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Octahedral Metal Carbonyls. XXXI.[1a] The Low Energy Raman Spectra of Monosubstituted Lewis Base Derivatives of the Group VIB Metal Carbonyls

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Polarized Raman spectra in methylene chloride have been obtained for a number of complexes of the type $LM(CO)_5$ (L = Lewis base; M = Cr, W) in the region 100–680 cm^{-1}. The spectral data, together with previously reported infrared data, have allowed assignment of the metal–carbon and ligand–metal stretching modes for these complexes. The assignments for these and other observed absorptions are discussed.

Introduction

The low energy vibrational spectra of metal carbonyls and their derivatives have been the subject of increasing attention in the past several years. Recently, the infrared spectra (300–700 cm^{-1}) of a large number of $LM(CO)_5$ complexes (L = Lewis base; M = Cr, Mo, W) were reported.[2] However, band assignments for the metal–carbon stretching modes and other low energy fundamental vibrations are still incomplete or are the subject of controversy. It was thus important to obtain the Raman spectra, including polarization data, to assist in the clarification of such assignments; some data for $LMo(CO)_5$ complexes (L = Lewis base) had previously allowed the partial assignment of the Mo–C stretching fundamentals.[3] The present report discusses the Raman spectra for a series of $LM(CO)_5$ complexes (M = Cr, W).

Experimental Section

Preparation of Complexes

The complexes $(C_6H_5)_3EM(CO)_5$ (E = P, As, Sb) were prepared by the method of Brown and Dobson.[2] The complexes $(C_6H_5O)_3PW(CO)_5$ and $(n\text{-}C_4H_9)_3P\text{-}W(CO)_5$ were synthesized employing the procedure of Strohmeier and Müller,[4] and were purified by chromatography of the residue after solvent removal on silica (n-heptane eluent) followed by removal of the n-heptane *in vacuo*. The method of Angelici and Malone[5] was employed in the preparation of (pyridine)$W(CO)_5$ and (cyclohexylamine)$W(CO)_5$. The complexes were determined to be pure by chemical analysis (carbon, hydrogen, and, where applicable, nitrogen; North Texas State University Analytical Service) and/or infrared analysis (Perkin Elmer Model 621 grating spectrophotometer) of their carbonyl stretching spectra (1850–2200 cm^{-1}).

Raman Spectra

Raman spectra were recorded on a Cary Model 82 Raman spectrophotometer equipped with a Coherent Radiation Model 52B krypton ion laser. Saturated solutions of the complexes in reagent grade dichloromethane in 0.2 mm capillary tubes were longitudinally excited employing the 647.1 nm red line of the laser. A focused beam of 250 milliwatts was employed in most instances; a 100 milliwatt defocused beam was required for some complexes to minimize decomposition. All scans were repeated to ensure that decomposition was not significant. The spectral band width employed was 3 cm^{-1}; the accuracy of the reported peak positions is judged to be ± 2 cm^{-1}.

Results and Discussion

The M–C–O Deformation Modes

Bands in the region 500–680 cm^{-1} are given in Table I. While six of the seven M–C–O deformation modes spanned for $LM(CO)_5$ complexes of formal C_{4v} symmetry are Raman-active ($A_1+B_1+B_2+3E$),[6] previous studies of related molecules have shown the deformation modes to be of weak intensity.[7] With one exception the weak bands observed for the $LM(CO)_5$ complexes cannot be assigned as M–C–O deformation modes. The derivatives containing the $(C_6H_5)_3E$–M grouping (E = P, As, Sb; M = Cr, W) all exhibit a polarized band of medium intensity at 655–685 cm^{-1}. These absorptions closely correspond to bands observed for the ligands which have been assigned as sym-

TABLE I. Raman spectra (500–680 cm^{-1}) for LM(CO)$_5$ complexes in dichloromethane (cm^{-1})[a].

