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Infrared Spectra of Group VI B Metal Carbonyls Containing Heterocyclic Diamines*

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Received June 21, 1969

The infrared spectra of $M(L-L)(CO)_4$ and $M(L-L)_2(CO)_2$ type compounds (M is Cr^0, Mo^0 or W^0 and L–L is 2,2′-bipyridine (bipy) or 1,10-phenanthroline (phen)) have been obtained from 4000 to 50 cm^{-1}. The CO stretching, M–C stretching, M–CO bending and M–N stretching bands have been assigned empirically. The infrared spectra of $Cr(bipy)_3$ and $Cr(phen)_3$ have been used to confirm the band assignments of the MN stretching modes of the carbonyl compounds.

Introduction

Infrared spectroscopy has been useful in elucidating the structure and bonding of metal carbonyl complexes. Thus far, a large number and variety of metal complexes have been studied in the carbonyl stretching region.[1] Normal coordinate analyses have been carried out on metal hexacarbonyl complexes.[2,3] Semi-empirical MO calculations have been done on simple carbonyls and these data correlated to the infrared data available.[4-6] Several authors[7-10] have discussed semi-quantitatively the bonding of more complexes molecules, such as metal carbonyl phosphines and amines, based on the spectra in the carbonyl stretching region. Far-infrared studies have been made on $M(L)_x(CO)_{n-x}$ type compounds where L is a phosphine or arsine ligand, $n = 4$ or 6, $x = 1$-3 and M is Cr, Mo, W, Fe, and Ni.[11-16,17]

This study reports the infrared spectra (4000-50 cm^{-1}) of a series of metal carbonyl complexes of $M(L-L)(CO)_4$ and $M(L-L)_2(CO)_2$ types where L–L is 2,2′-bipyridine (bipy), 1,10-phenanthroline (phen), or 4,4′-dimethyl-2,2′-bipyridine (44′dmbipy) and M is Cr, Mo and W. Of these compounds the $M(44'\text{-}dmbipy)(CO)_4$ type complexes were prepared for the first time. Previous infrared studies on other $M(L-L)(CO)_4$ type complexes have been reported only in the carbonyl stretching region.[7] Therefore, we have extended our studies to include the remainder of the infrared spectrum. The $M(L-L)_2(CO)_2$ type complexes were prepared by Behrens and Harder,[18] but no infrared studies have been made previously. The bipy and phen complexes of zero-valent chromium, $Cr(bipy)_3$ and $Cr(phen)_3$, were prepared and the infrared spectra obtained.

The infrared spectra of free bipy and phen have already been obtained for the whole region of the infrared spectrum.[19-21] The infrared spectrum of 44′-dmbipy has been reported in the region from 1600 to 700 cm^{-1}.[19] Many complex ions containing bipy and phen as ligands are known, and their infrared spectra studied.[21-23] Therefore a comparison of the spectra observed in this work with those of previous workers will serve as a guide in the identification of ligand and metal-ligand vibrations.

The lone pair electrons on the nitrogen atoms of these ligands form σ-bonds with the metal atom. The existence of metal-ligand π-bonding in these complexes has been demonstrated by Cotton and Kraihanzel[7] through an infrared study of $M(L-L)(CO)_4$ type compounds, where M is Cr, Mo, and W, and L–L is ethylenediamine (en) and bipy, and also by Taube and Herzog[24] for a number of transition metal complexes of low oxidation states with bipy and phen. The purpose of this work is to discuss the nature of the metal-ligand bonds in $M(L-L)(CO)_4$ and $M(L-L)_2(CO)_2$ type complexes based on their infrared spectra.

Experimental Section

Preparation of Compounds. The $M(bipy)(CO)_4$

(*) This work was supported by and ACS-PRF research grant (3318-C3,5) and an NSF research grant (GP-6789).

(1) D. M. Adams, « Metal-Ligand Vibrations », Arnold, London, 1967.

(2) H. Smith and L. H. Jones, *J. Mol. Spectra, 20,* 248 (1966).

(3) R. L. Amster, R. B. Hannan, and M. C. Tobin, *Spectrochim. Acta., 19,* 1489 (1963).

(4) K. Caulton and R. Fenske, *Inorg. Chem., 7,* 1273 (1968).

(5) D. G. Carrell and S. P. McGlynn, *Inorg. Chem., 7,* 1285 (1968).

