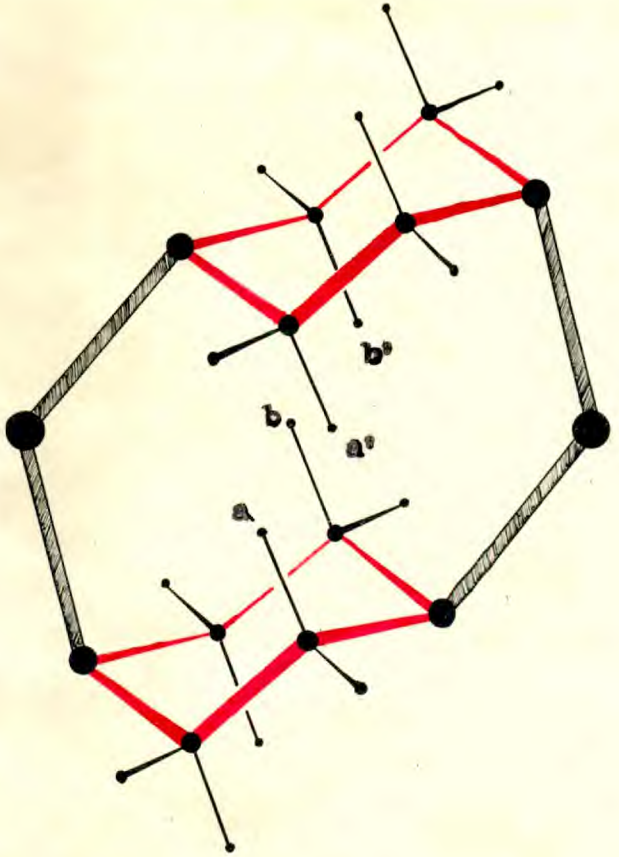


Plate 3.

5/a

other conformations are slightly more stable than the customary boat form. Similar considerations can be applied to the 1,4-dithian molecule and of particular interest is the conformation in which the bow and stern positions are occupied by carbon atoms instead of sulphur atoms. Two isomers can then arise. Plate 4 illustrates the meso-complex with two non-superimposable ligands, plate 5 the isomer with two superimposable ligands, which is optically active. In these structures there is much less interaction than in structures involving the conventional chair form between protons from two different 1,4-dithian molecules. In the meso-form the distances a - a' and b - b' are equal to 2.42 A. The closest proton distance, a - a', in the optically active isomer is 2.42 A. Both these distances are as great as the van der Waals' diameter of the hydrogen atom.

The only proton distance in an asymmetric boat conformation of 1,4-dithian, which is significantly less than than 2.40 A, is that between the axial hydrogens on the bow or stern carbon atoms. (cf. c - d in plate 4) This distance is calculated to be 1.86 A. There is, however, only one such proton interaction in each 1,4-dithian molecule of such conformation and it is unlikely to decrease the stability by more than about 5 kcal/mole. Furthermore, it is possible to deform the molecule from the strict asymmetric boat conformation without introducing angular strain (cf. the

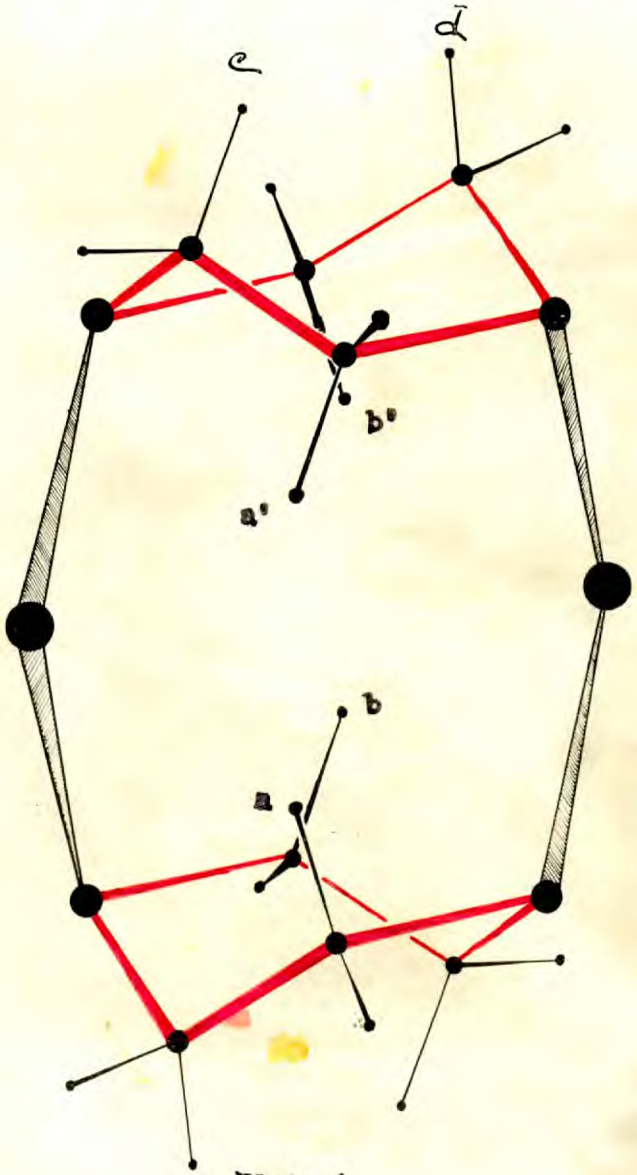


Plate 4.

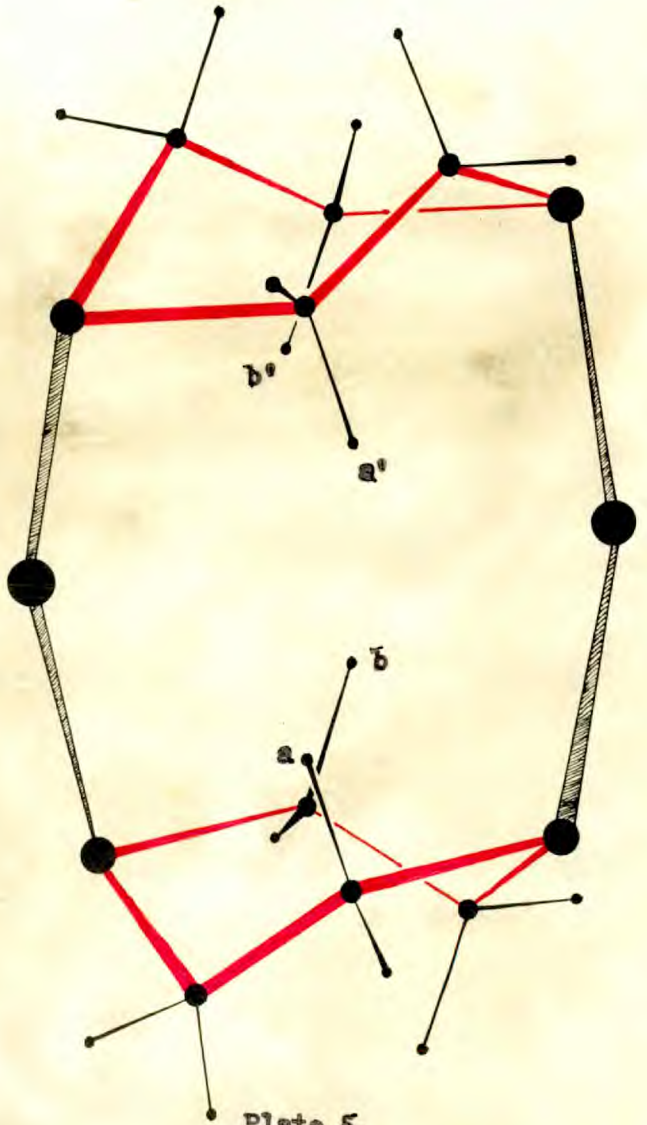


Plate 5.

52c

flexible form of cyclo-hexane)[55] in such a way that the distance between the interfering hydrogen atoms increases. This deformation also has the effect of drawing together the two different 1,4-dithian molecules in the metal complex so that their hydrogen atoms begin to interact : presumably a compromise will be reached in which each 1,4-dithian molecule is slightly distorted from the asymmetric boat form with a corresponding gain in stability. It is evident that the difference in energy between these isomers is quite negligible and that the energy barrier to their interconversion is so low as to preclude resolution at ordinary temperatures. The nuclear magnetic resonance spectra are shown in plate 6 and in table 7. Only one broad proton peak could be found.

Because of the small amount of strain already present in the complexes of molybdenum and tungsten, any reduction of the M - S bond length should bring the 1,4-dithian molecules closer together and decrease stability. It is noteworthy that chromium, which can be expected to give Cr - S bonds some 0.15 to 0.20 A shorter, does not seem to give complexes of this type.

The infra red non-carbonyl spectra of the ligand, its tetraiodide adduct, and its metal carbonyl and carbonyl halide complexes are shown in table 4 on the next page :

TABLE 4.

NON-CARBONYL SPECTRA OF 1,4-DITHIAN AND ITS COMPLEXES.

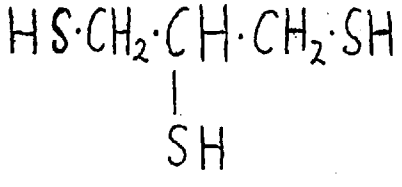
L Mulls NaCl	L CS_2, CH_2Cl_2 NaCl	L I_4 Mulls NaCl	L I_4 CS_2 NaCl	$(LMo(CO)_4)_x$ Mulls NaCl	$(LW(CO)_3)_2$ Mulls NaCl	$(LW(CO)_3)_2$ CS_2 NaCl	$(LW(CO)_3I_2)_2$ Mulls NaCl
						3050w	
2945w	2950m sh		2960w	2970w		2975w	
	2922s	2922w	2920w	2932w	2935w		
2840m						2850w	2850w
2800m							
-	-	-	-	cf. tables 8 and 9.			
					1416w		1430w
1400m	1415m	1408w		1413m	1411sh		1414m
	1355w					1328w	
1295m	1303m		1294m	1298m	1296w		
	1280s	1275w	1275m	1277m	1277w		
1255s		1255w				1237sh	1237w
	1203w				1205w		
				1160m	1162sh		1165w
1147m	1146s	1147w	1146m		1150m	1148sh	
	1100w			1094sh		1115w	
						1063w	
988w	995m	1000w	986w	995m	1000m	995sh	
		960w		967m			
940w	942m			936m	936w		
903sh				901sh	900sh		
892sh	898s	886m	898m	895m	892m	898sh	
					795w	823w	781w
760m	-	760m	-			730w	
						695m	
661s	662m	-1)	-1)	655m	660m		

1) The C-S stretching peaks of 2,5-dithiahexane tetraiodide were much weaker than those of the ligand itself.

