fluxed for 3 hr. Solvent then was removed from the reaction mixture at ~30 mm., leaving a brown residue.

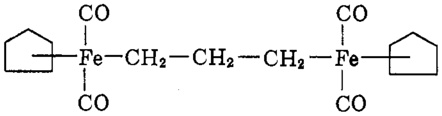
This residue was extracted with three 100-ml. portions of dichloromethane; the extracts were treated with ~50 g. of alumina (Merck) and the brownish extracts filtered by suction, this filtration being extremely slow. The filtrate was treated with dichloromethane to replace solvent that had evaporated during the slow filtration process. Hexane then was added and the solution filtered again. Slow removal of the solvent at ~30 mm. caused orange crystals of the product to separate from the solution. When the volume of the solution was ~40 ml. the evaporation was discontinued. The resulting crystals were filtered, washed with six 50-ml. portions of pentane, and dried to give 9.0 g. (39% yield) of orange crystalline $C_3N_3Cl[C_5H_5Fe(CO)_2]_2$. On heating this material darkened at about 150°.

Anal. Calcd. for $C_{17}H_{10}O_4N_3ClFe$: C, 43.7; H, 2.1; N, 9.0; Cl, 7.6; Fe, 23.9; mol. wt., 467. Found: C, 43.4; H, 2.3; N, 8.8; Cl, 7.7; Fe, 23.2; mol. wt., 483.

Infrared Spectrum.—C–H at 3120 (w) cm.$^{-1}$; carbonyl bands at 2040 (s) and 1970 (s) cm.$^{-1}$; other bands at 1770 (w), 1468 (s), 1435 (m), 1418 (m), 1390 (m), 1363 (s), 1350 (s), 1210 (s), 1190 (s), 1118 (vw), 1063 (vw), 1023 (w), 1009 (w), 965 (m), 855 (m), 839 (m), 806 (m), 786 (s), and 743 (s) cm.$^{-1}$.

Discussion

$(CH_2)_3[Fe(CO)_2C_5H_5]_2$ and higher homologs exhibit properties entirely compatible with σ-bonded structures such as I for the trimethylene derivative. The proton n.m.r. spectrum of $(CH_2)_3[Fe(CO)_2C_5H_5]_2$ shows in addition to a sharp peak for the ten cyclopentadienyl protons a second single sharp peak for all six of the methylene protons. The chemical shifts of both the α- and β-CH_2 groups thus appear to be identical. This is perhaps somewhat surprising but certainly not impossible for structure I.



I

The physical properties of the compounds $(CH_2)_n[Fe(CO)_2C_5H_5]_2$ resemble those of other compounds in which a $-Fe(CO)_2C_5H_5$ group is σ-bonded to a hydrocarbon residue such as the methyl derivative $CH_3Fe(CO)_2C_5H_5$.[3] Thus the trimethylene compound $(CH_2)_3[Fe(CO)_2C_5H_5]_2$ can be sublimed unchanged at 80° (0.1 mm.) and is soluble in organic solvents such as pentane, benzene, and dichloromethane. As compared with the methyl and ethyl derivatives which are reported to be rather air-sensitive, the compounds $(CH_2)_n[Fe(CO)_2C_5H_5]_2$ appear to be fairly stable in air, especially in the solid state. It is to be noted that the melting points of the $(CH_2)_n[Fe(CO)_2C_5H_5]_2$ compounds alternate with increasing values for n.

An attempt to prepare the compound $(CH_2)_2[Fe(CO)_2C_5H_5]_2$ from 1,2-dibromoethane and $C_5H_5Fe(CO)_2Na$ under conditions similar to those used for the preparation of the compounds $(CH_2)_n[Fe(CO)_2C_5H_5]_2$ described in this paper gave a quantitative yield of $[C_5H_5Fe(CO)_2]_2$ rather than the desired compound.

