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Complexes of Molybdenum Hexacarbonyl with Imidazolethione Molecules

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Introduction

Substitution reactions of Group VI hexacarbonyls with heterocyclic molecules produce complexes of the type $M(CO)_5L$ (M = Cr, Mo and W). When L is pyridine, pyrazine, pyridazine or pyrimidine the ligands are N-bonded to the metal [1–3] and when L is thiazolidine-2-thione [4] or thiomorpholine-2-thione [5] they are S-bonded to the metal. The behaviour of the latter, S,N-containing heterocyclic molecules, has encouraged us to extend our study [6–11] of the coordination chemistry of imidazolethione containing molecules to similar substitution reactions. We now report the behaviour of imidazolidine-2-thione (*Imdt*), imidazoline-2-thione (*Imt*), N(1)-methylimidazoline-2-thione (*MImt*) and N,N'-dimethylimidazoline-2-thione (*DMImt*) with molybdenum hexacarbonyl.

Experimental

The ligands *Imdt, Imt* and *MImt* were obtained from the Aldrich Chemical Company. *DMImt* was prepared by refluxing 1-methylimidazole (0.31 mol) and methyl iodide (21 ml) in ethyl acetate (8.3 ml) for 1.5 h. After removal of the ethyl acetate, methanol (300 ml), sulphur (11.2 g) and potassium carbonate (10.0 g) were added. The mixture was refluxed, with stirring, for 24 hours. Water (800 ml) was added and the product was extracted with methylene dichloride (8 X 100 ml) and dried over sodium sulphate. The solvent was removed and the pink/white crystalline product was identified by ^1H NMR, mass spectroscopy and infrared spectroscopy. The 1-methylimidazole was obtained from Emanuel Ltd., the remaining chemicals were reagent quality.

The complexes were prepared by dissolving equimolar ($1{:}1 \times 10^{-3}$) quantities of ligand and $Mo(CO)_6$ in purified, deaerated THF (40 ml). The reaction solution was warmed gently, a nitrogen blanket was introduced and the flask was sealed. The reaction solution was then irradiated with U.V. radiation for two hours. The course of the substitution reaction was accompanied by a colour change from colourless to lime-green to brown-yellow, on completion. The solid products were obtained after removal of the solvent. Yields were in the range 33–75%.

Element (C, H, N) analyses were performed by ICI Corporate Laboratory, Runcorn. Infrared spectra were obtained from mulls by means of a Perkin-Elmer 577 grating spectrophotometer in the range 4000–200 cm^{-1}. Electronic spectra in acetone or as mulls were obtained from a Unicam SP1700 spectrophotometer in the range 350–850 nm.

Results and Discussion

The complexes have a very similar physical appearance; their chemical analyses confirm that only one carbonyl group has been replaced by the ligand (Table I); preparations with greater, ligand/carbonyl, ratios produced essentially the same product.

Recrystallisation of the complexes was inhibited by their insolubility in aliphatic and aromatic hydrocarbons; as well as halogenated hydrocarbons; they do exhibit slight solubility in acetone and methanol however.

The major infrared bands of the ligands and the complexes are shown in Table II. The absence of any marked shift to ν(NH) as well as to those 'thioamide' bands [12] having their major contribution from the NH, CH and CN containing absorptions suggests that the imidazole-N atoms are not involved in coordination [13]. The major changes in the infrared spectra involve the thione containing frequencies in the range 780–335 cm^{-1}. In addition,

TABLE I. Analytical Data Found (Calc) %.

Compound	Colour	Mr	C	H	N	MP °C
$Mo(CO)_5Imdt$	Yellow-Brown	338.2	28.4(28.4)	1.96(1.78)	8.2(8.25)	120
$Mo(CO)_5Imt$	Yellow-Brown	336.1	28.4(28.6)	1.10(1.19)	8.6(8.33)	133
$Mo(CO)_5MImt$	Yellow-Brown	350.2	30.5(30.9)	1.83(1.72)	8.64(8.00)	120
$Mo(CO)_5DMImt$	Yellow-Brown	364.2	33.0(33.0)	2.20(2.21)	7.90(7.69)	190

TABLE II. Major Infrared Bands for the Ligands and Complexes ($\mathrm{cm^{-1}}$).