(6) D. A. Brown, *Transition Metal Chem., 3,* 1 (1967).

(7) C. S. Kraihanzel and F. A. Cotton, *Inorg. Chem., 2,* 533 (1963).

(8) W. A. Graham, *Inorg. Chem., 7,* 315 (1968).

(9) R. P. Stewart and P. M. Treichel, *Inorg. Chem., 7,* 1942 (1968).

(10) L. H. Jones, *Inorg. Chem., 7,* 1681 (1968).

(11) A. C. Vanderbroucke, Jr., D. G. Hendricker, R. E. McCarley, and J. G. Verkade, *Inorg. Chem. 7,* 1825 (1968).

(12) S. Singh, P. P. Singh, and R. Rivest, *Inorg. Chem., 7,* 1236 (1968).

(13) D. M. Adams, *J. Chem. Soc.,* 1771 (1964).

(14) M. A. Bennett and R. J. H. Clark, *ibid.,* 5560 (1964).

(15) A. Loutellier, and M. Bigorgne, *Bull. soc. chim. France,* 3186 (1965).

(16) G. Bouquet, A. Loutellier, and M. Bigorgne, *J. Mol. Structure, 1,* 211 (1968).

(17) A. A. Chalmers, J. Lewis, and R. Whyman, *J. Chem. Soc., (A),* 1817, (1967).

(18) H. Behrens and N. Harder, *Chem. Ber., 97,* 426 (1964).

(19) P. Cheuychit, R. Alan Jones, and W. H. F. Sasse, *J. Chem. Soc.,* 4557, (1964).

(20) J. R. Ferraro, R. Driver, W. R. Walker, and W. Wozniak, *Inorg. Chem., 6,* 1568, (1967).

(21) R. Inskeep, *J. Inorg. Nucl. Chem., 24,* 1763 (1962).

(22) A. A. Schilt and R. C. Taylor, *J. Inorg. Nucl. Chem., 9,* 211 (1959).

(23) J. R. Ferraro and . R. Walker, *Inorg. Chem., 4,* 1382 (1965).

(24) R. Taube and S. Herzog, *Z. Chem., 2,* 29 (1962).

type complexes, where M is Cr, Mo, and W, were prepared according to the method of Stiddard.[25] A similar method was used to prepare the corresponding phen and 44′dmbipy complexes. Complexes of the *cis*–M(L–L)$_2$(CO)$_2$ type, where M is Mo, and W, and L–L is bipy and phen, were prepared by the method of Behrens and Harder.[18]

The complexes, Cr(bipy)$_3$ and Cr(phen)$_3$, were prepared by using two different methods. Following the method of Behrens and Harder[18] 0.12 g of Cr(bipy)(CO)$_4$, prepared as mentioned above, and 0.7 g of bipy were placed in 30 ml. of dry, air-free decalin. After bubbling the solution with dry nitrogen gas for 15 minutes, the temperature of the solution was raised to the boiling point of decalin over a period of one hour. The solution was boiled for 15 minutes and cooled to room temperature. During the reaction the color of the solution changed from red to violet to very dark red. The cooled solution was filtered onto a sintered glass filter crucible, which had been dried in a nitrogen atmosphere. The black solid obtained was dried and stored in high vacuum. Cr(phen)$_3$ was prepared in a similar manner using non-hydrated phen.

The second method employed followed the procedure given by Brauer.[26] One gram of freshly prepared $\{$Cr(CH$_3$COO)$_2\}_2\cdot$2H$_2$O and 1.25 grams of bipy were plcaed in 30 ml of deaerated water and nitrogen gas was bubbled through the solution for 15 minutes, the flask was tightly stoppered and the solution shaken for six hours. After standing for a few minutes a black precipitate appeared on the bottom of the flask. This was filtered, dried, and stored in high vacuum.

Molybdenum, chromium, and tungsten hexacarbonyls were purchased from Alpha Inorganics, Beverly, Mass. 1,10-Phenanthroline, 2,2′-bipyridine and 1,10-phenanthroline hydrate were purchased from Aldrich Chemical Co., Milwaukee, Wis. 4,4′-Dimethyl-2-2′-bipyridine was donated by Reilly Tar and Chemical Co., Indianapolis, Indiana.