Complex	Ligand vibrations	δ MCO	Other bands
$(C_6H_5)_3PCr(CO)_5$	684(mw, p) 617(vw, d)		
$(C_6H_5)_3AsCr(CO)_5$	669.5(m, p) 617(vw, d)		
$(C_6H_5)_3SbCr(CO)_5$	658(m, p) 616(vw, d)		
$(C_6H_5)_3PW(CO)_5$	686(m, p) 618(w, d)		523(vw, p)
$(C_6H_5)_3AsW(CO)_5$	670(m, p) 617(w, d)		
$(C_6H_5)_3SbW(CO)_5$	658(ms, p) 616(w, d)		
$(C_6H_5O)_3PW(CO)_5$	616(ms, d)	597(vwbr, d)	544(vvw, d)
$(n\text{-}C_4H_9)_3PW(CO)_5$			531.5(vw, p)
$(C_5H_5N)W(CO)_5$			652(vw, d) 635(mw, ϱ = 0.5) 602(vwbr, d)
$(c\text{-}C_6H_{11}NH_2)W(CO)_5$			

[a] Relative band intensities and characteristics; s = strong; m = medium; w = weak; v = very; br = broad p = polarized; d = depolarized.

metrical ring deformations,[8] and which may confidently be assigned as such in these complexes. Additionally, complexes containing phenyl groups all exhibit a weak, depolarized absorption *ca.* 617 cm^{-1} which also corresponds to an observed ligand vibration.[8] It is of interest to note that in Cr complexes containing phenyl rings a weak absorption in the infrared at *ca.* 615 cm^{-1} was assigned as a M–C–O deformation mode by Brown and Dobson;[2] this assignment is probably incorrect. For $(C_6H_5O)_3P$, a very weak, depolarized absorption at 597 cm^{-1} which is coincident with a strong absorption in the infrared[2] may be assigned as a M–C–O deformation. The Raman spectra in the M–C–O deformation region are disappointing in that it was hoped that they might provide information with respect to the extent of changes in coupling between M–C–O deformation modes and M–C stretching modes as a function of the electronic nature of L.

The M–C Stretching Modes

Assignment of the metal–carbon stretching modes is best considered in light of the relationships between these modes and those of the metal hexacarbonyls, for which the assignments are unequivocal.[9] A correlation diagram relating the symmetries of the M–C stretching modes for $Cr(CO)_6$ and $W(CO)_6$ ($A_{1g}+E_g+T_{1u}$) to those of the corresponding $LM(CO)_5$ derivatives ($2A_1+B_1+E$) is presented in Figure 1. The absorptions (350–500 cm^{-1}) assigned as M–C stretching fundamentals are given in Table II.

M = Cr

The Cr–C stretching fundamentals for monosubstituted derivatives (C_{4v} symmetry) have only partially been assigned,[2] and those assignments were tenous in the absence of corroborating Raman data and in view of the very substantial differences in the metal–carbon stretching spectra observed for the corresponding complexes of Cr and W. The Raman data, together with the assigned M–C stretching modes for $Cr(CO)_6$ (A_{1g} = 381 cm^{-1}, E_g = 394 cm^{-1} and T_{1u} = 436 cm^{-1}, CCl_4 solution),[9] allow the assignment of all four Cr–C stretching fundamentals with a high degree of confidence. The T_{1u} mode of $Cr(CO)_6$ from which the E mode for $LCr(CO)_5$ complexes is derived (Fig. 1) lies higher in energy than do the A_{1g} and E_g modes, from which the $A_1{}^1$ and B_1 modes of the monosubstituted complexes are derived. It is thus reasonable, on the basis of the mechanics of the vibrations, to expect the E mode for the $LCr(CO)_5$ species to lie at relatively high energy. The band at medium inten-

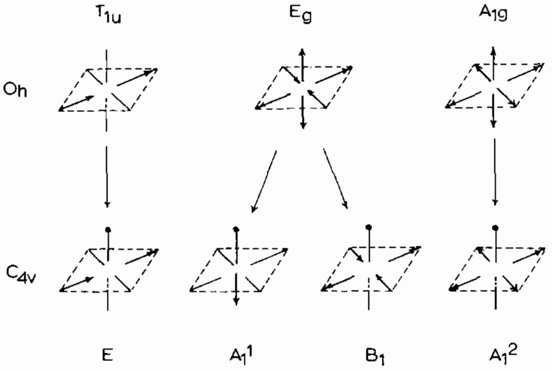

Figure 1. The Symmetries of the Metal–carbon stretching modes for $M(CO)_6$ and $LM(CO)_5$ complexes, and their relationships.

