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Zero-valent Mixed Tetracarbonyl-Xanthate and Dithiocarbamate Complexes of Group VI Metals

M. R. HOUCHIN* and K. MITSIOS

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

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Introduction

The patterns of bands produced by the infrared active stretching vibrations of metal carbonyl complexes are well known [1]. In some cases these patterns are diagnostic of both the number of carbon monoxide molecules coordinated to the metal centre, and of the geometry of the complex. Such is the case for monomeric *cis*-tetracarbonyl complexes at an octahedral metal centre.

Complexes of the type *cis*-[$M(CO)_4L_2$] (where L_2 represents one bidentate ligand or two monodentate ligands) possess C_{2v} symmetry and are expected to exhibit four infrared-active carbonyl stretching bands in the region 1700–2200 cm^{-1}. Orgel [1] suggests that a pair of bands, one very strong (B_1) and the other weak (A_1^{1a}) separated by ~120 cm^{-1} can be attributed to vibrations of the carbonyls *trans* to one another, while two bands of intermediate strength (A_1^{1b} and B_2) are due to vibrations of the *cis* pair of carbonyl groups (Fig. 1).

In the present study, the complexes *cis*-[$M(CO)_4$-L–L]$^-$ where M = Cr^0, Mo^0, W^0 and L–L = dedtc$^-$ and ex$^-$, were identified in DMSO solution by their IR spectra in the carbonyl stretching frequency region. DMSO is free from major absorption bands in this region of the IR, thus enabling solvent peaks to be cancelled (using a balanced reference cell) without loss of sensitivity to carbonyl absorptions. Further, many Group VI tetracarbonyl complexes are soluble in DMSO thereby allowing comparisons of carbonyl stretching frequencies free from solid state effects [2] and differential solvent effects [3].

Experimental

Solution IR spectra were obtained using a cell with barium fluoride windows. Approximately 0.03 mol dm^{-3} concentrations were found to be appropriate for a cell of 0.1 mm pathlength. An optically balanced reference cell filled with DMSO was used to cancel solvent peaks. Calibrated spectra were recorded on a Perkin-Elmer 457 Grating Infrared Spectrophotometer.

All reactions were performed under a nitrogen atmosphere.

Preparation of Complexes

Deoxygenated DMSO (30 cm^3) was added to a degassed reaction vessel containing 1.0 mmol of metal hexacarbonyl and 1.0 mmol of the ligand salt (potassium ethylxanthate or sodium diethyldithiocarbamate). The vessel was heated to 60–65 °C and as the reaction proceeded, the colour of the solution changed from pale yellow to red–brown. Reaction was generally complete in less than 30 minutes. The progress of the reaction was monitored by transferring small samples of the reaction solution to the cell *via* a syringe. The syringe, after removal of the needle, formed an air-tight seal with the cell inlet ports. An excess of solution was used to flush out any air or solvent present in the cell. The cell was then immediately sealed with polystyrene stoppers and the IR spectrum recorded in the carbonyl stretching frequency region.

The complexes *cis*-[$W(CO)_4$bipyr] and *cis*-[$W(CO)_4$tmen] (where bipyr = bipyridyl and tmen = N,N,N′,N′-tetramethylethylenediamine) were prepared by literature methods [4, 5].

Results and Discussion

Details of the IR spectra of the Group VI tetracarbonyl complexes and the Group VI hexacarbonyls (heated in DMSO at 65 °C) are presented in Table I. Also included in this table are the carbonyl stretching frequencies observed for the complexes *cis*-[$W(CO)_4$-bipyr] and *cis*-[$W(CO)_4$tmen] in DMSO solution (see also Fig. 2(c) and 2(d)).