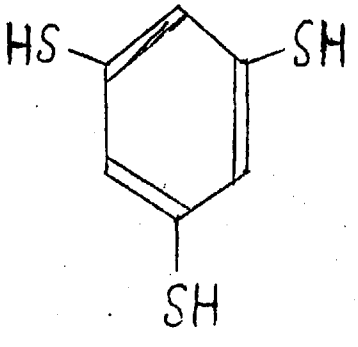
In the solid state 1,4-dithian and its tetraiodide adduct have a fairly strong band at 760 cm^{-1} in the CH_2-rocking region, which is not visible in solution spectra. This peak is also found in the mull spectra of the complexes but it is much weaker and shifted about 25 cm^{-1} upwards. In the CS_2 spectrum of 1,4-dithian tungsten tricarbonyl dimer. there is a fairly strong peak at 730 cm^{-1}. The C-S stretching peaks of the tetraiodide adduct can not be seen. Also in the case of the 2,5-dithiahexane tetraiodide adduct, the C-S stretching peaks are either very weak or missing. The 1147 cm^{-1} peak in 1,4-dithian and its tetraiodide is shifted 10 to 20 cm^{-1} upwards in the complexes, this peak could correspond to the CH_2-twisting region. On the whole the spectra of the ligand and its complexes are fairly similar. More careful spectra would be necessary to draw more definite conclusions concerning the conformation of the ligand.

3,6,9-TRITHIAUNDECANE COMPLEXES.

No complexes of the sulphur ligand 3,6,9-trithiaundecane, $(CH_3CH_2SCH_2CH_2)_2S$ (cf. fig. VII), seem to have been prepared prior to this work. Few metal organic compounds with tridentate sulphur ligands can be found in the literature. For instance, Carius[56] prepared the compounds $Ag_3C_3H_5S_3$, $Cu_3(C_3H_5S_3)_2$, and Pb $C_3H_5S_3$ from trithioglycerin (fig. XIX), but reported no molecular weights. Pollack and Carniol[57] obtained an orange precipitate when mixing lead acetate with trithiophloroglucin (fig. XX); again the complex was not investigated further.



XIX.



XX.

3,6,9-trithiaundecane sometimes acted as a bidentate ligand (cf. the reaction with manganese pentacarbonyl bromide, p.71), but in the reactions with the chromium or molybdenum hexacarbonyls it gave as the main product complexes in which all three sulphur stoms were coordinated giving the maximum stabilising effect of two five-membered chelate rings.

Another carbonyl compound was also found in the yellow petrol ether fraction separated from both tricarbonyl complexes L M $(CO)_3$. These other compounds could be partly purified by chromatography on alumina in petrol, a treatment which destroyed the tricarbonyls. The chromatographing complexes were most likely to be the bi-coordinated intermediates, L M $(CO)_4$, as the infra red carbonyl spectra were almost identical to those of the 2,5-dithiahexane tetracarbonyls. As the complexes were present in low yield and difficult to separate from an oily impurity, possibly the ligand, they could not be obtained pure. The weakly positive methyl iodide test for uncoordinated sulphur might thus not have been significant. In the case of molybdenum a small amount of yellow solid could be separated after careful washing of the material with carbon tetrachloride. There was, however, insufficient for the characterisation of the compound.

Several attempts were made to prepare the 3,6,9-trithiaundecane tungsten tricarbonyl from the hexacarbonyl and the ligand both directly and in a solvent. It was found that the tridentate sulphur ligand did not replace any carbonyl groups after 44 hours refluxing in petrol, 100-120°. After heating for one hour at 170° without a solvent the reaction products had decomposed. It thus appears that the complex formed with tungsten is less stable than those

obtained from molybdenum and chromium. In this respect this sulphur ligand ressembles benzene and its homologues rather than the other sulphur ligands studied in this work[62].

It was found that the tridentate sulphur ligand did not replace 2,5-dithiahexane in its chromium tetracarbonyl on heating in petrol 100-120°. After heating without solvent for one hour at 155° (conditions sufficiently intense for the formation of 3,6,9-trithiaundecane chromium tricarbonyl from the hexacarbonyl) the infra red carbonyl spectrum of the reaction mixture still showed only the bands typical of tetracarbonyl. It seemed unlikely that any replacement had occurred, as the tricarbonyl complex must form more easily from an intermediate, where two of the three sulphur atoms are already coordinated, than from the hexacarbonyl directly.

It would have been expected that sulphur complexes with two chelate rings should have been more stable than those with only one such ring. However, although the thermostabilities of the two types of carbonyls were similar, the complex with two chelate rings seemed less stable chemically as they could not be chromatographed on alumina like the 2,5-dithiahexane carbonyls.

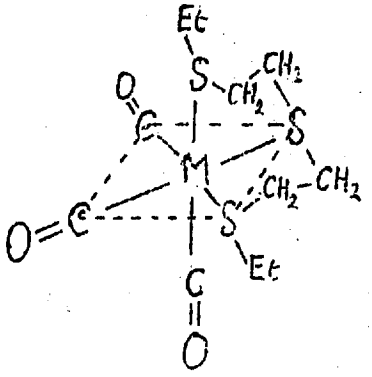
3,6,9-TRITHIAUNDECANE TRICARBONYLS OF CHROMIUM AND MOLYBDENUM.

Reaction between 3,6,9-trithiaundecane and chromium hexacarbonyl either directly at 135-150° or in petrol ether, 100-20° gave the hexacoordinate monomer as the main product. This yellow solid was, however, mixed with an oily fraction with a tetracarbonyl infra red carbonyl spectrum. The impurities could be removed by washing with benzene, this process, however, involved some loss of the product.

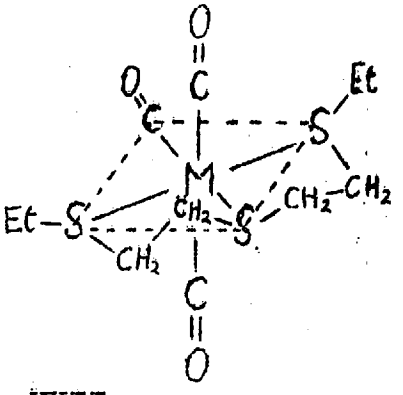
The reaction of the molybdenum hexacarbonyl was best carried out in 100-20°petrol. After cooling of the reaction mixture two liquid phases remained, the lower of which gave the tricarbonyl as a white precipitate on treatment with diethyl ether. The tricarbonyl was recrystallised from a 1 : 1 mixture of light petroleum and dichloromethane and gave a negative result in the methyl iodide test for uncoordinated sulphur. The upper petrol layer was found to give the same tetracarbonyl infra red spectrum.

Two possible octahedral structures of the tricarbonyls could exist and are shown in figs. XXI and XXII. Judging from group theory the cis-conformation, which has C_{3v} symmetry, should have two two infra red carbonyl peaks, the trans-isomer having C_{2v} symmetry should give rise to three carbonyl bands. As was the case with the tris-triphenyl phosphine molybdenum tricarbonyl prepared by Abel,

Bennett, and Wilkinson[13] only two bands were observed. (cf. table II).

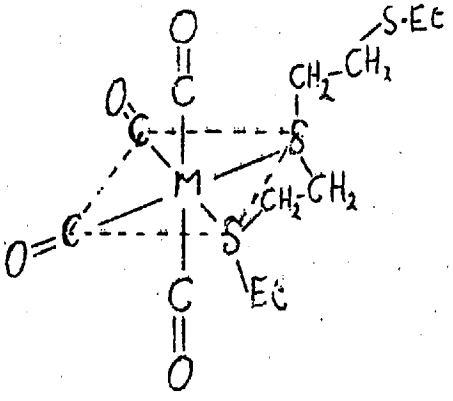


XXI.

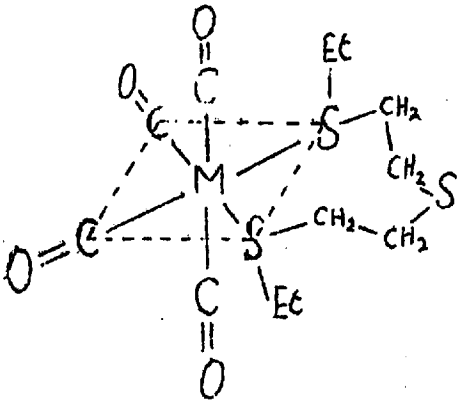


XXII.

In a complex where the tridentate sulphur ligand acts as a bidentate one, two different structures are possible as shown in figs. XXIII and XIV :



XXIII.



XXIV.

Structure XXIII seems most probable, as the possibility of attaching a second sulphur atom after the first sulphur atom of the molecule is coordinated is much greater, if the atoms are separated by a distance suitable for formation of a complex, in which the stabilising influence of a five-membered ring comes into play.

Reaction with iodine.

The 3,6,9-trithiaundecane molybdenum and chromium tricarbonyls reacted readily and without effervescence with iodine, but the tricarbonyl diiodides expected by analogy with the 2,5-dithiahexane and 1,4-dithian complexes, could not be isolated owing to their low stability. The reaction of the molybdenum compound could be followed in the infra red spectrum taken of the dichloromethane reaction mixture. The carbonyl bands of the tricarbonyl disappeared at once, and a new slowly disappearing spectrum was observed. This new spectrum was similar to that of the 2,5-dithiahexane molybdenum tricarbonyl diiodide, but two extra carbonyl bands were also present, as decomposition took place. (cf. table 9). The red-brown powder isolated after the reaction contained no carbonyl bands and could not be characterised.

The chromium tricarbonyl also reacted at once, but the complex formed decomposed immediately, so that no spectrum could be obtained. The non-carbonyl infra red spectra of the 3,6,9-trithiaundecane complexes are shown in table 5 on the next page together with that of the ligand. In the complexes new bands appear at about 830, 905, and 1280 cm^{-1}. The bands, which characterise the gauche form of 2,5-dithiahexane are at 840, 900, 1010, and 1272 cm^{-1}. It is thus likely that new peaks illustrate the fact that

TABLE 5.

NON-CARBONYL INFRA RED SPECTRA OF 3,6,9-TRITHIAUNDECANE AND ITS TRICARBONYLS OF MOLYBDENUM AND CHROMIUM.

L liquid, no solvent. NaCl.	L $Cr(CO)_3$ Mulls. NaCl.	L $Mo(CO)_3$ Mulls. NaCl.
3030m		
2935m	2954w	2982w
2900sh.	2925w	2924w
–	cf. table 11, p. 83.	
1450m		1443m
1423m	1425w	1435m
	1409m	1405m
		1396s
1373w		1375w
		1365w
		1289v w
	1285w*	1275w*
1260m	1248w	1240m
1200m		
	1164m	1169w
1129w	1123m	
1047w	1050m	1052w
960w	972m	967w
	911m*	905m*
	830s*	832m*
780w	771m	773w
755w	760m 1)	758w 1)
719m	–	–
683w	688m	664sh
646w	660w	640m

* denotes bands possibly indicative of the gauche conformations of the ligands two chelate rings.

1) bands in this part of the spectrum are obscured in Nujol.

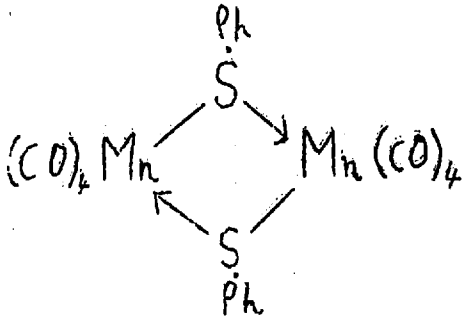
the middle sulphur atom in the tridentate ligand in the complexes is present in the gauche position with respect to the other two outer sulphur atoms. The fourth band derived from the gauche form of 2,5-dithiahexane at 1010 cm^{-1} and which was attributed to a C-C stretch by Sweeney et al.[16] is not visible in the 3,6,9-trithiaundecane complexes. The gauche conformation of the sulphur atoms fits in well with the distance between two cis-positions in an octahedral complex of chromium and molybdenum, so it is expected to be the preferred conformation.