TABLE II. Metal–carbon stretching absorption and band assignments for $LM(CO)_5$ complexes in dichloromethane.

Complex	Metal–carbon stretching modes[a] (frequencies in cm^{-1})			
	A_1^1	A_1^2	B_1	E
$(C_6H_5)_3PCr(CO)_5$	468*R*(m, p)	393*R*(s, p)	405*R*(w. d)	466*IR*(m)[b]
$(C_6H_5)_3AsCr(CO)_5$	473*R*(m, p)	393.5*R*(s, p)	407*R*(w, d)	466*IR*(m)[b]
$(C_6H_5)_3SbCr(CO)_5$	471*R*(m, p)	395*R*(s, p)	406*R*(w, d)	465*IR*(s)[b]
$(C_6H_5)_3PW(CO)_5$	449*R*(s, p) 450*IR*(w)[b]	431*R*(s, p)	425*R*(w, d)	383*IR*(s)[b]
$(C_6H_5)_3AsW(CO)_5$	453*R*(s, p)	431*R*(s, p)	425*R*(w, d)	384*IR*(s)[b]
$(C_6H_5)_3SbW(CO)_5$	451*R*(s, p)	431*R*(s, p) 431*IR*(vw)[b]	427.5*R*(w, d)	386.4*IR*(s)[b] 387*R*(vw, d)
$(C_6H_5O)_3PW(CO)_5$	423*R*(w,p)	435*R*(s, p) 432*IR*(sh)[b]		381.5*IR*(s)[b] 382*R*(vw, d)
$(n\text{-}C_4H_9)_3PW(CO)_5$	449*R*(sh, p)	436*R*(s, p)	428*R*(w, d) 430*IR*(mw)[b]	387*IR*(s)[b] 387*R*(vw,p?)
$(C_5H_5N)W(CO)_5$	473*R*(s, p)	431*R*(s, p) 428*IR*(vw)[b]	425*R*(w, d)	368.5*IR*(s)[b]
$(c\text{-}C_6H_{11}NH_2)W(CO)_5$	478*R*(mw, p)	429*R*(s, p) 429*IR*(w)[b]	420*R*(wsh, d)	371*IR*(vs)[b]

[a] Description of absorptions: *R* = observed in Raman spectrum; *IR* = observed in infrared spectrum. Relative intensities: s = strong; m = medium; w = weak; sh = shoulder; v = very. Polarizations: p = polarized; d = depolarized. [b] Ref. 2.

sity observed in the infrared and which is not coincident with a high energy Raman band thus would appear to be the E mode, as originally assigned by Brown and Dobson.[2] Of the two A_1 modes, easily discernible as strong, polarized absorptions in the Raman spectra, that at higher energy is expected to be the axial A_1 mode (= A_1^1)[10] on the basis of both mechanical considerations and the directional nature of π-bonding,[10] which is expected to increase the strength of the axial metal–carbon bond relative to that of the equatorial bonds in replacing a carbonyl in $Cr(CO)_6$ with a ligand which is a poorer π-acceptor.[10] The B_1 mode in the monosubstituted derivatives, derived from the E_g mode of the hexacarbonyl (Fig. 1), would be expected to be somewhat higher in energy than E_g with replacement of CO by L. Indeed, a weak, depolarized absorption is observed *ca.* 15 cm^{-1} higher in energy than is the E_g mode for the hexacarbonyl. This weak absorption can thus be assigned as the B_1 mode in these complexes.