Figure 2(a) shows the changes which occur in the carbonyl stretching frequency region of the IR as $Mo(CO)_6$ and ex$^-$ react to form *cis*-[$Mo(CO)_4$ex]$^-$. The single $Mo(CO)_6$ peak at 1965 cm^{-1} is progressively replaced by the four *cis*-[$Mo(CO)_4$ex]$^-$ bands at 1995 cm^{-1} (A_1^{1a}), 1878 cm^{-1} (B_1), 1850 cm^{-1} (A_1^{1b}) and 1808 cm^{-1} (B_2) over a period of ~15 minutes. There is a further peak at 1919 cm^{-1} (Fig. 2(a) (i) & (ii)). The origin of this band is uncertain. It may be due to initial formation of a xanthate pentacarbonyl complex (the other peaks expected for a pentacarbonyl complex being obscured by the tetracarbonyl and hexacarbonyl bands). An alternative explanation might be the formation of an inter-

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*Author to whom correspondence should be addressed. Present address: Division of Mineral Chemistry, Commonwealth Scientific and Industrial Research Organization, P.O. Box 124, Port Melbourne, Vic. 3207, Australia.

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TABLE I. IR Data for the Complexes.

Compound	νCO (cm^{-1})			
	T_{1u}			
$Cr(CO)_6$	1967			
$Mo(CO)_6$	1965			
$W(CO)_6$	1960			
	A_1^{1a}	B_1	A_1^{1b}	B_2
cis-$[Cr(CO)_4ex]^-$	1980	1870	1850	1805
cis-$[Cr(CO)_4dedtc]^-$	1978	1861	1835	1788
cis-$[Mo(CO)_4ex]^-$	1995	1878	1850	1808
cis-$[Mo(CO)_4dedtc]^-$	1991	1868	1838	1795
cis-$[W(CO)_4ex]^-$	1990	1863	1843	1802
cis-$[W(CO)_4dedtc]^-$	1981	1853	1831	1791
cis-$[W(CO)_4bipyr]$	1995	1887	1861	1818
cis-$[W(CO)_4tmen]$	1993	1858	1848(sh)	1805

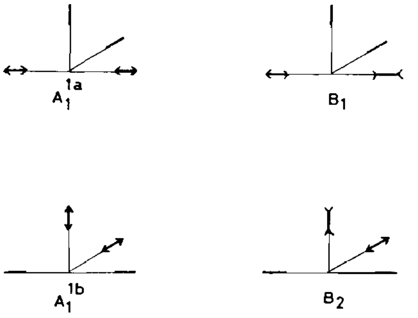

Fig. 1. Vibration modes of the carbonyl groups in complexes of the type *cis*-$[M(CO)_4L_2]$.

mediate molybdenum–carbonyl–DMSO complex. However, this seems less likely since $Mo(CO)_6$, when heated in DMSO in the absence of ex^-, showed no such peak. An analogous band appeared in the IR spectra during the formation of the Cr and W tetracarbonyl xanthate complexes, but not during the formation of any of the analogous dithiocarbamate tetracarbonyl complexes (see, for example, the formation of *cis*-$[Cr(CO)_4dedtc]^-$ in Fig. 2(b)).

Whilst all the above tetracarbonyl complexes appeared reasonably stable in DMSO solutions at moderate temperatures (~60 °C), higher temperatures caused a gradual collapse of the tetracarbonyl IR spectra.

To date all attempts to isolate these complexes have been unsuccessful. However, the IR spectra of the analogous bipyr tetracarbonyl complexes, whether isolated and dissolved in DMSO or prepared in DMSO solution as described above, showed similar spectra to the $dedtc^-$ and ex^- complexes (see Fig. 2(c)).