In the uncoordinated ligand the bands typical of the gauche conformations are absent and it seems most likely that the central sulphur atom is in the trans- or extended position relative to the outer sulphur atoms. As the molecule can take up different positions around the central sulphur atom, it is not surprising that a fairly complex pattern of bands are visible in the C-S stretching region and the lower CH_2-rocking region. No sulphur atoms are attached to methyl groups as in 2,5-dithiahexane, so that the bands are shifted a little relative to the bands of the bidentate ligand.

Sulphur complexes of manganese carbonyl bromides and attempted reactions of sulphur ligands with manganese penta-carbonyl.

It is known that manganese carbonyl halides react more readily with a number of ligands than does manganese carbonyl. Abel and Wilkinson[58], and Hieber and Schropp[10] have prepared a number of complexes of manganese carbonyl halides and have found that aromatic amines, isonitriles, triphenylphosphine, arsine, and stibine give non-polar complexes of the type $L_2 Mn(CO)_3X$, where L = ligand and X = halogen. NH_3 and KCN formed the polar complexes $(Mn(CO)_4(NH_3)_2 X$ and $K\,Mn(CO)_4(CN)_2$ respectively.

Much less is known about sulphur complexes of manganese carbonyl halides. Hieber and Schropp used thiophenol as a ligand and obtained the sulphur bridged dimer :



XXV.

from manganese chloride. This complex seems to be the only one reported so far of manganese carbonyl halides and a sulphur ligand.

In this thesis the reactions of five sulphur ligands with manganese carbonyl bromides have been investigated. With 2,5-dithiahexane, 1,4-dithian, and 3,6,9-trithiaundecane well defined air stable complexes were obtained on heating at 70° in petrol. On the other hand, the desired reaction with tetramethyl-biphosphine disulphide (cf. fig.VII, p. 6)did not take place in these conditions, the minimum S-S distance (3.7 A) being to great to fit in well with the distance between two cis-positions on octahedral manganese (about 3.10 A).

The reaction between manganese tetracarbonyl dibromide and thiourea afforded a small amount of a not very stable rose-red complex with a new carbonyl infra red spectrum (2052m, 2015m, and 1929m) after two hours' refluxing in petrol ether, 100-20° in one preliminary experiment. Owing to low yield this complex could not be characterised. Yamaguchi[59] found that thiourea, unlike urea, is coordinated through the sulphur atom in all complexes examined in the infra red judging from bands assigned to metal-nitrogen and metal-sulphur bonds. The thiourea complex obtained from manganese tetracarbonyl dibromide was thus unlikely to be stabilised by chelate ring formation.

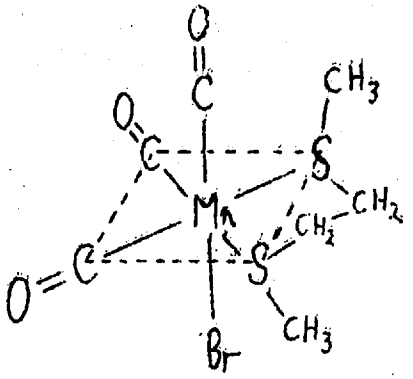
Although manganese carbonyl was expected to react less readily with the sulphur ligands, the reaction was attempted with 2,5-dithiahexane and 1,4-dithian. With

the former a flesh coloured product formed, but it was very unstable in air and mixed with much unreacted pentacarbonyl. After refluxing for two hours in 100-20° petrol most of the starting material was unchanged. The isolation of the new compound was not carried out and the reaction was only tried once. After heating of 1,4-dithian and manganese pentacarbonyl in petrol 100-20° the starting materials were recovered unchanged. At 160-90° without a solvent reaction took place and a small amount of a yellow but not very stable solid with infra red carbonyl bands at 2023m and 1993m cm^{-1} was separated but not characterised.

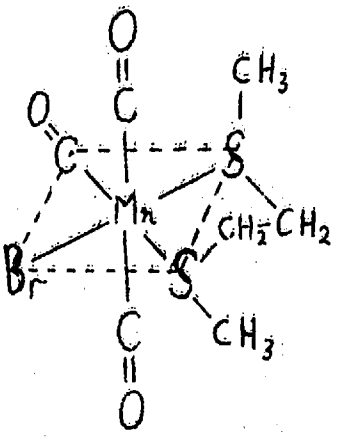
2,5-dithiahexane manganese tricarbonyl bromide.

2,5-dithiahexane reacted readily with both manganese pentacarbonyl bromide and tetracarbonyl dibromide at 75° in petrol and in both cases the identical complex formed. The stable orange yellow crystals could be purified in good yield by recrystallisation from diethyl ether or benzene. The complex was monomeric, non-conducting in nitrobenzene and contained no uncoordinated sulphur atoms. Unlike the other sulphur carbonyl complexes isolated in this work it melted, apparently without decomposition, at 135-6°. On heating in 100-20° petrol for two hours no polymerisation took place. In this respect the complex behaved like the manganese carbonyl halides with nitrogen, phosphorous,

arsenic, and antimony,[10,58] and not like the polymerising 1,4-dithian complex described later. Two structures can arise as shown in figs. XXVI and XXVII :



XXVI.



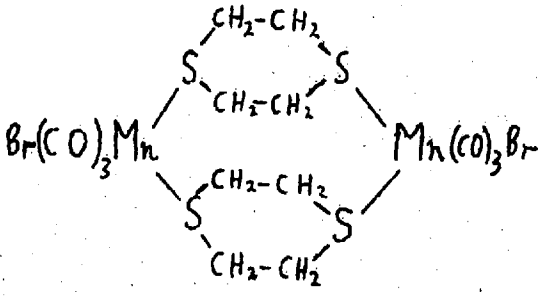
XXVII.

the former being most likely because of the known high trans effect of the carbonyl group. The proton magnetic spectrum differs from those of the 2,5-dithiahexane group VI carbonyls and will be discussed on p. 79.(cf. also plate 6).

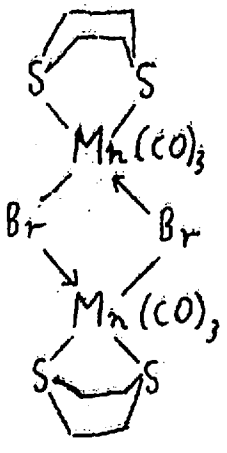
1,4-dithian manganese tricarbonyl bromide.

When 1,4-dithian was allowed to react with manganese pentacarbonyl bromide or with the tetracarbonyl dibromide, careful control of the temperature and time of the reaction was necessary in order to obtain the dimeric complex expected in analogy with the work on molybdenum and tungsten. At 65° in petrol ether $[C_4H_8S_2\ Mn(CO)_3Br]_2$ was the main product after heating for five minutes. With higher temperature and longer reaction time the reaction product or

products could not be recrystallised because of very low solubility in water and organic solvents. The more soluble dimer could be purified by recrystallisation from dichloromethane. It was a non-conductor in nitrobenzene. As there was no infra red evidence of bridging carbonyl groups, the following structures have been considered :



XXVIII.

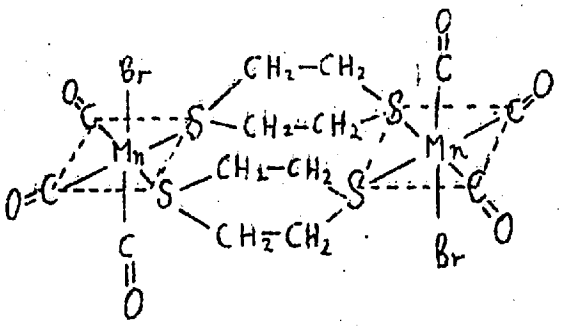


XXIX.

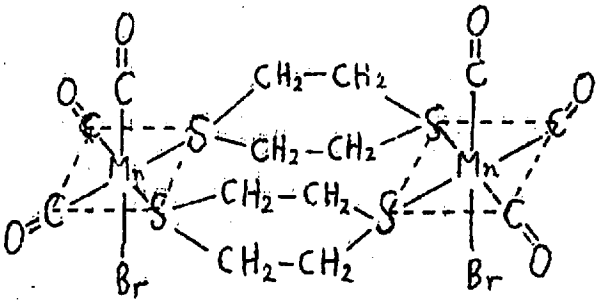
Structure XXVIII seems much more likely by analogy with the tungsten and molybdenum complexes of the same ligand already described, although the smaller size of the manganese atom, which is almost as small as the chromium one, causes more strain in the compound. The most important objection to structure XXIX lies in the fact that it would require seven-coordinate manganese, as the complex contains no uncoordinated sulphur. Also the strong tendency to polymerisation, which probably takes place through halogen bridge formation, makes structure XXVIII seem more likely.

In structure XXVIII the sulphur atoms are

again most likely to be attached trans to carbonyl groups because of the high trans directing effect of these groups. In this case two isomers can arise as shown in figs. XXX and XXXI :



XXX.



XXXI.

No attempts have been made to establish the presence of isomers. The complex was diamagnetic. Its infra red carbonyl spectrum in dichloromethane showed four bands. If certain carbonyl groups were present in an environment different from that of another carbonyl group on the metal, a more complex carbonyl spectrum could occur. The carbonyl spectrum is shown in table 12. The nuclear magnetic resonance spectrum is shown in table 7 and in plate 6. The dimer decomposed at about 200° in a closed tube as did also the polymeric material, which probably formed during the heating period.

The polymerisation product.

If the reaction between 1,4-dithian and either of the manganese carbonyl bromides was carried out at 85-100° in petrol for half an hour, a very insoluble yellow complex formed. As it could not be purified by recrystallisation, the material was not fully characterised, although it was found that it analysed a little higher for carbon and hydrogen and a little lower for oxygen than did the dimer. A very small amount obtained by extraction with much chloroform had no conclusive analysis either. An infra red spectrum taken of a dichlorometane extract showed three very weak bands, and also the nujol spectrum of the unrecrystallised material was somewhat simpler than the corresponding spectrum of the dimer. The bands were shifted downwards in the polymer, but the lowest band at 1902 cm^{-1} was too high up to indicate carbonyl bridges.[1] The hydrogen analysis, which was about 3 % indicated that two 1,4-dithian rings connected the manganese atoms, if only one ring were present, the analysis would be about 1.5 %.

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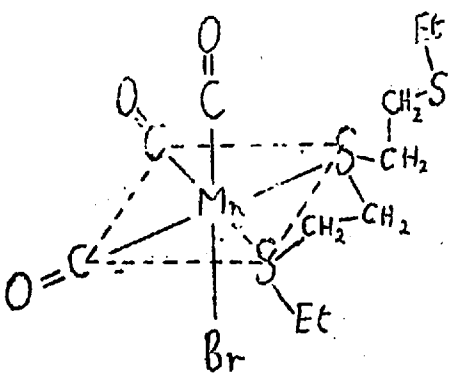
1) cf. table 12, p. 83

3,6,9-TRITHIAUNDECANE MANGANESE TRICARBONYL BROMIDE.

