

CARBONYL HALIDES OF THE GROUP VI TRANSITION METALS

X.* FURTHER DITHIOCARBAMATE DERIVATIVES OF MOLYBDENUM HALOCARBONYLS

By R. COLTON† and G. R. SCOLLARY†

[Manuscript received January 19, 1968]

Summary

The changes effected in the stability of molybdenum carbonyl compounds of the types $\text{Mo}(\text{CO})_2 \text{dte}_2$ and $\text{Mo}(\text{CO})_3 \text{dte}_2$ (dte = dialkyldithiocarbamate) and in their carbon monoxide carrying ability, by varying the alkyl group in the dithiocarbamate group, have been investigated.

The oxidation of the carbonyl dithiocarbamate complexes by oxygen to the known molybdenum(v) complexes of the type $\text{Mo}_2\text{O}_3 \text{dte}_4$ is reported. Extensive infrared and mass spectrometric studies on the latter compounds have been carried out.

Attempts to isolate the corresponding tungsten compounds have been unsuccessful.

INTRODUCTION

The carbonyl diethyldithiocarbamate complexes of the types $\text{Mo}(\text{CO})_2 \text{detc}_2$ and $\text{Mo}(\text{CO})_3 \text{detc}_2$ (detc = diethyldithiocarbamate) reported in Part V of this series¹ were shown to constitute a reversible carbon monoxide carrying system. By varying the size of the alkyl group it is possible to affect this carrier system and so stabilize either the tricarbonyl or dicarbonyl compound.

The diamagnetic molybdenum(v) dithiocarbamate complexes, $\text{Mo}_2\text{O}_3 \text{dte}_4$, were first prepared by Malatesta,² and an improved method has recently been reported.³ Both these methods involve reduction of molybdate ion. The oxidation of the molybdenum(II) carbonyl dithiocarbamates by air has now been shown to give the same species.

RESULTS AND DISCUSSION

Complexes of the type $\text{Mo}(\text{CO})_3 \text{dte}_2$ using the dimethyl, dibenzyl, and pyrrolidyl dithiocarbamate ligands are prepared by the interaction of the sodium salt of the ligand and dichlorotetracarbonylmolybdenum(II).⁴ The orange compounds thus formed are sensitive to oxygen and all carbonyl groups are lost when the compounds are dissolved in organic solvents, similar to the results briefly mentioned previously for the diethyldithiocarbamate compound.¹

* Part IX, *Aust. J. Chem.*, 1967, **21**, 1159.

† Department of Inorganic Chemistry, University of Melbourne, Parkville, Vic. 3052.

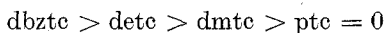
¹ Colton, R., Scollary, G. R., and Tomkins, I. B., *Aust. J. Chem.*, 1968, **21**, 15.

² Malatesta, L., *Gazz. chim. ital.*, 1939, **69**, 752.

³ Moore, F. W., and Larson, M. L., *Inorg. Chem.*, 1967, **6**, 998.

⁴ Colton, R., and Tomkins, I. B., *Aust. J. Chem.*, 1966, **19**, 1143.

The rate of loss of one molecule of carbon monoxide to form the corresponding dicarbonyl shows a dependence on the nature of the alkyl group in the ligand. With dibenzylidithiocarbamate (dbztc), carbon monoxide is lost very readily when the compound is pumped. The reverse reaction, i.e. absorption of carbon monoxide when damp, is very slow, but it does occur. This compound is thus a carbon monoxide carrier similar to the diethyldithiocarbamate compound.¹ With dimethyldithiocarbamate (dmtc), the loss of carbon monoxide occurs only very slowly and the reaction does not go to completion. However, the appearance of two additional peaks in the carbonyl stretching region of the infrared spectrum, superimposed on those of the tricarbonyl compound, indicates partial conversion into the dicarbonyl compound. The pyrrolidylidithiocarbamate (ptc) tricarbonyl compound does not lose carbon monoxide under these conditions at all. The rate of loss of carbon monoxide may be summarized as



This rate may be correlated with the size and steric hindrance of the alkyl group. The alkyl groups are free to move about and so may interact with the carbonyl groups. By increasing the size of the alkyl group, i.e. increasing the interaction, carbon monoxide is lost more readily and conversely for the addition of carbon monoxide to the dicarbonyls. However, with the pyrrolidyl group, the ring structure hinders movement of the group and so there is less interaction, and it is found that no carbonyl is lost in this case.