M = W

The positions of the assigned bands for $W(CO)_6$ are: $A_{1g} = 427.1$ cm^{-1}, $E_g = 412$ cm^{-1} and $T_{1u} = 374$ cm^{-1} in CS_2 solution.[9] Thus the E mode for $LW(CO)_5$ is expected to lie at relatively low energy on the basis of arguments similar to those employed in the assignment of that band in $LCr(CO)_5$ derivatives (see above). Indeed, the E mode has been assigned with little question from the infrared spectra of $LW(CO)_5$ complexes.[2] The assignment is supported by the observation of a weak, coincident absorption (depolarized) for several of the tungsten derivatives. The two A_1 modes are observed as strong, polarized bands at higher energy than the E mode, as expected on the basis of mechanical considerations through comparison with the spectra for $W(CO)_6$. Again, the higher energy of these bands is expected to be A_1^1, which should be strongly influenced by the identity of L since changes in L–W π-bonding are most strongly focused at the axial position. A_1^2, at lower energy, was previously assigned as an A_1 mode on the basis of weak absorptions observed in the infrared.[2] A band observed in the region 410–420 cm^{-1} was incorrectly assigned as an A_1 mode by Brown and Dobson.[2]

Large variations in the position of A_1^1 with the identity of L are observed, and, in fact, for the most strongly π-accepting ligand, $P(OC_6H_5)_3$,[2] A_1^1 is actually lower in energy than is A_1^2. Thus mechanical effects dominate in the determination of the band position for this strongly π-accepting ligand. The sensitivity of the position of $MC(A_1^1)$ to the π-bonding influences of the various L parallels that observed for the corresponding $\nu CO(A_1^1)$, as is illustrated in Figure 2. While data for $Mn(CO)_5Br$ suggest coupling of $\nu MC(A_1^1)$ with the MCO deformation mode of A_1 symmetry may be extensive,[11] influences of coupling effects upon $\nu MC(A_1^1)$ should be minimized through choice of a related series of complexes as in the present case. The observed "reciprocal relationship"[12] between $\nu MC(A_1^1)$ and $\nu CO(A_1^1)$ (Figure 2) has often been noted for vibrations whose relative positions are dominated by π-bonding effects, and may be contrasted to changes in the relative posi-

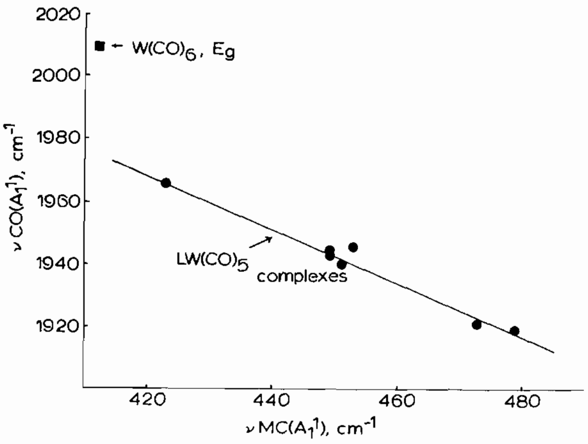

Figure 2. The plot of νCO(A_1^1) vs. νMC(A_1^1) for LW(CO)$_5$ complexes. Carbonyl stretching data are taken from Ref. 2. The point for the related Eg mode for W(CO)$_6$ (Ref. 9) is also shown.

tions of the equatorial carbonyl and metal–carbon stretching modes (A_1^2 and E) among which more complex relationships are observed.[2] These vibrational modes are more insensitive to changes in ligand bonding properties; thus νMC(A_1^2) for LW(CO)$_5$ complexes vary by less than 10 cm^{-1} (Table II).

As was the case for M = Cr, the B_1 mode is expected to be somewhat higher in energy than is the E_g mode from which it is derived. Weak polarized absorptions at *ca.* 425 cm^{-1} seen in the unpolarized spectra only as a weak shoulder employing a spectral bandwidth of 0.5 cm^{-1} but clearly visible in parallel polarization are therefore assigned as the B_1 modes.