The tetracarbonyl complexes are stable in a nitrogen atmosphere, but the dicarbonyl complexes and tris-bipy and tris-phen complexes of Cr(0) decompose upon exposure to air. Therefore, preparations and spectral measurements of these compounds were performed in a nitrogen atmosphere. All the solvents used were distilled over sodium under a nitrogen atmosphere. The carbon, hydrogen, and nitrogen contents of the complexes were determined by Weiler and Strauss, Microanalytical Laboratory, Oxford, England and Hoffman Laboratories, Denver, Colorado. The microanalytical data are presented in Table I.

Spectral Measurements. The infrared spectra were measured by using a Beckman IR-12 (4000-200 cm^{-1}) and a Beckman IR-11 (400-33 cm^{-1}) spectrophotometer. The frequencies were calibrated using polystrene and water vapor. The spectral resolution was approximately 2 cm^{-1} with an accuracy of ±1 cm^{-1}. Special precautions were taken in obtaining the spectra of air-sensitive compounds. Nujol mulls were prepared with Nujol through which nitrogen gas had been bubbled for twelve hours. The mulling procedure was preformed in a Wig–L Bug which had been flushed with dry nitrogen gas. Only after the mull was placed between the plates (CsI or polyethylene), the plates were exposed to the atmosphere. Oxidation or decomposition of the compound did not occur when this procedure was followed. This was confirmed by repeated runs of the mull spectra at different time intervals; no changes in the spectra were observed.

The solutions of these compounds were prepared in a nitrogen atmosphere using a solvent bubbled with dry nitrogen. No sign of decomposition or oxidation of the compound was noted for a solution prepared in this manner.

Results and Discussion

The 2100-1700 cm^{-1} Region (Carbonyl Stretching). Kraihanzel and Cotton[7] have investigated the infrared spectra of complexes of the type M(bipy)(CO)$_4$, where M is Cr, Mo, and W. In the present work this series was extended to include M(phen)(CO)$_4$ and M(44′dmbipy)(CO)$_4$ type compounds. These molecules belong to C_{2v} symmetry, and are expected to show four infrared active carbonyl stretching bands in this region. Table II lists the observed frequencies of these four carbonyl stretching bands for the nine compounds studied. The band assignments are given using Kraihanzel-Cotton's notation[7] throughout this section. The similarity of each frequency in the series indicates that the effect of ligand, L–L, on the CO bonds is similar for the three ligands studied.

Complexes of the type *cis*–M(L–L)$_2$(CO)$_2$ belong to C_2 symmetry and are expected to show two infrared active carbonyl stretching modes. Table II shows that this is the case for the four compounds studied. Cotton and Kraihanzel[27] have calculated the CO stretching force constants (k_1 for CO *trans* to N, and k_2 for CO *cis* to N) and the stretching-stretching interaction constant (k_i) from approximate normal coordinate analysis. For example, k_1, k_2 and k_i of Mo(bipy)(CO)$_4$ were calculated to be 13.92, 15.53 and 0.41 mdyn/A, respectively. Using the same approximations, we have obtained 12.35 and 0.54 mdyn/A for k_1 and k_i, respectively, for *cis*-Mo(bipy)$_2$(CO)$_2$.

If the CO groups of the M(CO)$_6$ type molecule are replaced by non-π-bonding ligand such as ethylenediamine or diethylenetriamine, more electrons become available to form the π–(M–CO) bonds. This results in a strengthening of the π–(M–C) bonds and a weakening of the π–(C–O) bonds. Thus the CO stretching frequencies become lower and the corresponding force constants become smaller. However, bipy and phen can form π–(M–N) bonds with transition metals. Therefore, substitution of the CO groups of hexacarbonyl compounds by these ligands does not weaken the π–(CO) bonds as much as ethylenediamine. Thus the order of the force constants

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[25] M. H. B. Stiddard, *J. Chem. Soc.*, 4712 (1962).

[26] G. Brauer, « Handbook of Preparative Inorganic Chemistry », Academic Press, New York, 1965.

[27] F. A. Cotton and C. S. Kraihanzel, *J. Am. Chem. Soc.*, *84*, 4432 (1962).