TABLE 1
INFRARED SPECTRA (cm^{-1}) OF CARBONYL DERIVATIVES (KBr DISKS)

Compound	$\nu(\text{CO})$	$\nu(\text{CN})$	$\nu(\text{Mo-S})$
$\text{Mo}(\text{CO})_3 \text{ dmtc}_2$	2020, 1920, 1882	1515	377
$\text{Mo}(\text{CO})_3 \text{ detc}_2^*$	2020, 1951, 1935, 1915, 1898	1500	363
$\text{Mo}(\text{CO})_3 \text{ ptc}_2$	2020, 1926, 1885	1498	328
$\text{Mo}(\text{CO})_3 \text{ dbztc}_2$	2030, 1950, 1920	1490m, 1475	385
$\text{Mo}(\text{CO})_2 \text{ dmtc}_2$	1930, 1840	—	—
$\text{Mo}(\text{CO})_2 \text{ detc}_2^{*\dagger}$	1925, 1842 [†]	1505	360
$\text{Mo}(\text{CO})_2 \text{ dbztc}_2$	2010, 1945, 1915w, 1900w	1493m, 1477	385

* See Part V, *Aust. J. Chem.*, 1968, **21**, 15.

† Incorrectly reported previously as 1865 cm^{-1} .

The principal infrared absorptions of these compounds are listed in Table 1. The carbonyl frequencies are generally lower than those reported for the tri- and di-carbonyl phosphine compounds.⁴ However, it would appear that there is no simple explanation for this observation in terms of electronic effects because there are no systematic trends in the C=O, C=N, and Mo-S stretching frequencies even within the dialkyldithiocarbamate series.

In addition it does not appear to be possible to explain the variation of the carbonyl peak positions on changing the alkyl group in terms of the electron releasing ability of the $-\text{NR}_2$ group. It has been shown that for a series of chromium(III) dithiocarbamates, Δ (splitting parameter) is independent of the $-\text{NR}_2$ group,

indicating that this group is too far away from the metal atom to have much effect on the electron distribution on the metal.^{5,6} However, the size of the alkyl group could possibly explain these results; the smaller the alkyl group, the less the interaction with the carbonyl groups and hence the lower the carbonyl stretching frequency. The appearance of two weak sidebands occurring in $\text{Mo}(\text{CO})_2\text{dbztc}_2$ cannot be explained, except to note that they are also known for some carbonyl pyridine complexes.⁷

The position of the CN stretching frequencies, whilst showing that there is partial double bond character, also shows a dependence on the nature of the alkyl group. Cotton and McCleverty⁸ have explained the difference in going from dimethyl to diethyldithiocarbamate in their compounds as being due to the higher electron releasing effect of the methyl group. However, it is generally accepted that the ethyl group has a higher releasing effect, if there is any difference at all, and it is felt that their explanation is in error. A better explanation can be made in terms of mass effects, i.e. the lighter the alkyl group, the higher the CN stretching frequency as observed.

All the carbonyl compounds reported here are diamagnetic. This can be explained for the seven-coordinate compounds as merely obeying the effective atomic number rule and for the six-coordinate compounds, splitting of the octahedral symmetry to give a lower doublet.⁷

An interesting property of all the carbonyl dithiocarbamates is their oxidation reaction. By dissolving in chloroform either the tri- or di-carbonyl compounds of the four dithiocarbamate ligands used (dimethyl, diethyl, dibenzyl, and pyrrolidyl), and passing oxygen through the solution for up to 2 hr, a deep purple compound is formed. The time required is dependent on the size of the alkyl group. The larger the alkyl group, the shorter the time required for oxidation. These compounds have been shown to be the oxo-bridged molybdenum(v) compounds, $\text{Mo}_2\text{O}_3 \cdot \text{dte}_4$. Previous attempts to prepare these molybdenum(v) complexes, by reduction of molybdenum(vi), with alkyl groups larger than ethyl, resulted in the formation of impure purple tars.³ However, the oxidation reaction described above yields pure compounds with alkyl groups as large as benzyl.