Imdt	Complex	*Imt*	Complex	*MImt*	Complex	*DMImT*	Complex	Assignments[a]
3350 3220	3200	3100	3100	3100	3100	–	–	ν(NH)
–	–	1580	1580	1565	1570	1570	1580	ν(C=C) + ν(C–N)
1480	1460	1460	1475	1455	1455	–	–	ν(C–N) + δ(NH)
	530	785	780	770	770	750	740	
515	510	730	730	730	740	730	730	ν(C–S)
					715			
335	330	335	335	410	410	500	500	δ(C–S)
–	360	–	365	–	365	–	350 365	ν(M–L)

[a]From references 12 and 20.

TABLE III. Infrared Data for the Carbonyl Groups.

Compound	Absorption Band ($\mathrm{cm^{-1}}$)	Assignment	k_1	k_2 mdyne/Å	k_i
$\mathrm{Mo(CO)_5}$*Imdt*	2060 w	A_1	14.33	15.91	0.43
	1985 vs	B_1			
	1830 s	E			
	1870 s	A_1			
$\mathrm{Mo(CO)_5}$*Imt*	2060 w	A_1	14.33	15.91	0.43
	1985 vs	B_1			
	1930 s	E			
	1870 m	A_1			
$\mathrm{Mo(CO)_5}$*MImt*	2060 w	A_1	14.33	15.91	0.39
	1985 vs	B_1			
	1935 s	E			
	1820 m	A_1			
$\mathrm{Mo(CO)_5}$*DMImt*	2060 s	A_1	14.26	15.32	0.29
	1985 ss	B_1			
	1910 vs	B_2			
	1890 vs	A_1			
	1870 vs	A_1			

all the complexes exhibit an absorption in the range 350–365 $\mathrm{cm^{-1}}$, indicative of a largely ν(Mo–S) band.

The carbonyl infrared bands have been assigned [14, 15] on the basis that the complexes have C_{4v} symmetry (Table III). An exception to this is the *DMImt* complex whose vibrational activity is consistent with C_{2v} symmetry. This arises because the *DMImt* molecule adopts a different orientation, with respect to the $\mathrm{Mo(CO)_5}$ fragment, than do the other molecules in this series. In addition, the Raman active B_1 absorptions are observed in the infrared for the C_{4v} complexes, presumably, because of the local symmetry in the solid. The CO stretching frequencies are higher than those of ammine molybdenum pentacarbonyls [16, 17] but are similar to those reported for substituted thiourea molybdenum pentacarbonyls [18]. Furthermore, the force constants k_1 and k_2 as well as the CO–CO interaction constants, k_i, (Table III), have been calculated [16] from the mull spectra. The values exhibit a trend similar to that observed for the CO stretching frequencies and are very similar to the data reported for the thiourea molybdenum pentacarbonyls [18]. These observations add further support to the contention that the imidazolethione molecules S-bond to

TABLE IV. Electronic Spectral Data (nm).

Compound	Band	Positions	Medium
$Mo(CO)_5$*Imdt*	336	390	acetone
$Mo(CO)_5$*Imt*	326	371	acetone
$Mo(CO)_5$*MImT*	350	410	acetone
$Mo(CO)_5$*DMImT*	310	–	mull

molybdenum in these complexes and that the resultant bond contains a significant degree of π-bonding. However, in view of the similarity of the k values to those of $Mo(py)(CO)_5$ it would seem that, as in the latter case, such π-bonding is likely to be weak because of competition for the dπ electrons from the five Mo–CO bonds [16].

The electronic spectra exhibit an intense charge-transfer band in the range 310–350 nm with a shoulder in the range 370–410 nm (Table IV). The former is often an indication of M–S bonding [9, 10]. The latter probably arises from the $^1E \leftarrow {}^1A_1$ transition expected of diamagnetic, pseudo-octahedral, $Mo(CO)_5L$ complexes [19].

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