1,4-Dichlorobutyne-2 was found to react with $C_5H_5Fe(CO)_2Na$ to give a mixture of $[C_5H_5Fe(CO)_2]_2$ and the compound $C_5H_5Fe(CO)_2CH_2C{\equiv}CCH_2Fe(CO)_2C_5H_5$, an unsaturated analog of the $(CH_2)_n[Fe(CO)_2C_5H_5]_2$ compounds. An attempt to hydrogenate this compound to $(CH_2)_4[Fe(CO)_2C_5H_5]_2$ instead gave $[C_5H_5Fe(CO)_2]_2$. The reaction between 1,4-dichlorobutene-2 and $C_5H_5Fe(CO)_2Na$ gave only $[C_5H_5Fe(CO)_2]_2$.

In an attempt to prepare a compound containing three $-Fe(CO)_2C_5H_5$ residues cyanuric chloride was allowed to react with $C_5H_5Fe(CO)_2Na$. The product, however, had the composition $C_3N_3Cl[Fe(CO)_2C_5H_5]_2$, only two of the three chlorine atoms being replaced with $-Fe(CO)_2C_5H_5$ groups. This material is an orange crystalline solid. Its air stability is comparable to that of the compounds $(CH_3)_n[Fe(CO)_2C_5H_5]_2$, but its solubility in organic solvents such as pentane is somewhat less.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND LABORATORY OF CHEMICAL AND SOLID STATE PHYSICS, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, CAMBRIDGE, MASSACHUSETTS

Vibrational Spectra and Bonding in Metal Carbonyls. II. Infrared Spectra of Amine-Substituted Group VI Carbonyls in the CO Stretching Region[1a]

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The method presented earlier for interpreting the CO stretching frequencies of substituted metal carbonyls of the type $ML_n(CO)_{6-n}$ in terms of CO stretching and stretch–stretch interaction force constants is applied to molecules in which M = Cr, Mo, and W and the L's are supplied by cyclohexylamine, ethylenediamine, diethylenetriamine, pyridine, and α,α-dipyridyl. The results are discussed in terms of the π-bonding abilities of these ligands. Several of the compounds studied are new and their preparation and characterization are described in detail.

Introduction

In part I[2] a method of analyzing and correlating the CO stretching modes of substituted group VI carbonyls was developed on the basis of valence theory and its applicability demonstrated by applying it to a variety of phosphine-substituted compounds. In this paper we report data and analysis thereof, using the same princi-

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(1) (a) Supported by the U. S. Atomic Energy Commission. (b) Fellow of the Alfred P. Sloan Foundation.

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

ples, for some amine-substituted group VI carbonyls. The present work serves to confirm the correctness and extend the practicability of the method and provides further semiquantitative support for the generally accepted views concerning the nature of metal–ligand bonding in metal carbonyls and similar compounds of low-valent metals.

Compounds with Aliphatic Amines

The compounds with aliphatic amines are directly analogous to the phosphine compounds previously[2] treated and no new theoretical considerations are required. However, it is generally believed that while phosphines have significant ability to accept $d\pi$ electrons (using their $3d\pi$ orbitals), aliphatic amines have no ability to do so except by a hyperconjugation mechanism which should be relatively ineffectual. Thus we might expect significant differences in force constants and perhaps also some qualitative differences in the appearance of the spectra of stoichiometrically and structurally analogous phosphine- and (aliphatic) amine-substituted compounds. Both of these expectations are confirmed in such ways as to substantiate the assignments previously made of the spectra of the phosphine-substituted compounds. Three types of aliphatic amine-substituted group VI carbonyls were prepared and studied, *viz.*, $M(Am)(CO)_5$, *cis*-$M(Am)_2(CO)_4$, and *cis*-$M(Am)_3(CO)_3$.

Relatively few $M(Am)(CO)_5$ compounds have been reported[3,4] and the methods were undesirably elaborate in one way or another. We therefore prepared some new ones in which Am = cyclohexylamine by a straightforward thermal reaction of Am with $M(CO)_6$.

The ethylenediamine derivatives, $M(en)(CO)_4$, apparently have not been reported before. They too were obtained easily by direct reaction. The preparation of the diethylenetriamine compounds, $M(trien)(CO)_3$, of Cr and W by direct reaction already has been reported[5]; we also have prepared the molybdenum compound in this way.