The principal infrared absorptions of these compounds are listed in Table 2. The CN stretching frequency shows a dependence on the alkyl group—by increasing the size of this group, lowering of the stretching frequency occurs. This can be best explained by mass effects as described for the carbonyl compounds above.

The Mo-S stretching frequencies are not in agreement with those obtained by Moore and Larson.³ However, for reasons described in Part V,¹ it is felt their assignments are incorrect. However, the frequencies assigned to the Mo-O absorptions are in agreement with the trends observed by these workers for other dithiocarbamate and xanthate complexes of molybdenum(v),³ and for some oxo-bridged chloro species of molybdenum(v).⁹ The strong absorptions near 930 cm^{-1} are readily

⁵ Jørgensen, C. K., *J. inorg. nucl. Chem.*, 1962, **24**, 1571.

⁶ White, A. H., Ph.D. Thesis, University of Melbourne, 1966.

⁷ Colton, R., and Rix, C. J., *Aust. J. Chem.*, 1968, **21**, 1155.

⁸ Cotton, F. A., and McCleverty, J. A., *Inorg. Chem.*, 1964, **3**, 1398.

⁹ Colton, R., and Rose, G. G., *Aust. J. Chem.*, 1968, **21**, 883.

assigned to the molybdenum-oxygen double-bond stretching frequencies,¹⁰ the bands near 750 cm^{-1} (not observed by Moore and Larson³) assigned to antisymmetric molybdenum-oxygen-bridge stretching frequencies, and the bands near 430 cm^{-1} assigned to symmetric molybdenum-oxygen-bridge stretching frequencies. The weak band observed at 877 cm^{-1} in $\text{Mo}_2\text{O}_3\text{ detc}_4$ cannot be assigned in the above scheme, but a peak occurs at this position in the corresponding molybdenum(VI) compound, and this probably indicates that slight oxidation to the molybdenum(VI) compound occurred. The antisymmetric stretch in $\text{Mo}_2\text{O}_3\text{ dbztc}_4$ was not observed, but an intense ligand absorption occurs near 750 cm^{-1} , and this probably obscured any weak molybdenum-oxygen stretch.

TABLE 2
INFRARED SPECTRA (cm^{-1}) OF OXYGEN-BRIDGED COMPLEXES (KBr DISKS)

Compound	$\nu(\text{CN})$	$\nu(\text{Mo-S})$	$\nu(\text{Mo=O})$	$\nu(\text{Mo-O-Mo})$
$\text{Mo}_2\text{O}_3\text{ dmtc}_4$	1534	365	933	758w, 426m
$\text{Mo}_2\text{O}_3\text{ detc}_4$	1508	363	930, 877w	745w, 430m
$\text{Mo}_2\text{O}_3\text{ ptc}_4$	1498	334	927	745w, 428m
$\text{Mo}_2\text{O}_3\text{ dbztc}_4$	1498m, 1478	385	940	427m

As noted above, the positions of the metal-oxygen frequencies agree closely with those observed for a series of dialkyldithiocarbamates and xanthates of the general type $\text{Mo}_2\text{O}_3\text{L}_4$.³ A full structural determination for the compound where L is ethyl xanthate¹¹ has confirmed that the complex contains a linear metal-oxygen-metal arrangement and that the terminal oxygen atoms are *cis* to the bridging atom. Because of the similarity of the infrared spectrum of this compound to those of the dithiocarbamate complexes prepared in this work, it can be inferred that the dithiocarbamate complexes have a similar structure.