Table I. Analytical Data

Compound	%C Calcd	%C Found	%H Calcd	%H Found	%N Calcd	%N Found
Cr(bipy)(CO)$_4$	52.55	52.33	2.5	2.72	8.8	8.79
Mo(bipy)(CO)$_4$	46.6	46.21	2.6	2.42	7.60	7.42
W(bipy)(CO)$_4$	37.2	37.31	1.8	2.04	6.2	5.91
Cr(phen)(CO)$_4$	55.78	56.47	2.34	2.39	8.13	8.24
Mo(phen)(CO)$_4$	49.46	49.52	2.07	1.88	7.21	7.23
W(phen)(CO$_4$)	39.50	40.39	1.66	1.64	5.76	5.64
Cr(44′dmbipy)(CO)$_4$	55.15	55.01	4.02	4.05	8.04	8.06
Mo(44′dmbipy)(CO)$_4$	48.97	48.95	3.57	3.18	7.14	7.70
W(44′dmbipy)(CO)$_4$	40.00	40.71	2.91	2.36	5.83	6.74
Mo(bipy)$_2$(CO)$_2$	56.91	56.15	3.47	3.57	12.07	11.87
W(bipy)$_2$(CO)$_2$	47.80	46.80	2.92	2.66	10.14	9.57 [a]
Mo(phen)$_2$(CO)$_2$	50.64	59.82	3.15	3.32	10.93	10.71
W(phen)$_2$(CO)$_2$	51.02	51.55	2.85	3.23	9.33	9.00 [a]
Cr(en)(CO)$_4$	31.15	31.54	3.60	3.73	12.50	13.31
Mo(en)(CO)$_4$	22.88	22.70	3.00	3.29	10.45	10.72
W(en)(CO)$_4$	20.24	20.79	2.25	2.53	7.86	9.46
Cr(bipy)$_3$	69.22	69.59 [a]	4.65	4.54	16.14	15.89
Cr(phen)$_3$	72.96	72.68	4.08	4.61	14.18	14.52

[a] Obtained in separate analysis

Table II. CO Stretching Frequencies of Amine Substituted Metal Carbonyls (cm^{-1})

Compound	Solvent	$A_1^{(2)}$	$B_1^{(2)}$	$A_1^{(2)}$	$B_2^{(1)}$
Cr(bipy)(CO)$_4$	CHCl$_3$	2010 m	1911 vs	1884 sh	1835 s
Mo(bipy)(CO)$_4$	CHCl$_3$	2019 m	1910 vs	1885 sh	1835 s
W(bipy)(CO)$_4$	CHCl$_3$	2010 m	1900 vs	1874 m	1832 s
Cr(phen)(CO)$_4$	CHCl$_3$	2010 s	1904 vs	1886 m	1835 s
Mo(phen)(CO)$_4$	CHCl$_3$	2016 s	1911 vs	1883 m	1835 s
W(phen)(CO)$_4$	CHCl$_3$	2008 s	1890 s	1865 vs	1842 m
Cr(44′dmbipy)(CO)$_4$	ChCl$_3$	2005 s	1900 vs	1870 m	1812 m
Mo(44′dmbipy)(CO)$_4$	CHCl$_3$	2014 s	1910 vs	1886 s	1825 m
W(44′dmbipy)(CO)$_4$	CHCl$_3$	2006 s	1895 vs	1872 s	1810 m
				A	B
cis—Mo(bipy)$_2$(CO)$_2$	mull [a]			1785 s	1712 s
cis—W(bipy)$_2$(CO)$_2$	CS$_2$			1778 vs	1719 s
cis—Mo(phen)$_2$(CO)$_2$	mull			1780 vs	1715 s
	mull			1784 s	1724 s
cis—W(phen)$_2$(CO)$_2$	mull			1780 s	1740 s

[a] Mull spectra are shown because of the insolubility of these complexes in organic solvents

Table III.[a] Absorption Bands of M(L—L)$_x$(CO)$_{6-x}$ in the 300-700 cm^{-1} Region