It is very desirable, wherever possible, to use in the force constant calculations frequencies for molecules in solution rather than in the solid phase since intermolecular interactions can have appreciable effects upon the frequencies and can even cause drastic *qualitative* changes in the appearance of the spectra.[6] It is an interesting irony that the more insoluble a compound is, the stronger must be the intermolecular interactions and hence the more necessary that solution spectra be obtained; that is, the difficulties tend to increase in proportion to the need. The $M(en)(CO)_4$ and $M(dien)(CO)_3$ compounds all are extremely insoluble in commonly used infrared solvents. We reasoned that the important intermolecular interactions were probably due to NH···OC hydrogen bonding. Therefore the most desirable sort of solvent would be one which could supplant the CO groups as proton acceptors without at the same time forming hydrogen bonds to the CO groups for the latter action would have an unwanted effect on the CO stretching frequencies. Another requirement of a suitable solvent is the obvious but rather restrictive one that it not absorb strongly in the 1700–2200 cm.$^{-1}$ region. With these requirements in mind, polyethers (*e.g.*, glyme and diglyme) and nitromethane were tried. The last proved most generally satisfactory and can be recommended as a useful solvent for study of CO stretching frequencies in metal carbonyl compounds. Unfortunately, $W(dien)(CO)_3$ and $Cr(dien)(CO)_3$ are insufficiently soluble even in CH_3NO_2 and thus only mull spectra were obtained. Fortunately a comparison of the spectra of $Mo(dien)(CO)_3$ in CH_3NO_2 and in a mull was possible. The mull spectra of the three compounds are similar and show splitting of peaks and fine structure not present in the spectrum of $Mo(dien)(CO)_3$ in CH_3NO_2.

TABLE I

OBSERVED AND CALCULATED CO STRETCHING FREQUENCIES AND FORCE CONSTANTS FOR CYCLOHEXYLAMINE METAL PENTACARBONYLS

Compound	Observed bands,[a] cm.$^{-1}$	Calcd. frequencies, cm.$^{-1}$	Force constants[b]		
			k_1	k_2	k_i
$Cr(Cy)(CO)_5$	2067 ± 5	2064	14.59	15.77	0.32
	1980 ± 5	1976			
	1935 ± 5	1937			
	1890 ± 10	1890			
$Mo(Cy)(CO)_5$	2072 ± 5	2068	14.65	15.83	.32
	1983 ± 5	1980			
	1938 ± 5	1939			
	1895 ± 10	1895			
$W(Cy)(CO)_5$	2071 ± 5	2072	14.65	15.74	.35
	1974 ± 5	1974			
	1929 ± 5	1929			
	1894 ± 15	1892			

[a] All data from chloroform solutions. [b] In mdynes per Å.

$M(Am)(CO)_4$ Compounds.—The frequencies of the absorption peaks of the CO stretching modes in these compounds are recorded in Table I. The spectrum of the molybdenum compound is shown in Fig. 1; the spectra of the chromium and tungsten compounds are identical in all qualitative features. An assignment of the normal modes was made by analogy to the assignment for the $M((C_6H_5)_3P)(CO)_5$ compounds, by using qualitative considerations about intensities, and by considering the shifts expected on changing from a phosphine, which can form π-bonds, to an amine which cannot. Here and subsequently, the symmetry considerations and secular equations of Table I, part I,[2] will be used.

The secular equations show that band 1 must be due to the A_1 mode which is largely localized in the $CO^{(2)}$ group; the weakness of the band is consistent with this.[2,7] It has been shown that in the $M((C_6H_5)_3P)(CO)_5$ compounds, band 2 is due to the B_1 mode (Ra-

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(3) H. Behrens and J. Köhler, *Z. anorg. allgem. Chem.*, **300**, 51 (1959).

(4) W. Strohmeier, K. Gerlach, and G. Matthias, *Z. Naturforsch.*, **15b**, 621 (1960).

(5) E. Abel, M. Bennett, and G. Wilkinson, *J. Chem. Soc.*, 2325 (1959).

(6) The solid state spectrum of $Mo(en)(CO)_4$ is strikingly different from the solution spectrum and would be grossly misleading if subjected to the kind of interpretations made in this paper.

(7) L. E. Orgel, *Inorg. Chem.*, **1**, 25 (1962).