The diamagnetism of the oxo-bridged compounds cannot be rationalized directly in terms of the Dunitz and Orgel scheme¹² for $(\text{Ru}_2\text{OCl}_{10})^{4-}$ since on the basis of the scheme the last two electrons should be accommodated in degenerate orbitals, resulting in a paramagnetic complex. For the corresponding ethyl xanthate, a series of energy levels has been devised¹¹ on the basis of the two metal orbitals used in the bridge bonding system being non-planar. This series of orbitals effectively describes the diamagnetism of the complexes.

The solution chemistry of the dithiocarbamate complexes is unusual. With the exception of the dibenzyl compound, the complexes are rather insoluble in most organic solvents, and the purple-red solutions, when prepared, oxidize slowly to give a yellow solution, indicating the formation of the molybdenum(VI) compound. No oxidation was observed with the dibenzyl complex unless benzoyl peroxide or hydrogen peroxide was added. The solution then turned yellow, indicating the existence of a molybdenum(VI) species, but no pure compound could be isolated from the solution.

¹⁰ Barraclough, C. G., Lewis, J., and Nyholm, R. S., *J. chem. Soc.*, 1959, 3552.

¹¹ Blake, A. B., Cotton, F. A., and Wood, J. S., *J. Am. chem. Soc.*, 1964, **86**, 3024.

¹² Dunitz, J. D., and Orgel, L. E., *J. chem. Soc.*, 1953, 2594.

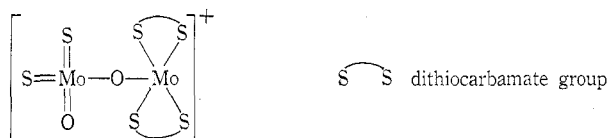
The ultraviolet and visible spectra of the oxo-bridged compounds are recorded in Table 3. Because of the insolubility of these compounds and their tendency to oxidize in solution, the molar extinction coefficients have been quoted to the nearest thousand. The assignment of these bands is rather difficult. The band centred around 508–520 $m\mu$ disappears with time; for the diethyldithiocarbamate complex it disappears in $1\frac{1}{2}$ hr¹³ and the band near 375–380 $m\mu$ increases in intensity. The bands near 508–520 $m\mu$ have been assigned by Moore and Larson³ to a $^2B_2 \rightarrow ^2B_1$ transition and by Mackey¹³ to a $b_{2u} \rightarrow b_{3u}^*$ transition on the basis of the energy diagram calculated for the corresponding ethyl xanthate complex.¹¹ The band at 519 $m\mu$ in the dibenzylthiocarbamate complex is of a much higher intensity and

TABLE 3
ULTRAVIOLET AND VISIBLE SPECTRA IN CHLOROFORM
 λ_{\max} in $m\mu$; ϵ to nearest thousand

Compound	Concn. (M)	λ_{\max} (ϵ)
$\text{Mo}_2\text{O}_3 \text{ dmtc}_4$	0.9×10^{-4} , 1.8×10^{-5}	513 (2000); 378 (5000); 326sh (16000); 265 (44000)
$\text{Mo}_2\text{O}_3 \text{ detc}_4$	0.9×10^{-4} , 1.8×10^{-5}	508 (2000); 375 (5000); 306sh (19000); 260 (59000)
$\text{Mo}_2\text{O}_3 \text{ ptc}_4$	0.9×10^{-4} , 1.8×10^{-5}	508 (2000); 378 (5000); 317sh (19000); 255 (59000)
$\text{Mo}_2\text{O}_3 \text{ dbztc}_4$	1.4×10^{-4} , 5.5×10^{-6}	519 (7000); 375 (8000); 300 (27000); 262 (75000)

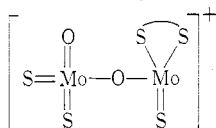
appeared to be anomalous. However, since this is the only compound of the series which is readily soluble in organic solvents, and whose spectrum can be obtained immediately, its spectrum may be more reliable than the spectra of the other compounds. It would seem likely therefore that this band, and also the band at 375 $m\mu$, may be due to sulphur-to-molybdenum charge transfer. The bands around 300–326 $m\mu$ and 255–265 $m\mu$, because of their intensities and position, are most likely due to electron transfer within the ligand molecule.