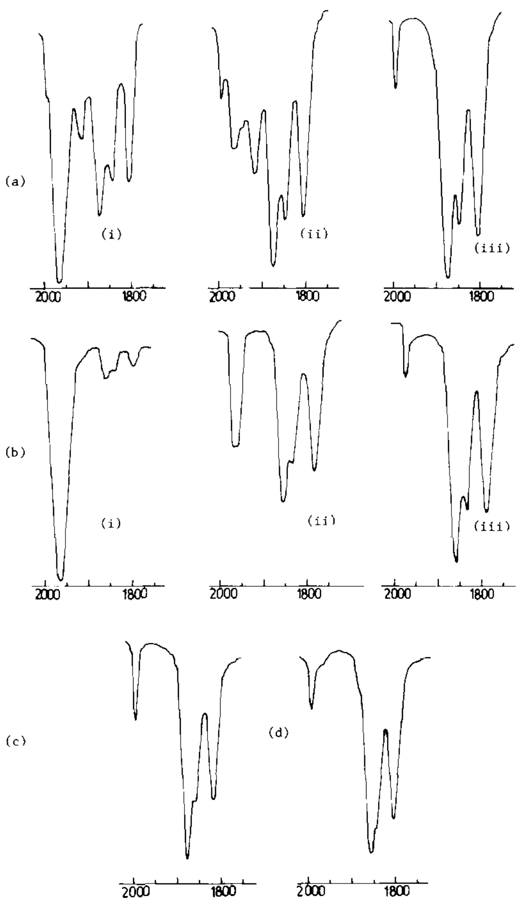

Fig. 2. IR spectra in the carbonyl stretching frequency region showing the formation of: (a) *cis*-$[Mo(CO)_4ex]^-$; (b) *cis*-$[Cr(CO)_4dedtc]^-$; (c) *cis*-$[W(CO)_4bipyr]$; (d) *cis*-$[W(CO)_4tmen]$.

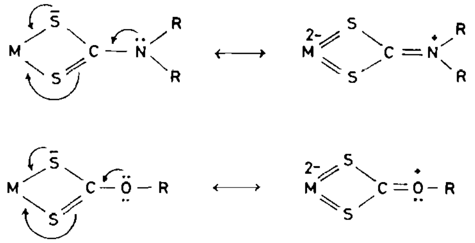

Fig. 3. π-Effects for dithiocarbamate and xanthate ligands.

The ease with which $dedtc^-$ and ex^- react with the group VI hexacarbonyls in DMSO solution is surprising. Reaction temperatures of ~60 °C are sufficient to promote rapid reaction of the xanthate and dithiocarbamate anions with $Cr(CO)_6$ and $Mo(CO)_6$, while reaction with $W(CO)_6$ is somewhat slower. (This order of reactivity has been attributed to the stronger W–C σ bonds in $W(CO)_6$ [6]). Attempts to prepare the tetracarbonyl complex anions in boiling chloroform, toluene and xylene using solvent-soluble ligand salts, all proved unsuccessful.

In the series of complexes *cis*-$[W(CO)_4L{-}L]$ where L–L = bipyr, tmen, ex^- or $dedtc^-$ (Table I), bipyr is a π electron accepting ligand whereas tetramethylethylenediamine is not capable of either accepting or donating π electron density to a coordinated metal. Dithiocarbamate and xanthate ligands can accept π electron density into the empty 3d orbitals of the sulphur donor atoms. They can also donate π electron density (Fig. 3). The negative charge on the xanthate and dithiocarbamate ligands should enhance ligand to metal electron donation.

The data in Table I show that *cis*-$[W(CO)_4$bipyr] exhibits higher carbonyl stretching frequencies than *cis*-$[W(CO)_4$tmen], as would be expected. The carbonyl stretching frequencies of *cis*-$[W(CO)_4ex]^-$ are, on average, slightly lower than those for the tmen complex, while *cis*-$[W(CO)_4dedtc]^-$ has considerably lower carbonyl stretching frequencies. Assuming the variations in the σ electron donating abilities of the ligands to be small, the results imply that, in the above series of complexes, the π accepting and donating properties of ethylxanthate approximately cancel. For diethyldithiocarbamate, the π donating effects predominate. This observation is consistent with the presence of the more electronegative oxygen atom in ex^- compared to the nitrogen atom in $dedtc^-$. This results in less electron density being transferred to the coordinated metal in the ex^- complex compared with the $dedtc^-$ complex (Fig. 3).

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