TABLE II

CO STRETCHING FREQUENCIES OF AMINE–SUBSTITUTED GROUP VI CARBONYLS

Compound[a,b]	Frequencies,[c] cm.$^{-1}$ Band 1	Band 2	Band 3	Band 4	Solvent
Cr(Cy)(CO)$_5$	2067	1980	1935	1890*	CHCl$_3$
Mo(Cy)(CO)$_5$	2072	1983	1938	1895*	CHCl$_3$
W(Cy)(CO)$_5$	2071	1974	1929	1894*	CHCl$_3$
Cr(en)(CO)$_4$	2004	1873*	1855*	1810	CH$_3$NO$_2$
Mo(en)(CO)$_4$	2015	1890	1864*	1818	CH$_3$NO$_2$
W(en)(CO)$_4$	2006	1867	1852*	1809	CH$_3$NO$_2$
Cr(dien)(CO)$_3$	1884	1735			Mull
Mo(dien)(CO)$_3$	1898	1758			CH$_3$NO$_2$
Mo(dien)(CO)$_3$	1887	1734			Mull
W(dien)(CO)$_3$	1877	1727			Mull
Cr(py)(CO)$_5$	2073	1986	1938	1905*	CHCl$_3$
Mo(py)(CO)$_5$	2079	1987	1944	1890*	CHCl$_3$
W(py)(CO)$_5$	2076	1980	1933	1895*	CHCl$_3$
Cr(py)$_2$(CO)$_4$	2020	1899	~1878	1837	CH$_3$CN
Mo(py)$_2$(CO)$_4$	2025	1907	~1881	1839	CH$_3$CN
W(py)$_2$(CO)$_4$	2012	1888	1869	1828	CHCl$_3$
Cr(dipy)(CO)$_4$	2012	1905	1880	1828	CHCl$_3$
Mo(dipy)(CO)$_4$	2017	1909	1878	1829	CHCl$_3$
W(dipy)(CO)$_4$	2010	1899	1873	1826	CHCl$_3$

[a] All data were obtained using CaF$_2$ optics; frequencies were calibrated using polystyrene film and are believed accurate to ±5 cm.$^{-1}$ except for the starred ones which may be uncertain to ±10 cm.$^{-1}$ because of poor resolution and those preceded by ~ where limits of error are probably still greater. [b] Cy = cyclohexylamine; en = ethylenediamine; dien = diethylenetriamine; py = pyridine; dipy = α,α′-dipyridyl. [c] Band numbering is purely sequential for purposes of reference; *cf.* Fig. 1, 2, 3, and 4.