The mass spectra of the molybdenum(v) dithiocarbamates have been obtained and the main fragments are listed in Table 4. Because of the high mass numbers, the spectrum of the dibenzylthiocarbamate compound is unresolved and no interpretation has been given. The fragments clearly indicate the dimeric oxo-bridged nature of the complex. The fragments containing two molybdenum atoms occur in two series of three ranges, each range containing 16 peaks (molybdenum has 7 naturally occurring isotopes spanning nine mass numbers); the lower fragments contain seven peaks indicating one molybdenum atom per fragment. This pattern may be explained if we assume that an unsymmetrical ion occurs and that the dithiocarbamate group can cleave at one C–S bond and one Mo–S bond. The first ion obtained, $\text{Mo}_2\text{O}_2\text{S}_2 \text{ dtc}_2^+$, may be represented as



¹³ Mackey, D. J., personal communication.

although this is not the only stereoisomer which would fit the facts. The next two ions are obtained by loss of one oxygen or one sulphur from this ion. The second series may be obtained by the loss of one dithiocarbamate group less one sulphur atom [that is loss of (dtc—S)] and the first ion $\text{Mo}_2\text{O}_2\text{S}_3 \text{ dtc}^+$ may be represented as



and the next two ions are formed by loss of an oxygen or a sulphur atom from this ion. It is possible of course that these ions may be formed by loss of (dtc—S) from each of the ions in the first series. The third series contains only one molybdenum atom and shows loss of one oxygen atom in each of two steps from $\text{MoO}_2 \text{ dtc}^+$ to Mo dtc^+ . It is clear that if this fragmentation scheme is realistic there should be a large peak at the resonance-stabilized (dtc—S) fragment in each mass spectrum; this is in fact the case as shown in Table 4.

TABLE 4
MASS NUMBER RANGES

Compound	$\text{Mo}_2\text{O}_3 \text{ dmtc}_4$	$\text{Mo}_2\text{O}_3 \text{ dtc}_4^*$	$\text{Mo}_2\text{O}_3 \text{ ptc}_4$
$\text{Mo}_2\text{O}_2\text{S}_2 \text{ dtc}_2^+$	520-536	576-592	572-588
$\text{Mo}_2\text{OS}_2 \text{ dtc}_2^+$	504-520	560-576	556-572
$\text{Mo}_2\text{O}_2\text{S dtc}_2^+$	488-504	544-560	540-556
$\text{Mo}_2\text{O}_2\text{S}_3 \text{ dtc}^+$	432-448	460-476	458-474
$\text{Mo}_2\text{OS}_3 \text{ dtc}^+$	416-432	444-460	442-458
$\text{Mo}_2\text{O}_2\text{S}_2 \text{ dtc}^+$	400-416	428-444	426-442
$\text{MoO}_2 \text{ dtc}_2^+$	364-372	420-428	416-424
MoO dtc_2^+	348-356	404-412	400-408
Mo dtc_2^+	332-340	388-396	—
(dtc—S)	88	116	114

* Spectrum obtained from Mr D. J. Mackey, although our assignments are given.

Attempts to prepare the corresponding tungsten diethyldithiocarbamate have been unsuccessful. On mixing dichlorotetracarbonyltungsten(II) and sodium diethyldithiocarbamate in ethanol, a mixture of compounds was formed; one compound is yellow and the other white. An infrared spectrum of the mixture showed five carbonyl peaks with a splitting pattern identical to that reported for the molybdenum compound.¹ However, repeated extraction of the mixture with chloroform did not yield any pure carbonyl compound. The same preparation was carried out using chloroform as a solvent. The rather impure compound which formed could not be further purified. The impure compound showed three carbonyl bands in the infrared spectrum.

Malatesta² was unable to prepare tungsten(V) dithiocarbamates or xanthates corresponding to the molybdenum(V) compounds. Hence, it seems that dithio-

carbamates of tungsten, while capable of existence, are rather intractable and will not be easily characterized.