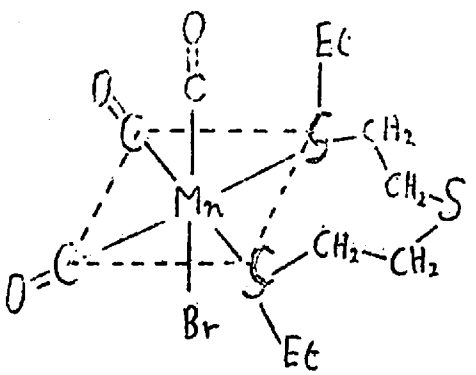
A very viscous deep red oil formed readily in high yield when manganese pentacarbonyl bromide reacted with $(CH_3CH_2SCH_2CH_2)_2S$. This oil could be purified by twice repeated chromatography in diethyl ether on alumina and analysed correctly for the complex $(CH_3CH_2SCH_2CH_2)_2S\ Mn(CO)_3Br$ As a seven-coordinated manganese complex is much less likely to exist than a six-coordinated one, it was not surprising that the compound contained uncoordinated sulphur in the methyl iodide test. Reaction with B_2H_6 took place and about 80 % of the amount required for one uncoordinated sulphur atom was taken up in about an hour. The addition compound was fairly stable under nitrogen and an infra red spectrum could be recorded. This spectrum contained a very strong band at 2400 cm^{-1} and a carbonyl region with four bands, one more than the red oil. After ten minutes the the B_2H_6 adduct band at 2400 cm^{-1} had almost disappeared and the carbonyl spectrum only contained three bands as in the case of the red oil, these bands were shifted about ten cm^{-1} downwards, possibly because of the diglym solvent. The red oil could be recovered after the decomposition of the B_2H_6 adduct, which on exposure to air gave rise to strong effervescence. The decomposed adduct was extracted with ether, which contained the recovered red oil. There was an orange residue after the ether extraction. This orange solid had an infra red carbonyl

spectrum with three bands at 2055w, 1961m, and 1882w, but was not characterised.

The 3,6,9-trithiaundecane manganese tricarbonyl bromide was a non-conductor in nitrobenzene and its infra red carbonyl spectrum showed no bridging carbonyl bands. As it is a monomer, the following two structures have been considered :



XXXII.



XXXIII.

Structure XXXII is much more likely to form as it is stabilised by a five-membered chelate ring. Because of the trans effect of the carbonyl group the two sulphur atoms coordinated are most likely to be attached trans to carbonyl groups.

REACTIONS BETWEEN IRON CARBONYLS AND SULPHUR LIGANDS.

Much of the previous work on reactions between iron carbonyls and sulphur ligands appears in the following references : 7,8,9,11,14, and 15. (cf. p. 2). In this thesis are reported some reactions between $Fe(CO)_5$ and $[Fe(CO)_4]_3$, which took place readily, but the results were disappointing because of low yields, and instability in some cases. Usually orange red complexes formed and mostly there were two carbonyl complexes, as could be seen when the reaction products were chromatographed in petrol on alumina. The first band contained a purer product than did the second band, which was contaminated with the sulphur ligand used. Infra red carbonyl spectra were recorded of the products obtained from both bands.

Hieber, Bader and Riess[7] prepared the complex 2,5-dithiahexane iron dicarbonyl diiodide from 2,5-dithiahexane and $[Fe(CO)_4]_3$. This iron carbonyl was allowed to react with 1,4-dithian in this work, but only the tetraiodide adduct of the ligand formed at room temperature. The results of the reactions attempted in this work are shown briefly in table 6 on the next pages :

TABLE 6.

REACTIONS BETWEEN IRON CARBONYLS AND SULPHUR LIGANDS.

Ligand	Carbonyl	Conditions (in N_2)	Results
Toluene 3,4-dimethyl thioether. (cf. fig. IX)	$Fe(CO)_5$	Reflux in 100-20° petrol or in the iron carbonyl for 4 to 16 hrs. Ratio 1 : 1.	First carbonyl off column : MP 122-24. C 37.0,37.1; H 2.97, 2.87; O 16.29; Fe 22.76,2292 % in two consecutive runs; MW 450. IR : 2016s,2056s,2088m second band off column : intense red carbonyl, IR : 2053m,2008s,1977m, 1945m and ligand.
2,5-dithiahexane (cf. fig. IV)	$Fe(CO)_5$	Heating 2 hrs at 140° in an excess of the ligand	a red oily product came off the column. It decomposed in an attempted vacuum destillation at 80°.
"	"	Heating 3.5 hrs in diglym at 105° Ratio 1 : 1.	After the solvent was filtered off the residue was extracted with THF From the concentrated solution a non carbonyl, light olive green solid precipitated on acetone addition, Fe +, S +.
"	$[Fe(CO)_4]_3$	Heating 1 hr in excess of ligand at 80-115°.	First red carbonyl off column IR: 2085m,2048s,2002m, 1896m second band : red oil + ligand.

TABLE 6 CONTINUED.

Ligand	Carbonyl	Conditions (in N_2)	Results.
2,5-dithiahexane	$[Fe(CO)_4]_3$	heating 1 hr in petrol at at 80° (1:1)	Two fractions came off the column, the second contained orange crystals.
1,4-dithian (cf. fig. V.)	$Fe(CO)_4I_2$	in ether at room temperature (1:1)	tetraiodide of 1,4-dithian fell out.
3,6,9-trithia-undecane (cf. fig. VI)	$[Fe(CO)_4]_3$	Heating 1 hr in petrol at 100° . (1:1)	First orange carbonyl off the column had IR : 2080s, 2038s, 2000s and the analysis : C 26.89 H 1.56 O 23.85 Fe 22.91 %, MW 784. It had been recrystallised once from petrol. second band off the column contained a red oil. IR : 2035s, 2020s, 1973vs, 1939vs.

NUCLEAR MAGNETIC RESONANCE SPECTRA AND ASSIGNMENTS.

The nuclear magnetic resonance spectra of some of the complexes prepared in this thesis have been examined on a Varian instrument at 56.45 mc/sec. and 22° ±1. The line positions are given in τ-values (10.00 minus the position in ppm on the low field side of tetramethylsilane as internal reference). (cf. table 7 and plate 6). The solvents used are mentioned in each case.

As can be seen from table 7 the shifts of the methyl and methylene peaks of 2,5-dithiahexane on complex formation are very small, especially for the methylene group. A similar result was found by Li, Johnson, and Shoolery,[63] who studied the methylene proton peaks of glycylglycinate and glycinamide before and after chelate formation with zinc or magnesium chloride. On complexing, the proton peak of the methylene group involved in the ring shifted a little, about 0.30 ppm and 0,36 ppm respectively.[1)] The shifts obtained with 2,5-dithiahexane on complex formation with the group VI metals and manganese were even smaller indicating weaker chelate bonds. The methyl proton peak of the 2,5-dithiahexane complexes shifted approximately 0.25 to 0.30 ppm. These shifts could be due to restriction of torsional movement of the alkyl groups because of chelation.

Whereas the two peaks expected from 2,5-dithiahexane had a similar shape and the areas under them

---

1) on Zn

could be estimated to have the expected ratio of 6 : 4 in the group VI tetracarbonyls; the manganese tricarbonyl bromide complex had a very sharp methyl peak and a broad methylene peak with some structure. The ratio of the areas of two so different peaks was very difficult to determine with accuracy. This changed spectrum may depend on distortion of the symmetry of the chelate ring. The size of the metal seemed to be unimportant, as the chromium tetracarbonyl of the 2,5-dithiahexane had a spectrum very similar to that of molybdenum.

When two iodine atoms are attached to 2,5-dithiahexane molybdenum tetracarbonyl, the spectrum changes to give a large double peak at the methylene proton region and a somewhat smaller peak at the methyl proton region. On further recrystallisation one more peak appears at τ = 6.73. This peak is probably due to the formation of a decomposition product, as a similar one is the only peak seen in the chloroform spectrum of the tricarbonyl dibromide, which was found to decompose extensively in this solvent.

The ligand 1,4-dithian has methylene group protons in both the axial and the equatorial positions, and as extensive spin-spin coupling occurs in molecules of this type, only one broad unresolved band was found at room temperature in this ligand and its complexes. This band shifted downwards on complex formation and in the case of

the tungsten complex the shift was about 0.5 ppm.

3,6,9-trithiaundecane gave the three expected peaks. The methyl peak from the ethyl gave a triplet with a splitting of about 7 cps. The methylene group from the ethyl part gave a quadruplet with the same splitting. Those two peaks were found to be about 0.15 ppm lower than those of diethyl sulphide, but at a similar distance from one another.[64,65] The bridging methylene peak appeared unresolved a little lower on the τ-value scale, but partly overlapping the ethyl methylene peak. On complex formation the methyl group peak was shifted a little downwards, but the other peaks remained almost unchanged on formation of two chelate rings. The 3,6,9-trithiaundecane manganese tricarbonyl bromide was not investigated.

TABLE 7.

NUCLEAR MAGNETIC RESONANCE SPECTRA OF SULPHUR COMPLEXES.

Compound	τ-value methyl H	τ-value methylene H	solvent
2,5-dithiahexane	7.85	7.28	$CHCl_3$
chromium tetracarbonyl complex	7.65	7.35	"
molybdenum tetracarbonyl complex	7.58	7.28	"
molybdenum tricarbonyl diiodide, 2 × recrystallised	7.58	7.27, 7.22, 6.73	"
molybdenum tricarbonyl dibromide, once recrystallised	7.83[1]	7.38[1] 6.81[2]	"
manganese tricarbonyl bromide	7.52[3]	7.26[4]	"
1,4-dithian		7.15[4]	CCl_4
tungsten tricarbonyl dimer		6.64[4]	$CHCl_3$
manganese tricarbonyl dimer		6.98[4]	CH_2Cl_2
3,6,9-trithiaundecane	8.75 ethyl bridge	7.49, 7.33[5]	CCl_4
	8.65 bridge	7.35	$CHCl_3$
molybdenum tricarbonyl	8.59 ethyl bridge	hidden 7.30	"

1) very weak bands. 2) very strong band. 3) very narrow band.
4) broad band. 5) unresolved.