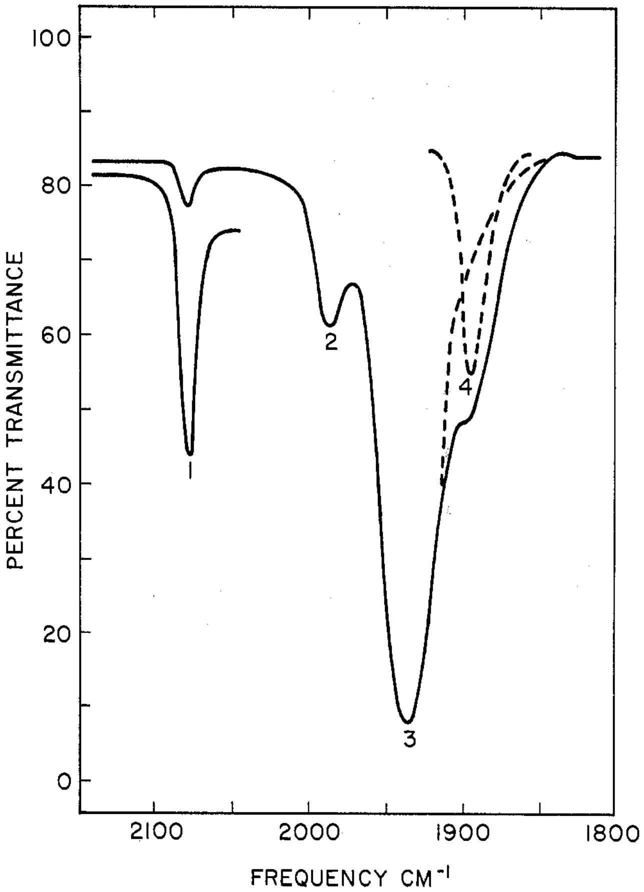

Fig. 1.—The infrared spectrum of $C_6H_{11}NH_2Mo(CO)_5$ in the CO stretching region. Upper solid curve: 6 mg./ml. in CHCl$_3$, cell thickness, 0.1 mm. Lower solid curve: ~35 mg./ml. in CHCl$_3$; cell thickness, 0.1 mm. Dotted curves show theoretical resolution of low-energy region. The numbers of the bands correspond to those in Table I.

man active only, in strict C_{4v} symmetry) which gains some infrared intensity because the structure of the ligand makes it impossible for the molecule to have perfect C_{4v} symmetry. A similar assignment seems justified here. Bands 3 and 4 must be due to the E mode and to that A_1 mode which is mainly localized in $CO^{(1)}$. In $M((C_6H_5)_3P)(CO)_5$ it was found that these two modes are accidentally degenerate, or so nearly so that the bands are entirely unresolved. It would be expected that lowering the π-acceptor strength of the substituent would lower the force constant k_1 more than it would lower k_2 and from the secular equation it follows that the A_1 mode would therefore become lower in frequency than the E mode. Thus we assign band 3 as due to the E mode and band 4 as due to the A_1 mode.

Using this assignment the force constants in Table I were calculated by a procedure of successive approximations in which k_2 and k_i were adjusted to minimize the sum of the squares of the deviations in the frequencies for bands 1–3 while simultaneously adjusting k_1 to provide an exact fit for band 4.

M(en)(CO)$_4$ Compounds.—For these *cis*-disubstituted compounds all four non-degenerate CO stretching modes are infrared active. The frequencies of the observed bands are recorded in Table II and a typical spectrum is shown in Fig. 2. As noted previously in connection with the analogous diphosphine compounds, band 1 can be assigned unequivocally from the secular equations to that A_1 mode which mainly involves the $CO^{(2)}$ groups, but no other certain assignments can be obtained simply by inspection of the secular equations; examination of the force constants calculated for each of the six possible assignments in the phosphine compounds showed that only one appeared acceptable, namely

Band 1: A_1, mainly in $CO^{(2)}$ groups
Band 2: A_1, mainly in $CO^{(1)}$ groups
Band 3: B_1, mainly in $CO^{(2)}$ groups
Band 4: B_2, mainly in $CO^{(1)}$ groups

Since the amine nitrogens are less able to accept dπ electrons from the metal than are phosphorus atoms, we should expect certain qualitative changes in the spectrum on replacing P by N. The force constant for the $CO^{(1)}$ groups should drop more than the force constant of the $CO^{(2)}$ groups.[8] Therefore, the lower frequency A_1 mode should move from a frequency slightly above the B_1 mode to a frequency somewhat below it and the frequency difference between the B_1 and B_2 modes should become greater. These considerations thus suggest the following assignment for Mo(en)(CO)$_4$

Band 1: A_1, mainly in $CO^{(2)}$ groups
Band 2: B_1, mainly in $CO^{(2)}$ groups
Band 3: A_1, mainly in $CO^{(1)}$ groups
Band 4: B_2, mainly in $CO^{(1)}$ groups

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(8) Empirical support for this prediction is obtained from the force constants of the ML(CO)$_5$ compounds. On replacing $(C_6H_5)_3P$ by $C_6H_{11}NH_2$ the k_1 values drop by about 0.9 while the k_2 values drop by ~0.15.