Compound	Ligand Band					δ(M—CO)						ν(M—C)		
Cr(CO)^b						664 (T_{1u}), [534] (T_{2g})						448 (T_{1u}), [424] (E_g)		
Mo(CO)^b						593 (T_{1u}), [468] (T_{2g})						370 (T_{1u}), [389] (E_g)		
W(CO)$_6$^{b}						584 (T_{1u}), [481] (T_{2g})						373 (T_{1u}), [415] (E_g)		
Bipy	650 s		623 s	510 w	404 m									
Cr(bipy)(CO)$_4$	649 s		630 m	510 w	404 s	638 sh		554 s	492 w			472 s	454 vs	
Mo(bipy)(CO)$_4$	658 s		639 m	511 w	411 w	600 m	580 s	552 m	498 m	474 m	451 m	394 m	384 sh	375 vs
W(bipy)(CO)$_4$	658 w	649 w	628 m	511 w	408 vw	590 m	578 s	562 m	510 w	490 w	458 w		386 sh	378 vs
Phen			626 s		411 m									
Cr(phen)(CO)$_4$	650s		636 m	519 m	413 m	648 sh	585 w	550 m	500 m			462 m	448 s	396 w
Mo(Phen)(CO)$_4$	645 m			519 m	411 w	602 m	582 s	552 m	478 m	464 m	453 m	399 w	384 sh	372 vs
W(phen)(CO)$_4$	645 w		626 m	420 w	411 w	591 m	578 s	561 m	495 w	468 w	454 w		386 sh	379 vs
44Dmbipy	672 s		521 w	427 m	418 m									
Cr(44′dmbipy)(CO)$_4$		645 m	521 m	518 w	417 m	632 m		557 m	497 m			457 vs	431 w	
Mo(44′dmbipy)(CO)$_4$	672 m	645 s		423 w	422 m	601 m	582 m	558 m	501 w	485 w	465 m	407 w	376 vsb	320 w
W(44′dmbipy)(CO)$_4$	670 m	628 s		438 w	427 m	590 w	580 s	568 m	510 w	486 w	471 m	411 m	378 vs	320 w
Mo(bipy)$_2$(CO)$_2$	648 s		625 s	422 w	411 w	590 m	533 m	498 m		462 sh	454 s	369 s	364 sh	
W(bipy)$_2$(CO)$_2$	650 s		623 m	422 w	410 w	575 m	540 m	530 m		469 w	460 m	370 m	368 sh	
Mo(phen)$_2$(CO)$_2$		631 s	623 m	510 w	427 m	591 s	556 m	541 m		472 m	451 m	370 m		

[a] All spectra run as Nujol mulls. [b] Taken from References 2,3 [ ] Raman active vibrations.

becomes

$$\begin{array}{ccc} W(CO)_6 > W(bipy)(CO)_4 > W(en)(CO)_4 \\ 16.41 > 13.87, \quad 15.38 > 13.68, \; 15.01 \; (mdyn/A) \\ k_1 \quad\quad k_2 \quad\quad k_1 \quad\quad k_2 \end{array}$$

If the two CO groups of M(bipy)(CO)$_4$ are substituted by bipy, the carbonyl force constant decreases further. It is not possible, however, to compare M(bipy)$_2$(CO)$_2$ with M(en)$_2$(CO)$_2$, since the latter has not yet been prepared. We may conclude, however, that k$_1$ of *cis*—Mo(en)$_2$(CO)$_2$ would be less than that of *cis*—Mo(bipy)$_2$(CO)$_2$ (12.35 mdyn/A).

Table IV. Comparison of B_2 ν(M–C) Frequencies in Nitromethane and Nitrobenzene (cm^{-1})

Compound	Symmetry Species	Cr	Mo	W	Solvent
$M(CO)_6$	T_{1u}	441	368	374	vapor[a]
		447	368	374	nitrobenzene
$M(en)(CO)_4$	B_2	460	373	374	nitrobenzene
		460	373	383	nitromethane
$M(bipy)(CO)_4$	B_2	451	371	378	nitrobenzene
$M(phen)(CO)_4$	B_2	450	372	380	nitrobenzene
$M(44'dmbipy)(CO)_4$	B_2	452	371	378	nitrobenzene