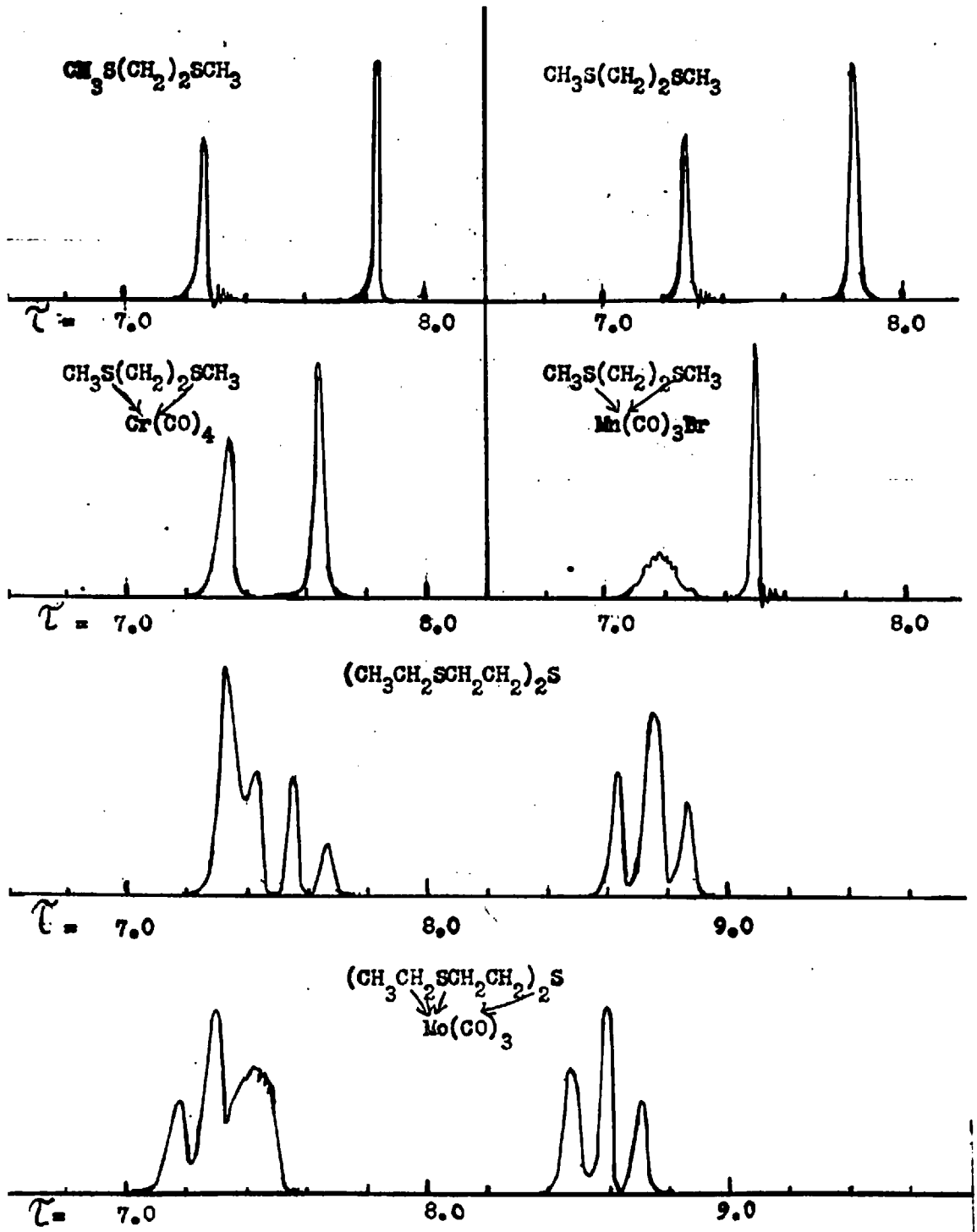


Plate 6. Nuclear magnetic resonance spectra.

TABLE 8.

TETRACARBONYL SPECTRA OF GROUP VI METAL COMPLEXES.

COMPLEX.	CARBONYL STRETCHING FREQUENCIES	MEDIUM	OPTICS
2,5-dithiahexane chromium tetracarbonyl	2020m, 1914s, 1898s, 1869s	$CHCl_3$,	CaF_2
	2022m, 1896s, 1862s	CH_2Cl_2,	"
molybdenum analogue	2030m, 1919s, 1905s, 1868s	$CHCl_3$,	"
	2033s, 1906s, 1863s	CH_2Cl_2,	"
tungsten analogue	2023m, 1910s, 1896s, 1867s	$CHCl_3$,	"
	2025m, 1900s, 1861s	CH_2Cl_2,	"
1,4-dithian molybdenum tetracarbonyl	2033m, 1900s, 1860s	CH_2Cl_2,	NaCl
3,6,9-trithiaundecane reaction byproduct with $Cr(CO)_6$	2020m, 1900s, 1862s	CH_2Cl_2,	NaCl
$Mo(CO)_6$	2037m, 1898s, 1890sh, 1860sh	CCl_4,	"
dipyridyl molybdenum tetracarbonyl[27]	2022m, 1906vs, 1877s, 1826s	$CHCl_3$,	NaCl
cis-bis-triphenylphosphine molybdenum tetracarbonyl[27,32]	2026m, 1933vs, 1910vs	CCl_4,	CaF_2
1,2-bisdiethyl phosphinoethane	of Cr 2000s, 1905sh, 1880vs		
	of Mo 2012s, 1909sh, 1891vs, 1873sh		
	of W 2008s, 1901sh, 1882vs, 1866 sh		
o-phenylenebisdimethylarsine chromium tetracarbonyl, 6a	2012, 1922, 1898	$CHCl_3$,	
molybdenum analogue, 6a	2026, 1938, 1923, 1914	cyclohexane	
tungsten analogue, 6a	2016, 1923, 1905, 1885	$CHCl_3$	

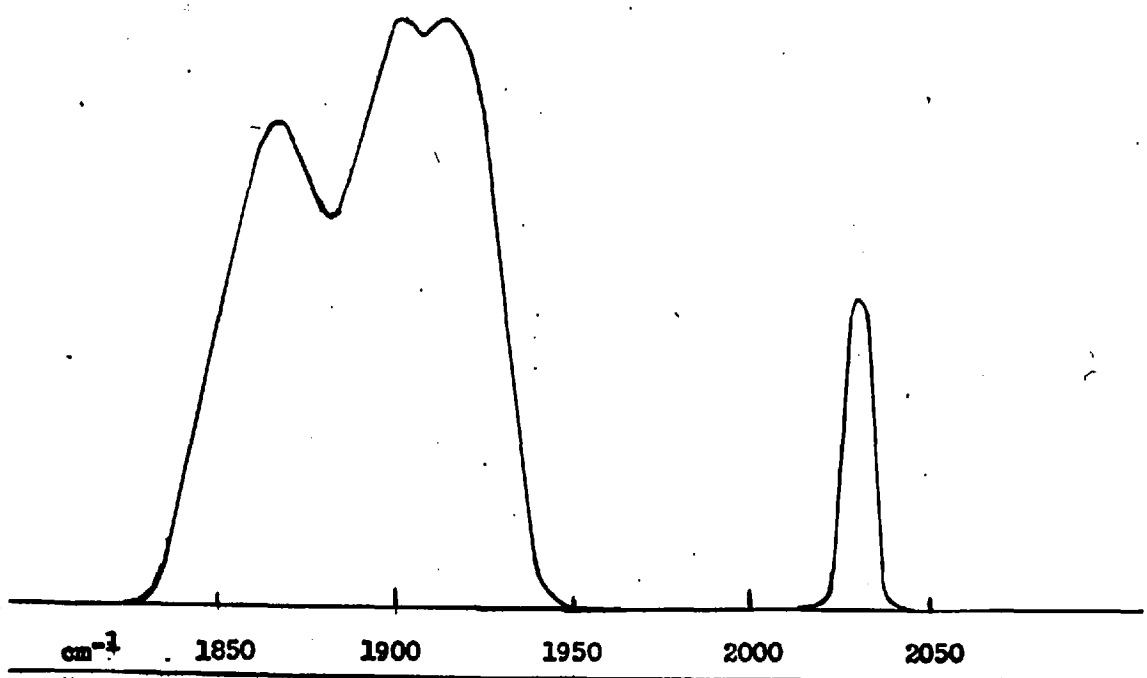


Plate 7. Typical infra red tetracarbonyl spectrum of complexes with two cis-coordinated sulphur atoms.

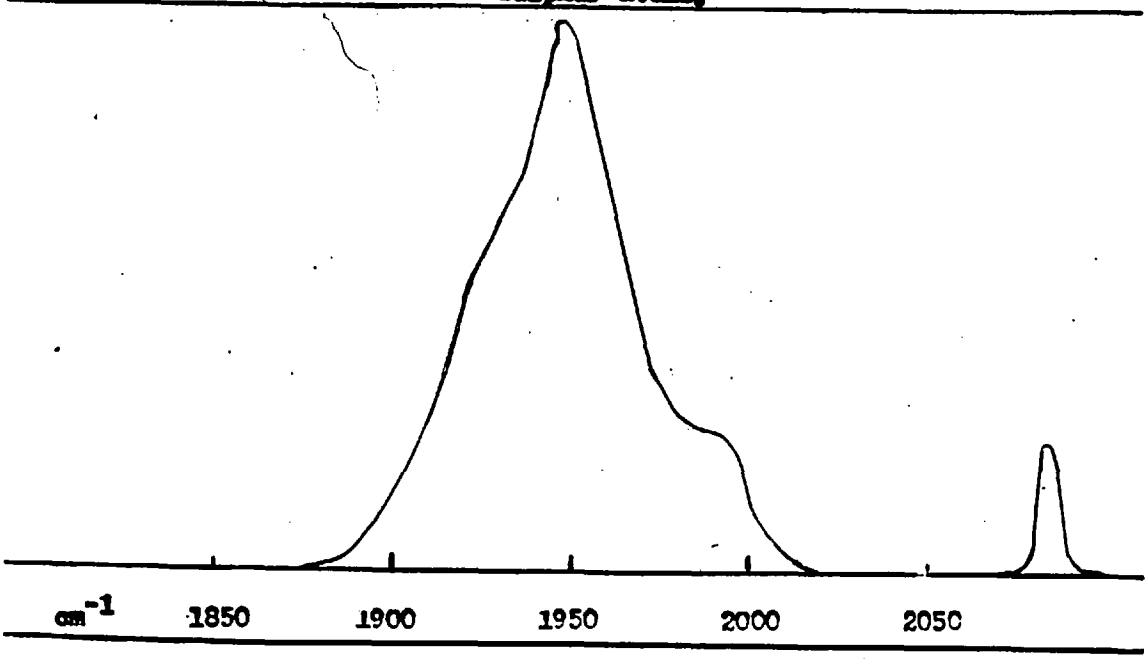


Plate 8. Infra red carbonyl spectrum of 1,4-dithian tungsten tricarbonyl dimer and complexes shown in table 10.

INFRA RED SPECTRA.

TABLE 9.

CARBONYL HALIDE SPECTRA OF THE GROUP VI METAL COMPLEXES.

COMPLEX	CARBONYL FREQUENCIES	MEDIUM	OPTICS
2,5-dithiahexane molybdenum tricarbonyl diiodide	2046s, 1988low sh, 1960s	CS_2	"
tungsten analogue	2033m, 1943s, 1906w	"	"
molybdenum dibromide analogue	2044m, 1990 low sh, 1955m	"	"
tungsten dibromide analogue	2054s, 1977s, 1912s	Nujol,	"
reaction mixture of 2,5-dithiahexane chromium tetracarbonyl and iodine	2083m, 1980 low sh, 1970m	$CHCl_3$,	"
2,5-dithiahexane molybdenum dicarbonyl iodide, diner	2000w, 1945w, 1866m	"	"
1,4-dithian tungsten tricarbonyl diiodide, diner	2054m, 1972s, 1911m	CH_2Cl_2	"
reaction mixture of 1,4-dithian molybdenum tetracarbonyl and iodine	2062s, 1991s, 1932s	"	"
o-phenylenebisdimethyl arsine molybdenum tricarbonyl diiodide, 6b	2053, 1982, 1925	Nujol	
dibromide analogue, 6b	2023, 1971, 1921	"	

INFRA RED SPECTRA.