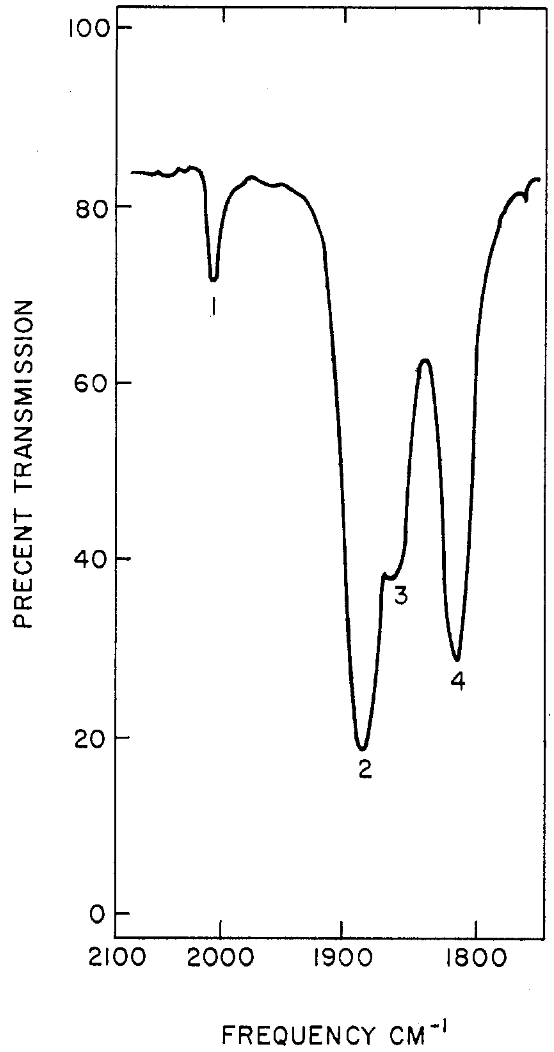

Fig. 2.—The infrared spectrum of Mo(en)$(CO)_4$ in the CO stretching region: ~5 mg./ml. in CH_3NO_2; 0.1 mm. cell thickness.

In order to test further the validity of this assignment, we have, as before,[2] calculated force constants for all six possible assignments. The frequencies of bands 1, 2, and 4 (Table II) were used for this purpose since they can be measured most accurately. The acceptability of a given assignment then was judged both on the relative values of the force constants and on the accuracy with which these force constants produced the frequency of band 3. Table III gives the results for Mo(en)$(CO)_4$; results for the Cr and W compounds were essentially the same. It may be seen that all assignments other than the sixth (the one proposed above) fail in one or more ways. The first leads to $k_1 >> k_2$; the second grossly miscalculates the unused frequency; the fourth fails in both of these respects; the fifth gives $k_1 > k_2$. Assignment six is entirely satisfactory in giving $k_1 < k_2$, a reasonable value of k_i, and a satisfactory frequency for the unused band.

Table III

Force Constants Obtained with Six Assignments of the CO Stretching Bands of Mo(en)$(CO)_4$

	Assignment				Calcd. force constants			Calcd. freq. of band 3 (1864 cm.$^{-1}$)
No.	A_1	A_1	B_1	B_2	k_1	k_2	k_i	
1	2015	1890	1818	1864	15.80	14.02	0.34	1857
2	2015	1818	1890	1864	13.28	15.28	0.43	1777
3	2015	1890	1864	1818	Imaginary roots obtained			
4	2015	1818	1864	1890	15.06	12.76	0.64	1687
5	2015	1864	1818	1890	14.92	14.35	0.50	1887
6	2015	1864	1890	1818	13.76	15.25	0.42	1858

M(dien)$(CO)_3$ Compounds.—The mull spectra of these compounds have been reported previously[5] and our results agree satisfactorily with the earlier ones. As noted above, only the Mo compound was sufficiently soluble to provide a solution spectrum. Since the frequencies here were 11 and 24 cm.$^{-1}$ higher for bands 1 and 2, respectively, than those of the mull spectrum, the mull frequencies of the Cr and W compounds were increased by these amounts before inserting them into the secular equations. This was done to make the resulting force constants more suitable for direct comparison with those of other compounds, all of which have been measured in solution. We follow Abel, Bennett, and Wilkinson[5] in inferring from the appearance of only two strong CO stretching bands that these molecules have *cis*-configurations. Since k_i is required to be positive[2] the assignment and calculation of force constants follows straightforwardly. The results are given in Table IV.

Compounds with Heterocyclic Amines

The chief difference between compounds of this class, *i.e.*, those containing pyridine (py) and α,α'-dipyridyl (dipy), and all those previously treated is that the heterocyclic amines have an asymmetry built directly into their π-bonding orbital systems. Thus, applicability of the secular equations of part I, which assume axial symmetry in the metal–substituent bonds, to these molecules, cannot be taken for granted. On the contrary, it will be important to look carefully for inconsistencies which might be manifestations of anisotropy in the π-bonding.