Absorptions Below 300 cm^{-1}

The Raman spectra for the $(C_6H_5)_3EM(CO)_5$ complexes (E = P, As, Sb; M = Cr, W) in this region are characterized by two polarized absorptions in the region 140–255 cm^{-1} (Table III). That absorption which varies with L but which is invariant to M, at higher energy, is assigned as a ligand vibration, a ring–E deformation mode.[8] The bands at lower energy are assigned as the M–E stretching modes; their positions are consistent with those previously reported for M–P bonds[13] and with mass effects. Bands attributable to the P–W stretch also are observed for $(n\text{-}C_4H_9)_3P$-W(CO)$_5$ and $(C_6H_5O)_3PW(CO)_5$, but no absorptions which can be assigned as the W–N stretching modes are noted in the 120–400 cm^{-1} spectral region for (pyridine)W(CO)$_5$ and (cyclohexylamine)W(CO)$_5$; it is possible that these absorptions are obscured by solvent absorptions (270–300 cm^{-1}).

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References

1 a. Part XXX: M.N. Memering and G.R. Dobson, *Inorg. Chem., 12,* 2490 (1973).
b. Texas A & M University:
c. North Texas State University.
2 R.A. Brown and G.R. Dobson, *Inorg. Chim. Acta, 6,* 65 (1972), and references cited therein.

TABLE III. Raman spectra (<400 cm^{-1}) for LW(CO)$_5$ complexes in dichloromethane (cm^{-1})[a].

Complex	νML	δ E–C$_6$H$_5$	Other bands
$(C_6H_5)_3PCr(CO)_5$	185.5(ms, p)	253(m, p)	
$(C_6H_5)_3AsCr(CO)_5$	176(ms, p)	238.5(m, p)	
$(C_6H_5)_3SbCr(CO)_5$	174(ms, p)	222(m, p)	
$(C_6H_5)_3PW(CO)_5$	161.5(m, p)	254.5(mw, p)	
$(C_6H_5)_3AsW(CO)_5$	146(m, p)	240(m, p)	
$(C_6H_5)_3SbW(CO)_5$	139(ms, p)	223(m, p)	186.5(w, d)
$(C_6H_5O)_3PW(CO)_5$	168(ms, p)		~238(vwbr, d) ~211(vwbr, ϱ = 0.55)
$(n\text{-}C_4H_9)_3PW(CO)_5$	180(vwbr, p)?		~250(vwbr, p) ~218(vwbr, p) 158(vwbr, p)
$(C_5H_5N)W(CO)_5$			172.5(mw, ϱ = 0.63)
$(c\text{-}C_6H_{11}NH_2)W(CO)_5$			

[a] Relative band intensities and characteristics: s = strong; m = medium; w = weak; v = very; br = broad; p = polarized; d = depolarized.

3 R. Poilblanc and M. Bigorgne, *Bull, Soc. Chim. France,* 1301 (1962).
4 W. Strohmeier and F.J. Müller, *Chem. Ber., 102,* 3608 (1969).
5 R.J. Angelici and M.D. Malone, *Inorg. Chem., 6,* 1731 (1967).
6 G.R. Dobson, I.W. Stolz and R.K. Sheline, *Adv. Inorg. Chem. Radiochem., 8,* 1 (1966).
7 D.M. Adams and A. Squire, *J. Chem. Soc., A,* 2817 (1968).
8 F.W. Parrett, *Spectrochim. Acta, 26A,* 1271 (1970).
9 L.H. Jones, R.S. McDowell and M. Goldblatt, *Inorg. Chem., 8,* 2348 (1969).
10 See, e.g., F.A. Cotton and C.S. Kraihanzel, *J. Amer. Chem. Soc., 85,* 4432 (1962).
11 D.K. Ottesen, H.B. Gray, L.H. Jones and M. Goldblatt, *Inorg. Chem., 12,* 1051 (1973).
12 See, e.g., L.M. Haines and M.H.B. Stiddard, *Adv. Inorg. Chem. Radiochem., 12,* 53 (1969).
13 A.C. Vandenbroucke, Jr, D.G. Hendricker, R.E. McCarley and J.G. Verkade, *Inorg. Chem., 7,* 1825 (1968); A.A. Chalmers, J. Lewis and R. Whyman, *J. Chem. Soc., A,* 1817 (1967).