EXPERIMENTAL

Analyses

Samples for molybdenum were fused in sodium hydroxide-sodium peroxide mixtures and molybdenum was determined gravimetrically as its 8-hydroxyquinolate.¹⁴ Carbon, hydrogen, nitrogen, and sulphur analyses were performed by the Australian Microanalytical Service, Melbourne.

Ligands

Dimethyl, dibenzyl, and pyrrolidyl dithiocarbamates were prepared by shaking together an equimolar mixture of the corresponding amine and an aqueous sodium hydroxide solution, followed by the addition of an excess of carbon disulphide. The solution was allowed to evaporate and the resulting solids were recrystallized from an alcohol-ether mixture.

Preparation of Carbonyl Compounds

All of the tricarbonyl complexes are prepared in an identical manner, so that only the preparation of tricarbonylbis(dimethyldithiocarbamato)molybdenum(II) will be described in detail. This preparation is carried out in a nitrogen atmosphere.

Dichlorotetracarbonylmolybdenum(II)⁴ (1 g) and sodium dimethyldithiocarbamate (1.2 g) were mixed in methanol (20 ml) and the solution stirred for 5 min. The brown-orange precipitate was filtered, washed with methanol, and dried under a carbon monoxide stream.

TABLE 5
ANALYTICAL DATA

Compound	Found (%)					Calc. (%)				
	C	H	Mo	N	S	C	H	Mo	N	S
Mo(CO) ₃ dmtc ₂	25.4	3.1	22.9	7.0		25.7	2.9	22.9	6.7	
Mo(CO) ₃ ptc ₂	32.4	3.6	20.6	5.8		33.0	3.4	20.4	5.9	
Mo(CO) ₃ dbztc ₂	54.1	3.9	13.0	3.6		54.8	3.9	13.3	3.9	
Mo(CO) ₃ dbztc ₂	54.8	4.2	14.2	3.8		55.2	4.0	13.8	4.0	
Mo ₂ O ₃ dmtc ₄	19.7	3.5	26.1	7.4	35.0	20.0	3.2	26.6	7.8	35.5
Mo ₂ O ₃ detc ₄	28.3	4.8	23.3	6.6	30.3	28.8	4.8	23.1	6.7	30.8
Mo ₂ O ₃ ptc ₄	29.2	4.0	23.1	6.8	30.7	29.1	3.9	23.4	6.8	31.1
Mo ₂ O ₃ dbztc ₄	53.5	4.3	14.6	4.1	18.8	54.3	4.2	14.5	4.2	19.3

Dicarbonylbis(dibenzylthiocarbamato)molybdenum(II) was prepared from the corresponding tricarbonyl complex by merely pumping under vacuum for about 30 min. The analytical data for all the carbonyl compounds are given in Table 5.

Molybdenum(V) Dithiocarbamates

The procedure to obtain all of the oxidation products of the carbonyl derivatives is identical except for the time factor. Thus only the preparation of the diethyldithiocarbamate compound will be described in detail. Dicarbonylbis(diethyldithiocarbamato)molybdenum(II) was dissolved in acetone and oxygen was bubbled through the solution for 2 hr. The deep purple precipitate was filtered, washed several times with acetone, and dried under vacuum. The analytical data for these compounds are also given in Table 5.

¹⁴ Hollingshead, R. G. W., "Oxine and its Derivatives." (Butterworths: London 1954.)

Physical Measurements

Infrared spectra were recorded on Perkin-Elmer 327 and 421 instruments. Visible spectra were recorded on a Beckman DK-2A spectrophotometer and mass spectra on an AEI MS9 spectrometer.

ACKNOWLEDGMENTS

The authors are indebted to Mr D. J. Mackey, of this Department, for the loan of his mass spectrum of the diethyldithiocarbamate compound and his helpful discussions on the ultraviolet and visible spectra of the molybdenum(v) compounds.

One of us (G.R.S.) thanks the University of Melbourne for a postgraduate scholarship.