TABLE 10.

COMPOUNDS WITH THE CARBONYL SPECTRUM SHOWN IN PLATE 8 .

COMPLEX	CARBONYL FREQUENCIES	MEDIUM	OPTICS
(2,5-dithiahexane tungsten tricarbonyl)$_x$, C and H analysis only.	2087m, 1990 low sh, 1942s	CH_2Cl_2	NaCl
1,4-dithian molybdenum tricarbonyl dimer, 1)	2080w, 1980 low sh, 1950s	"	"
1,4-dithian tungsten tricarbonyl dimer	2080w, 1985 low sh, 1945s	CS_2	"
Reaction product of 1,4-dithian and chromium hexacarbonyl, not purified	2075m, 1995 low sh, 1938s	CH_2Cl_2	"
Reaction product of tetramethyl biphosphine disulphide and molybdenum hexacarbonyl, 2),3)	2082w, 1995 low sh, 1952s	"	"
Reaction product of trithioformaldehyde and molybdenum hexacarbonyl at 80°, 2 hrs 2)	2087m, 1990 low sh, 1952s	"	"

1) C analysis 1.25 % too high
2) the carbonyl complex could not be separated from the sulphur ligand.
3) 1 hr in bomb at 220°, carbonyl sublimes at 115° with ligand

All these complexes were obtained in low yield and with the exception of the 1,4-dithian tungsten tricarbonyl dimer they were all fairly unstable, as could be expected from potentially five-coordinated complexes of molybdenum, tungsten, and chromium.

TABLE 11.

CARBONYL SPECTRA OF 3,6,9-TRITHIAUNDECANE AND TRIS-TRIPHENYL-PHOSPHINE MOLYBDENUM AND TUNGSTEN TRICARBONYLS.

COMPLEX	CARBONYL FREQUENCIES	MEDIUM	OPTICS
3,6,9-trithiaundecane molybdenum tricarbonyl	1919s, 1788s	HCBD	NaCl
	1932s, 1812s	CH_2Cl_2	"
3,6,9-trithiaundecane chromium tricarbonyl	1907s, 1790s	Nujol	"
	1932s, 1818s	CH_2Cl_2	CaF_2
Tris-triphenylphosphine molybdenum tricarbonyl [13]	1949s, 1835s	Nujol	

TABLE 12.

CARBONYL SPECTRA OF MANGANESE CARBONYL BROMIDES.

COMPLEX	CARBONYL FREQUENCIES	MEDIUM	OPTICS
2,5-dithiahexane manganese tricarbonyl bromide	2052s, 1970s, 1922s	$CHCl_3$	NaCl
1,4-dithian manganese tricarbonyl bromide dimer	2048s, 2025 sh, 1968s, 1920s	CH_2Cl_2	"
polymer	2027w, 1953w, 1902w	"	"
3,6,9-trithiaundecane manganese tricarbonyl bromide	2046s, 1965s, 1920s	"	"
Bis-triphenylphosphine manganese tricarbonyl bromide, 58	2046 , 1955 , 1916	$CHCl_3$	"
Bis-triphenylarsine manganese tricarbonyl bromide, 58	2055s, 2025s, 1958w, 1918w	"	"

DISCUSSION OF THE INFRA RED CARBONYL SPECTRA.

As can be seen from the tables 8 and 11 and the work of Cotton and Zingales[12] sulphur ligands lower the carbonyl frequencies much less than nitrogen ligands and a little more than phosphine, arsine, or stibine ones. A comparison of the carbonyl frequencies of the 2,5-dithiahexane complexes and the very similar bidentate phosphine ligand shows, however, that this tendency is not always pronounced but can perhaps be slightly reversed. Bouquet and Bigorgne[60] also found little difference in the carbonyl frequencies of phosphorous, arsenic, and sulphur complexes, although a careful study of their results reveals the carbonyl frequencies of the sulphur complexes to be a little lower than those of the arsenic complexes. The tendency is most pronounced for the lower peaks of the carbonyl spectrum. The sulphur to metal bond should thus have a little more double bond character than the metal to phosphorous and the metal-to arsenic bonds. Table 8 also shows that the carbonyl frequencies of the molybdenum tetracarbonyls tend to be a little higher than those of the chromium and tungsten analogues. As many variables are involved, it is not possible to explain this tendency satisfactorily.

In the carbonyl halide complexes the electron withdrawal effected by the halogen groups brings about a great change of the electron density around the metal,

so that nothing can be said of the different π-bonding abilities of the ligands judging from these spectra.

All tetracarbonyls with two coordinated sulphur atoms were found to have approximately the same spectrum with the same shape, which is shown in plate 7. As in most of the cases the two sulphur atoms must be attached cis to one another, an octahedral complex should have C_{2v} symmetry as in fig. XIII on page 20. This configuration ought to give rise to four carbonyl bands, which were indeed observed in chloroform or carbon tetrachloride. In dichloromethane, however, only three bands were observed in all cases both with NaCl and CaF_2 optics. As the tetracarbonyl of molybdenum obtained with 1,4-dithian has a very similar four-band spectrum, it thus seems very likely that the two sulphur atoms from two molecules of the ligand are attached cis to one another. The trans-isomer gives rise to only one strong band, and this spectrum was never observed.

The only other carbonyl spectrum obtained with carbonyl complexes, which had only two sulphur atoms attached to the metal, is shown in plate 8. This spectrum, which appears in table 10, was obtained in a number of cases for a compound formed together with a tetracarbonyl or formed by the reduction of a tricarbonyl halide. In some reactions between the group VI metal hexacarbonyls and 1,4-dithian this spectrum was the only new one observed.

If the reaction product could be isolated, there was always analytical evidence of tricarbonyl formation, which seemed reasonable, as the spectrum contained one band less than those of the tetracarbonyls. As five-coordinated complexes are known to be unstable, it was not surprising that most of these complexes were unstable and difficult to purify. The existence of the 1,4-dithian tungsten tricarbonyl dimer seems fairly certain. In the not very satisfactory reactions between molybdenum hexacarbonyl and the ligands tetramethylbiphosphine disulphide or trithioformaldehyde this tricarbonyl spectrum was the only indication of the formation of a metal organic carbonyl complex. As the reaction conditions had to be rather drastic in the case of the phosphorous containing ligand, it was possible that complexes could have formed from decomposed starting material.

Table 11 shows the two carbonyl bands expected from the configuration shown in fig. XXI on page 60. The only other carbonyl spectrum derived from the reaction of the tridentate sulphur ligand with the group VI hexacarbonyls was a tetracarbonyl type spectrum shown in table 8. No evidence of structure XXII was found.

Of the sulphur complexes with manganese shown in table 12 all but the 1,4-dithian dimer complex have the three band carbonyl spectrum, which was found for the similar manganese and rhenium complexes prepared by Abel et al.[58] Only two of the manganese complexes prepared in

the work by Abel et al. had a different four band carbonyl spectrum, which was found in the case of the bis-triphenylarsine manganese tricarbonyl bromide and iodide, whilethe chloride had the usual three band spectrum. The 1,4-dithian manganese tricarbonyl bromide dimer has a very similar arrangement of its four bands, and it is conceivable that the three complexes with a four band spectrum may have a configuration different from that of the complexes with a three band spectrum. Perhaps the sulphur and arsine ligands could be attached trans to the halogen in the complexes with the less usual four band carbonyl spectrum. Although this conformation seems less likely because of the great trans effect of the carbonyl group, it is maybe preferred for steric or other reasons. The 1,4-dithian manganese tricarbonyl bromide, dimer differs in its chemical behaviour from the other manganese sulphur complexes in its ease of polymerisation. The triphenylarsine complexes, however, did not seem to polymerise in the same way, as they were prepared at 120° in petrol and could be heated for half an hour without changing.

All preparations were carried out in nitrogen atmosphere. The microanalyses were made by the Microanalytical Laboratory, Imperial College. Infra red spectra were recorded on a Perkin Elmer, Model 21 spectrometer, using NaCl and CaF_2 optics. The nuclear magnetic resonance spectra were studied on a Varian Associates Model 4300 B spectrometer operating at 56.4 mcs/sec. Magnetic measurements on solids were made using the Gouy method.

Group VI metal carbonyls and carbonyl halides.

2,5-dithiahexane chromium tetracarbonyl.

$Cr(CO)_6$ (1 g, 4.5 mmoles) was heated at 150-65° with excess of 2,5-dithiahexane (5 ml) until no more gas was evolved (2 hrs). The reaction mixture was allowed to cool, the solid material was filtered off and washed well with light petrol. Some unreacted $Cr(CO)_6$ was sublimed off on 0° C cold finger at 70°/0.1 mm Hg. The residue was recrystallised from $CHCl_3$ to give deep yellow crystals, yield 64 %. (Found C 33.81 H 3.83 O 22.40 Cr 18.22 %, M = 285 (ebull. in benzene); $C_8H_{10}S_2CrO_4$ requires : C 33.50 H 3.51 O 22.30 Cr 18.17 %, M = 286). The compound decomposes at about 130° in a closed tube. It is soluble in $CHCl_3$ and benzene, very slightly soluble in petroleum ether. It can be chromatographed on alumina.

2,5-dithiahexane molybdenum tetracarbonyl and 2,5-dithiahexane tungsten tetracarbonyl were prepared like the chromium analogue in 43 and 26 % yield respectively. They are both

yellow. The tungsten complex was less soluble and was best recrystallised from acetone. (Found for the Mo complex : C 29.54 H 3.30 O 19,51 Mo 29.22 %, M = 339 (ebull. in benzene); $C_8H_{10}S_2MoO_4$ requires : C 29.05 H 3.15 O 19.38 Mo 29.07% M = 330. It decomposes at about 150° in a closed tube) (Found for the W complex : C 23.48 H 2.71 O 15.80 W 43.5 %; $C_8H_{10}S_2WO_4$ requires : C 23.01 H 2.41 O 15.30 W 43.9 %.) The complex is too insoluble in benzene for molecular weight determination. It decomposes at about 160° in a closed tube. Both complexes can be chromatographed on alumina in $CHCl_3$.

2,5-dithiahexane molybdenum tricarbonyl diiodide.

2,5-dithiahexane molybdenum tetracarbonyl (1 g, 1.8 mmoles) in 50 ml benzene was allowed to react with I_2 in 100 ml benzene (0.43 g, 1.7 mmoles) gradually with good stirring for half an hour. Deep orange crystals precipitated from the solution on concentration in vacuo. Recrystallisation from benzene gave 85 % yield of the analytically pure compound. Recrystallisation from $CHCl_3$ or acetone also gave the analytically pure compound, but the complicated infra red carbonyl spectrum in chlorinated solvents showed that decomposition took place in these conditions. The CS_2 spectrum was less complex. (Found : C 14.95 H 1.98 O 8.78 Mo 17.54 %, M = 506 (isopiestic in tetrahydrofuran); $C_7H_{10}S_2MoO_3I_2$ requires : C 15.11 H 1.81 O 8.63 Mo 17.23 %, M = 556) The compound started to decompose at about 40° in solution or in a closed tube. It is non-conducting in nitrobenzene (Λ = 0.8 mhos).