[a] Taken from Ref. 28

The 700 to 300 cm^{-1} Region. In this region one would expect the metal-carbonyl bending δ(M–CO), metal-carbon stretching ν(M–C), and ligand vibrations. The δ(M–CO) and ν(M–C) vibrations are often grouped together because their frequency regions overlap in some cases, and because they may couple with each other in the same symmetry species. As a result, the number of observed bands is in some cases different than that theoretically expected. It was possible, however, to make reasonable empirical assignments using the following criteria. (1) Bands which occur very near the frequencies of δ(M–CO) and ν(M–C) of $M(CO)_6$[1,3] were assigned to the corresponding modes. (2) Normal coordinate analyses[28] on $M(CO)_6$ type compounds show that δ(M–CO) frequencies are generally higher than ν(M–C) frequencies. This order of frequencies is also retained in substituted metal carbonyls.[11,12,14,15] (3) According to Loutellier and Bigorgne,[15] vibrational coupling between δ(M–CO) and ν(M–C) in $Ni(CO)_xL_{4-x}$ where $x = 1\text{-}3$ and $L = PF_3$ is not appreciable. Although this result may not be applicable to other systems, it is reasonable to neglect the effect of coupling as a first approximation.

Table III lists the band assignments derived from these considerations. Compounds of the type M(L–L)-$(CO)_4$, where M is Mo and W, show six bands between 450 and 610 cm^{-1}. Three of these bands occur between 550 and 610 cm^{-1} as a triplet and are assigned to the δ(M–CO) modes. This agrees with the assignments made on the corresponding tetracarbonyl complexes containing phosphine.[13] The other three bands can also be assigned to δ(M–CO) because their frequencies fall in the δ(M–CO) region and the theoretical number of infrared active δ(M–CO) modes is six. The $Cr(L\text{–}L)(CO)_4$ type complexes exhibit δ(Cr–CO) vibrations in the region where ligand vibrations are normally found (625-670 cm^{-1}). Thus the lack of several bands may be due to overlap of δ(Cr–CO) and ligand vibrations.

Theoretically, four bands are expected for the ν(M–C) vibrations of $M(L\text{–}L)(CO)_4$ type complexes. Table III shows that in most cases only three bands are identified as ν(M–C) bands. It is probable that ligands bands which appear in the 430-400 cm^{-1} region also overlap on some of the ν(M–C) bands. As is seen in Table III, each compound exhibits a strong band at a slightly higher frequency than the ν(M–C) mode of the corresponding hexacarbonyl. These strong bands can be assigned to the B_2 ν(M–C) vibrations.[16] Bennett and Clark[14] noted that this particular vibration is sensitive to changes in oxidation state and X in $M(CO)_5X$ type complexes. A study of the solution spectra (Table IV) shows that this bands shifts by 3 to 6 cm^{-1} toward higher frequencies relative to $M(CO)_6$ and by 1 to 10 cm^{-1} toward lower frequencies relative to $M(en)(CO)_4$. These shifts, though small, are uniform in direction. As discussed previously, this result is interpreted as indicating that the M–C bond becomes stronger when more π-electrons are available for M–C back bonding and becomes weaker when competition for back-bonding occurs.

The dicarbonyl complexes of the type *cis*–$M(L\text{–}L)_2$-$(CO)_2$ exhibit complex spectra between 600 and 350 cm^{-1}. These complexes belong to C_2 symmetry and four δ(M–CO) and two ν(M–C) vibrations are expected. Table III shows that six bands occur in the δ(M–CO) region. The occurrence of these additional bands may be due to the presence of both *cis* and *trans*- isomers or the splitting of the fundamental bands in the solid state or the appearance of bands other than δ(M–CO). There is no evidence for the presence of the *trans* isomer in the carbonyl stretching region; two strong bands were observed although only one band is expected for the *trans* isomer. Solution spectra could not be obtained due to low solubility of the complexes in organic solvents, instability of the complexes, and relatively low intensity of the bands in this region. Hence, we were not able to ascertain whether the solution spectra would show fewer bands than the mull spectra.

The 300-50 cm^{-1} Region. Table V lists the observed frequencies between 300 and 50 cm^{-1}. The metal-nitrogen stretching ν(M–N), skeletal bendings δ(C–M–C), δ(C–M–N), and δ(N–M–N) and ligand vibrations may appear in this region. In addition, lattice vibrations are also expected to appear in the same region if the spectrum is obtained in the crystalline state. To distinguish lattice from internal vibrations we have measured the spectra both in the crystalline state and in solution. The spectra were almost identical in two physical states for all the compounds studied. Therefore the frequencies listed in Table V do not seem to include lattice vibrations. Previously, the δ(C–M–C) vibrations have been assigned between 115 and 70 cm^{-1}.[3,11] Other bending modes such as δ(N–M–N) and δ(C–M–N) also occur in approximately the same region. No attempt has been made to distinguish these bands in Table V.