The diiodide analogue of tungsten and the dibromide analogues of molybdenum and tungsten were prepared in the same way. The dibromides, which were less stable than the diiodides, were best obtained by direct crystallisation from the filtered and concentrated reaction solution and they decomposed rapidly in chlorinated solvents or acetone. All the tricarbonyl dihalides were orange, they were obtained in yields of about 85 %. They were more soluble than the tetracarbonyls.

2,5-dithiahexane tungsten tricarbonyl diiodide.

(Found : C 13.26 H 1.75 O 7.17 I 39.72 %, M = 631 (ebull. in benzene.) $C_7H_{10}S_2WO_3I_2$ requires : C 13.06 H 1.57 O 7.46 I 39.40 %, M = 644.) The complex decomposes at about 135° in a closed tube and is non-conducting in nitrobenzene (Λ= 0mhos).

2,5-dithiahexane molybdenum tricarbonyl dibromide.

(Found : C 17.72 H 2.18 O 10.44 Mo 20.96 Br 34.53 %, M = 478. (ebull. in benzene). $C_7H_{10}S_2MoO_3Br_2$ requires : C18.18 H 2.18 O 10.39 Mo 20.75 Br 34.55 %, M = 462). The complex decomposes at about 125° in a closed tube and is non-conducting in nitrobenzene (Λ= 1.5mhos).

2,5-dithiahexane tungsten tricarbonyl dibromide.

(Found C 15.49 H 2.03 O 8.89 Br 28.54 %. M could not be done in benzene. $C_7H_{10}S_2WO_3Br_2$ requires : 15.31 H 1.83 O 8.74 Br 29.06 %). The complex decomposes at about 145° in a closed tube and is non-conducting in nitrobenzene (Λ= 0mhos).

Attempted preparation of the chromium iodine analogue.

When 2,5-dithiahexane chromium tetracarbonyl was allowed to react with iodine in CH_2Cl_2, the orange reaction solution

had an infra red spectrum similar to the tricarbonyl dihalide complexes of molybdenum and tungsten. The infra red carbonyl bands disappeared in about one hour and the complex was not isolated. (cf. table 9) Reaction in benzene was not tried.

2,5-dithiahexane molybdenum dicarbonyl iodide dimer from decomposition of 2,5-dithiahexane molybdenum tricarbonyl diiodide.

2,5-dithiahexane molybdenum tricarbonyl diiodide (8 g,10 m-moles) was heated in benzene for two hours in an oil bath at 110°. The benzene solution was filtered off and the solid residue was extracted with several 50 ml portions of $CHCl_3$ until a newly added portion was transparent and light red brown. The red brown crystalline dimer could be obtained pure. if well formed crystals were recrystallised from much $CHCl_3$, in which solvent it is stable and slightly but slowly soluble. (Found C 17.58 H 2.46 O 8.19 Mo 24.30 I 31.73 %, M = 792 (obtained by heating the tricarbonyl diiodide in benzene, by the ebulloscopic method). Attempts to determine the molecular weight of the dimer isopiestically in tetrahydrofuran failed owing to decomposition. $C_{14}H_{20}S_4Mo_2O_4$ requires : C 17.98 H 2.51 O 8.0 Mo 23.92 I 31.65 %, M = 802). The dimer decomposes at about 85° in a closed tube. Its conductivity in nitrobenzene is low (Λ=2.7mhos). The yield, which could be as high as 50 % of not quite analytically pure material varied and it was difficult to prepare larger amounts of really pure complex.

Reaction of 2,5-dithiahexane molybdenum dicarbonyl iodide dimer with p-toluidine.

The dimer was allowed to react with two equivalents of p-toluidine in benzene. At 40° there seemed to be very little interaction as the starting materials were recovered. After refluxing in benzene for 15 minutes reaction took place and a brown solid, which could not be characterised and which contained no carbonyl bands in the infra red, was obtained. If during the refluxing the bath temperature was raised above 100°, two fractions of solids could be obtained. An intensely violet solid could be separated from the brown solid by seven times repeated centrifuging in benzene. The violet complex was concentrated on top of the brown solid. The violet complex contained Mo, I, and N, but no S. (Found : C 29.93 H 3.44 N 5.24 Mo 16.20 %; bis-p-toluidine molybdenum diiodide requires : C 29.70 H 3.55 N 4.96 Mo 16.92 %.) The violet complex was very insoluble and probably di- or polymeric. It contains no carbonyl groups. It loses its colour slowly, when heated above 150° in a closed tube.
The brown solid had no infra red carbonyl bands.

Reduction of 2,5-dithiahexane tungsten tricarbonyl diiodide.

2,5-dithiahexane tungsten tricarbonyl diiodide reacted readily with reducing agents such as sodium amalgam, KOH in ethanol, $NaBH_4$, and $LiAlH_4$. No reaction products could be obtained with the first three reducing agents, but with $LiAlH_4$ in tetrahydrofuran the hydride-containing reaction

mixture gave two carbonyl complexes after exposure to air. These carbonyl complexes could be isolated by evaporation of the solvent, extraction of the solid residue with benzene and subsequent chromatography on alumina. The first yellow band off the column contained a small amount of a yellow solid carbonyl, which after careful washing with a small amount of light petrol and pumping down, analysed in the following way : C 21.87 H 2.24%; 2,5-dithiahexane tungsten tricarbonyl requires : C 21.55 H 2.58%. No more analyses could be done owing to low yield. This complex seemed identical to the complex obtained by direct reaction of 2,5-dithiahexand and tungsten hexacarbonyl in a bomb at 220° for two hours. (Found after chromatography on alumina in benzene : C 21.20 H 1.90%) The second band off the column in both cases contained 2,5-dithiahexane tungsten tetracarbonyl.

Reduction of 2,5-dithiahexane molybdenum tricarbonyl diiodide.

The molybdenum analogue reacted readily with $NaBH_4$, $LiAlH_4$, and KOH in ethanol to give in all cases a yellow solid with the same spectrum as 2,5-dithiahexane molybdenum tetracarbonyl. No other carbonyl bands were observed, although the analysis repeatedly indicated a tricarbonyl. Chromatography lead to decomposition and recrystallisation did not change the analysis, which in all cases showed the presence of a monomer. (Found : C 29.5 ± 0.35 H 3.3 ± 0.3 O 16.40 ± 0.4 Mo 31.4 ± 0.5 %, M = 314 ± 3; 2,5-dithiahexane molybdenum tetracarbonyl requires : C 29.05 H 3.16 O 19.38 Mo 29.07 %, the tricarbonyl : C 27.85 H 3.34 O 15.90 Mo 31.72 %, M = 303.

Direct reaction of 2,5-dithiahexane and molybdenum hexacarbonyl at 220-250°.

Molybdenum hexacarbonyl was allowed to react with excess 2,5-dithiahexane in a bomb for three hours at 220-250°. Only one carbonyl complex was found. This complex had the 2,5-dithiahexane molybdenum tetracarbonyl spectrum and the same anomalous tricarbonyl analysis as the material obtained by reduction of the tricarbonyl diiodide. (Found : C 29.86 H 3.43 O 16.56 %, M = 371.)

Direct reaction of 2,5-dithiahexane and tungsten hexacarbonyl at 220°.

Tungsten hexacarbonyl reacted with 2,5-dithiahexane in a bomb at 220° to give both the 2,5-dithiahexane tungsten tetracarbonyl and a suspected tricarbonyl, which were separated by chromatography on alumina in benzene. No other carbonyl complexes were observed. The suspected tricarbonyl seemed to be identical to the carbonyl obtained by reduction of the tricarbonyl diiodide. (cf. analyses given in connection with reduction reactions).

Replacement of 2,5-dithiahexane by norbornadiene.

2,5-dithiahexane chromium tetracarbonyl (0.5 g, 1.75 mmoles) in 25 ml petrol ether 100-20° was heated at 80-100° for two hours with norbornadiene (0.2 g, 0.22 mmoles). In the case of chromium no polymerisation was observed. After cooling the the petrol ether solution was combined with the petrol ether extract of the small solid residue. The solvent was

evaporated in vacuo and the norbornadiene chromium tetracarbonyl was sublimed on to a cold finger kept at -80° at 100°/0.1 mm Hg. The yellow complex was recrystallised from light petrol and melted at 89-91°. (Found : C 50.99 H 3.25 O 24.91 %, M = 255 (ebull. in benzene); $C_{11}H_8CrO_4$ requires : C 51.60 H 3.14 O 24.99 %, M = 256).

Replacement of 2,5-dithiahexane by triphenylphosphine.

About 2 g of the 2,5-dithiahexane tetracarbonyls of chromium, molybdenum, or tungsten were allowed to react with two equivalents of triphenylphosphine for three to five hours. The colour of the reaction mixture changed from yellow to light yellow and a small amount of effervescence was observed in the beginning of the experiment. The reaction temperature was 120° and about 30 ml of petrol ether 100-20° was sufficient as a solvent. After cooling the solid material was filtered off and washed well with light petrol. The solid was chromatographed on alumina in a 1 : 1 mixture of benzene and light petrol. The first fraction coming off the column contained about 30 % yield of bis-triphenylphosphine metal tetracarbonyl, which contained no sulphur but could not be obtained pure in spite of recrystallisation from benzene or CH_2Cl_2 or repeated chromatography. There was infra red evidence of the formation of small amounts of the hexacoordinated tri- and pentacarbonyl derivatives with the trans isomer of the tetracarbonyl being the main reaction product.

Replacement of 2,5-dithiahexane by pyridine.

1,5 g (4.5 mmoles) of 2,5-dithiahexane molybdenum tetracarbonyl was heated in an excess of pyridine (25 ml) at 60° for half an hour. After cooling of the orange red reaction solution the solvent was evaporated so that about 10 ml remained. The deep yellow crystals, which separated, were recrystallised from pyridine, washed with pyridine, then with a 2 : 1 mixture of light petrol and pyridine, and finally with light petrol. The complex contained no sulphur. (Found : C 45.98 H 2.93 N 7.55 O 17.30 %, M = 367 (ebull. in benzene); $C_{14}H_{10}N_2MoO_4$ requires : C 45.90 H 2.75 N 7.64 O 17.48 %, M = 366.) (Yield about 90 %). Before recrystallisation infra red carbonyl bands typical of the tris-pyridine molybdenum tricarbonyl were visible.

1,4-DITHIAN COMPLEXES.

1,4-dithian molybdenum tetracarbonyl and tricarbonyl dimer.

1,4-dithian (0.6 g, 4.9 mmoles) was well mixed with molybdenum hexacarbonyl (1.3 g, 4.9 mmoles) and heated at 140-50° for half an hour. After cooling, the unreacted start materials were sublimed off onto a liquid nitrogen probe at 50-110°/0.1 mm Hg. The residue was extracted with two portions of 50 ml benzene from which the white tricarbonyl was crystallised in 1 % yield. (Found : C 29.26 H 2.28 O 16.38 %, M = 534 (ebull. in benzene using on a minimun amount of material); $C_{14}H_{16}S_4Mo_2O_6$ requires : C 28.10 H 2.65 O 16.00 %, M = 600). Attempts to recrystallise the yellow crystalline tetracarbonyl residue from benzene, $CHCl_3$, or acetone failed owing to decomposition. Crystals separated by hand from the residue after careful washing with benzene and light petrol were found to be pure. (Found C 28.91 H 2.69 O 19.44 %; $C_{16}H_{16}Mo_2O_8$ requires : C 29.11 H 2.44 O 19.50 %). (Yield 37 %). The tetracarbonyl decomposes at 135° in a closed tube. Both carbonyls decompose slowly in air. (cf. table 9, p. 81 for iodine reaction).

1,4-dithian tungsten tricarbonyl diner.

1,4-dithian (3.5 g, 2.9 mmoles) was well mixed with tungsten hexacarbonyl (10.4 g, 2.9 mmoles) and heated at 145-60°. The effervescence ceased after one hour and the reaction could be resumed after extraction of the cooled reaction mixture with three 50 ml portions of benzene. The benzene was evaporated in vacuo and the extracted starting materials were sublimed off onto a liquid nitrogen probe at 50-110°/0.1 mm Hg and combined with the unextracted starting materials, which were pumped free of solvent and allowed to react again. A one hour reaction gave about 0.5 g (about 5 %) yellow carbonyl complex, which was washed with two 50 ml portions of benzene. The residue was recrystallised from about 750 ml of benzene, in which solvent the complex was slowly soluble. (Found : C 21.81 H 1.70 O 12.47 W 47.08 %, M = 796 (ebull. in benzene); $C_{14}H_{16}S_4W_2O_6$ requires : C 21.60 H 2.07 O 12.33 W 47.30 %, M = 776). The complex decomposed at about 155° in a closed tube. It was very soluble in CH_2Cl_2.

1,4-dithian tungsten tricarbonyl diiodide diner.

1,4-dithian tungsten tricarbonyl diner (90 mg, 0.11 mmoles) was dissolved in 10 ml CH_2Cl_2 and allowed to react at room temperature with iodine (51 mg, 0.2 mmoles). After 30 minutes when all iodine had been consumed, the reaction mixture was filtered and concentrated in vacuo to a volume of about 2 ml. The diiodide was precipitated carefully with about 2 ml of light petrol and washed well with light petrol after

centrifuging. (Found : C 13.31 H 1.31 O 7.39 I 39.52 %, M = 1264 (ebull. in benzene); $C_{14}H_{16}S_4W_2O_6I_4$ requires : C 13.10 H 1.25 O 7.47 I 39.45 %, M = 1284). The complex decomposed at about 85° in a closed tube. It could be recrystallised from benzene, but decomposed in $CHCl_3$ or acetone.

3,6,9-trithiaundecane chromium tricarbonyl.

Chromium hexacarbonyl (2.8 g, 12.7 mmoles) in 20 ml 100-120° petroleum ether was heated with 3,6,9-trithiaundecane (3 ml, 14 mmoles) at a bath teperature of about 140° for 3 hours. After cooling the deep yellow crystals were filtered off and washed well with light petrol. A small amount of chromium hexacarbonyl was sublimed off onto a 0° probe at 60°/0.1 mm Hg. The crystals were extracted with four 5 ml portions of benzene, which contained both tetra- and tricarbonyl. The rest of the crystals were recrystallised from benzene. (Yield 33 %) (Found : C 38.13 H 5.15 O 13.95 %, M = 355 (ebull. in benzene); $C_{21}H_{18}S_3CrO_3$ requires : C 38.15 H 5.23 O 13.82 %, M = 347). The complex decomposed at about 130° in a closed tube. It was very soluble in benzene and CH_2Cl_2.

This tricarbonyl reacted readily with iodine to give an orange complex, which was so unstable that the infra red spectrum of the reaction mixture contained no carbonyl peaks.

3,6,9-trithiaundecane molybdenum tricarbonyl.

Molybdenum hexacarbonyl (1 g, 3.8 mmoles) in 5 ml 100-20° petroleum ether was allowed to react with 3,6,9-trithiaundecane (0.8 ml, 3.8 mmoles) for two hours at 115°. After cooling two liquid phases separated in the reaction vessel. Most of the petrol layer on top was decanted off. The lower oily layer was washed with four 3 ml portions of diethyl ether and a white solid precipitated out. It was recrystallised from a 1 : 1 mixture of $CHCl_3$ and light petrol and washed well with light petrol. (Yield 30 %) (Found : C 33.39 H 4.55 O 12.20 Mo 24.27 %, M = 378 (ebull. in benzene); $C_{21}H_{18}S_3MoO_3$ requires : C 33.80 H 4.62 O 12.30 Mo 24.52 %, M = 390). The complex decomposed at about 145° in a closed tube.

Bis-(2,5-dithiahexane) uranium tetrachloride.

Uranium tetrachloride (1,2 g, 3.17 mmoles) in 50 ml dry tetrahydrofuran was allowed to react at room temperature with 2,5-dithiahexane (0.53 ml, 6.34 mmoles) for 24 hours with occasional shaking. The solvent was then evaporated in vacuo and the grey-green solid formed was washed well with light petrol under nitrogen. (Yield about 95 %). (Found : C 15.28 H 3.51 (U 37.88 from green U_3O_8 residue) Cl 22.10 %; $C_8H_{20}S_4UCl_4$ requires : C 15.40 H 3.23 U 38.20 Cl 22.70 %). The complex decomposed at about 150° in a closed tube under nitrogen. It could be kept for several months in a stoppered flask under nitrogen without decomposition, which

took place rapidly in air. The complex was not soluble in benzene but was fairly soluble in tetrahydrofuran. It is essentially non-conducting in nitrobenzene (Λ = 5 mhos). It had the following infra red spectrum : 2930w, 1595w, 1463 low sh, 1452m, 1420m, 1370 low sh, 1313w, 1295 low sh, 1282w, 1265w*, 1028w*, 1015w, 971m, 913w, 840w*. The bands marked * were assigned to the gauche form of the sulphur ligand.[16]

MANGANESE CARBONYL BROMIDE COMPLEXES.

2,5-dithiahexane manganese tricarbonyl bromide.

Manganese pentacarbonyl bromide (1 g, 3.6 mmoles) was allowed to react with an excess of 2,5-dithiahexane (3 ml, 24 mmoles) at 75° for half an hour. After cooling an orange air stable solid was filtered off and washed well with light petrol. Traces of manganese pentacarbonyl bromide were sublimed off onto a 0° probe at 80°/0.1 mm Hg. The new complex was recrystallised from diethyl ether. (Found : C 24.60 H 3.12 O 13.65 Br 23.47 %, M = 345 (ebull. in benzene); $C_7H_{10}S_2MnO_3Br$ requires : C 24.65 H 2.95 O 14.06 Br 23.41 %, M = 341). The complex had a definite melting point at 135-6°. It was very soluble in $CHCl_3$. It was non-conducting in nitrobenzene (Λ = 0 mhos).

The reaction of manganese tetracarbonyl dibromide and 2,5-dithiahexane gave the identical complex, which on heating in 100-20° petroleum ether at 110° remained monomeric.

1,4-dithian manganese tricarbonyl bromide dimer.

Manganese pentacarbonyl bromide (0.7 g, 2.5 mmoles) was allowed to react in 5 ml 80-100° petroleum ether at 65° for 5 minutes. Careful control of the reaction conditions was found to be necessary, as polymerisation easily occurred. After cooling, the orange yellow solid was filtered off and washed well with light petrol. It could be recrystallised from CH_2Cl_2. (Found : C 24.90 H 2.43 O 14.07 %, M = 662 (ebull. in benzene); $C_{14}H_{16}S_4Mn_2O_6Br_2$ requires : C 24.85 H 2.38 O 14.13 %, M = 678). The complex decomposed at about 200° in a closed tube and was non-conducting in nitrobenzene. (Λ = 0 mhos). With manganese tetracarbonyl dibromide the identical complex was obtained in the same reaction conditions.

Polymer

When the reaction was carried out at 100° for half an hour the reaction product was an orange yellow very insoluble solid, which could not be recrystallised. A very small amount of yellow solid was extracted with much $CHCl_3$ and analysed as follows : C 21.55 H 1.44 O 17.21 Mn 19.7 %, M = 558 (ebull. in benzene). The residue had the following analysis : C 26.44 H 3.10 O 13.62 Mn 11.37 %; no conclusions were drawn concerning the structure of these compounds or mixtures of compounds. The polymeric material was non-conducting in nitrobenzene. (Λ = 0 mhos).

3,6,9-trithiaundecane manganese tricarbonyl bromide.

Manganese pentacarbonyl bromide (2.5 g, 9.1 mmoles) in 10 ml 100-20° petroleum ether was allowed to react with an excess of 3,6,9-trithiaundecane (3 ml, 14 mmoles) at 100° for one hour. All the manganese pentacarbonyl reacted and a deep red and very viscous oil sank to the bottom of the reaction vessel. The oil was purified by twice repeated chromatography on alumina in diethyl ether. (Found : C 31.69 H 4.33 O 11.30 Mn 12.61 Br 18.01, 19.03 %, M = 442 (ebull in benzene); $C_{11}H_{18}S_3MnO_3Br$ requires : C 31.58 H 4.24 O 11.19 Mn 12.80 Br 18.58 %, M = 429 (ebull. in benzene). The complex was non-conducting in nitrobenzene (Λ = 0 mhos). The methyl iodide test for uncoordinated sulphur was positive and 380 mg of the oil (0.887 mmoles) in 2.5 ml diglym took up 0.71 equivalents (0.305 mmoles) of B_2H_6 corresponding to 80 % of the amount required for on uncoordinated sulphur atom/molecule. When the B_2H_6 adduct was exposed to air, much effervescence was observed and the 3,6,9-trithiaundecane manganese tricarbonyl bromide could be recovered pure after chromatography on alumina in diethyl ether.

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2,5-dithiahexane was obtained from Light Chemicals and could be used directly. The density was very near to 1 g/ml. In spite of the nauseating smell of this compound no ill effects were found after long exposure to high concentrations of its fumes.

1,4-dithian was prepared from sodium sulphide and ethylene bromide in ethanol. On heating on a steam bath white polymer precipitated and was subsequently depolymerised by boiling with phenol at 160°. The 1,4-dithian was extracted from the reaction mixture, which was first liberated from phenol by washing with NaOH solution. In order to get pure 1,4-dithian the extraction was best carried out with petrol ether and the ligand was chromatographed on alumina in petroleum ether.[45-47] MP 111-112° . (Found : C 39.50 H 6.93 %, M = 123 (ebull. in benzene); $C_4H_8S_2$ requires : C 39.95 H 6.66 %, M = 120). Oxygen containing impurities often accompanied the ligand.

3,6,9-trithiaundecane was prepared from mustard gas, yperite, according to the method by Helfrich and Reid.[67] The liquid ligand was twice distilled and the fraction 144-46°/ 1 mm Hg was retained. (Bath temperature = 195°) (Found : C 46.5 H 8.8%; $C_8H_{18}S_3$ requires : C 45.3 H 9.4 %). This purity was found sufficient for the reactions carried out. This tridentate ligand seemed to cause slight stomach upset when handled with bare hands, the same effect was noticed on handling the tridentate trithioformaldehyde. (cf. ref. 68).

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