The ν(M–N) vibrations may appear between 300 and 120 cm^{-1}. Table V shows that eight complexes

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(28) L. H. Jones, *Spectrochim. Acta, 19,* 329 (1963).

Table V. Far Infrared Spectra[c] in the 300 to 50 cm^{-1} Region (cm^{-1})

Compound	Ligand Band		ν(M–N)				δ(X–M–Y)[b] or Ligand Band		
bipy	(238)	168[a]					99 m		
$Cr(bipy)(CO)_4$			195 m	178 vw			105 m		
$Mo(bipy)(CO)_4$	255 vw		210 m	184 s			94 m		
$W(bipy)(CO)_4$	254 vw		204 m	177 s			92 m		
cis–$Mo(bipy)_2(CO)_2$	249 w		277 m	266 m	209 m	186 m	115 m	102 m	
cis–$W(bipy)_2(CO)_2$	252 vw		262 m	232 m	204 m	180 w	140 m	127 m	107 m
	247 sb						124 w	112 w	97 w
$Cr(phen)(CO)_4$	306 m	247 m	226 m	193 vw			106 w		
$Mo(phen)(CO)_4$	292 m	244 m	204 s	183 m			102 w		
$W(phen)(CO)_4$	303 m	247 m	206 s	188 m			102 w		
cis–$Mo(phen)_2(CO)_2$	304 m	249 sh	280 m	254 s	228 w	189 w			
cis–$W(phen)_2(CO)_2$	305 m	249 w	240 m	288 s	190 w	175 w			
44′dmbipy	230 w						143 s		
$Mo(44'dmbipy)(CO)_4$	225 w		201 m	178 m			145 m	94 m	
$W(44'dmbipy)(CO)_4$	270 vw		205 w	185 w			136 m	94 m	
$Cr(CO)_5(N(C_2H_4)_3CH)$[d]			185				120	106	
$Mo(CO)_5(N(C_2H_4)_3CH)$[d]			170				107	89	
$W(CO)_5(N(C_2H_4)_3CH)$[d]			168				101	88	
$Cr(bipy)_3$			311 m	228 w	204 w	184 w	70 vs		
$Cr(phen)_3$	204 w		287 w	263 m		186 w	76 m		

( ) Raman band. [a] This ligand band is not usually observed in metal complexes.[3,4] [b] X or Y = C or N. [c] Spectra in Nujol mulls. [d] Taken from Ref. 11.

of the type M(L–L)$(CO)_4$ exhibit two bands each in the region 178 to 226 cm^{-1} and their frequencies are fairly constant although those of other bands vary with the ligands. Since two ν(M–N) bands are predicted from symmetry considerations, these two bands were assigned to the metal-nitrogen stretching modes.

Complexes of the type *cis*–M$(L–L)_2(CO)_2$ exhibit two additional bands in the region between 230 and 280 cm^{-1}. Since four ν(M–N) are infrared active in this type, these two bands, together with those in the 178 to 226 cm^{-1} region are assigned to ν(M–N). As is seen from the carbonyl stretching bands, the CO bond order is reduced appreciably in these dicarbonyl complexes. This indicates that more electrons are available for the M–N bond. Thus the occurence of the ν(M–N) at higher frequencies in dicarbonyl complexes is indicative of stronger M–N bonds in the former.

The complexes, $Cr(dipy)_3$ and $Cr(phen)_3$, enable us to study a spectrum free of ν(M–C), δ(C–M–C), and any vibrations due to carbonyl group vibrations. Both complexes belong to D_3 symmetry which would predict three ν(M–N) to be infrared active (A_2+2E). Table V indicates the bands for these complexes in the 184-311 cm^{-1} region which are not due to ligand vibrations. These bands are tentatively assigned to ν(M–N). Bands which occur at lower frequency may be due to the δ(N–M–N) or ligand vibrations. Recently Vanderbroucke *et al.*[11] have obtained the far-infrared spectra of complexes of the type $M(CO)_5$-$(N(C_2H_4)_3CH)$, where M is Cr, Mo, and W. Although they did not assign the M–N stretching modes they report that these compounds exhibit a band between 185 and 168 cm^{-1}, which may be due to ν(M–N).