M(py)$(CO)_5$ Compounds.—The CO stretching frequencies for these compounds are listed in Table II and the spectrum of the Mo compound which is nearly identical with those of the Cr and W compounds is shown in Fig. 3. The most striking feature of these spectra, seen upon comparison of the data in Table II and especially upon comparing Fig. 1 and 3, is that they are not significantly different from those of the M(Am)$(CO)_5$ compounds. Therefore, an analogous assignment has been made, and the force constants in Table IV obtained. It may be seen that these agree, in *every* case, to within ±0.1 unit, which is about their estimated precision, with force constants in the analogous M(Am)$(CO)_5$ species.

***cis*-M$(py)_2(CO)_4$ and M(dipy)$(CO)_4$ Compounds.**—Figure 4 shows the spectra of the tungsten compounds of these types and the frequencies of all compounds are listed in Table II. It may be seen that these spectra very closely resemble those of the M(en)$(CO)_4$

TABLE IV

FORCE CONSTANTS IN AMINE-SUBSTITUTED GROUP VI CARBONYLS

Compound type	Cr			Mo			W		
	k_1	k_2	k_i	k_1	k_2	k_i	k_1	k_2	k_i
$M(CO)_6$	...	16.49	0.22	...	16.52	0.27	...	16.41	0.29
$M(en)(CO)_4$	13.68	15.07	.45	13.76	15.25	.42	13.68	15.01	.47
$M(dien)(CO)_3$	13.10	...	.70	13.13	...	.73	13.05	...	.67
$M(py)(CO)_5$	14.56	15.93	.38	14.56	15.94	.34	14.59	15.83	.37
cis-$M(py)_2(CO)_4$	14.05	15.41	.42	14.07	15.52	.42	13.92	15.25	.43
$M(dipy)(CO)_4$	13.91	15.48	.41	13.92	15.53	.41	13.87	15.38	.41

compounds, though not quite so closely as the $M(py)(CO)_5$ spectra resemble the $M(Am)(CO)_5$ spectra. The resemblance, however, is such as to leave little doubt that the same assignments should be made as in the $M(en)(CO)_4$ compounds; the force constants thus obtained are recorded in Table IV.

Interpretation.—The foregoing data and results must now be interpreted in a manner consistent with the following considerations:

(1) The heterocyclic amine ligands have some potentiality to accept metal dπ electrons (as compared to the aliphatic amines which have none, or what we shall take to be none).

(2) The ability of the heterocyclic amine ligands to accept dπ electrons is anisotropic, being finite for a dπ orbital oriented perpendicularly to the plane of the amine ring but zero with respect to a dπ orbital lying in the plane of the amine ring.

(3) There are two limiting cases for the orientation of a pyridine ring relative to the $M(CO)_5$ moiety in $M(py)(CO)_5$, as shown in Fig. 5. In structure 5a the plane of the ring bisects opposite $M(CO)_2$ angles while in 5b the ring plane extended includes a pair of *trans* CO groups.

We may first consider structure 5a. This has only C_{2v} symmetry, which means that the degeneracy of the E mode for an $ML(CO)_5$ molecule of C_{4v} symmetry must, in principle, be lifted, giving modes of B_1 and B_2 symmetry in C_{2v}. However, if the secular equations are set up according to the procedure described in part I, the B_1 and B_2 modes turn out to have the same secular equation and this is identical with that for the E mode in C_{4v} symmetry. In fact, all the secular equations are identical in the two cases. That this should be so is not difficult to appreciate when it is noted that in structure 5a all four CO groups in the *xy* plane are equivalent just as they are in the C_{4v} case and we obtain the secular equations by considering only CO–CO couplings *via* the F matrix. Thus if structure 5a is assumed, the *qualitative* similarity of the $M(py)(CO)_5$ and $M(Am)(CO)_5$ spectra can be accounted for irrespective of the magnitude of the metal–pyridine π-bonding. However, the nearly *quantitative* aspect of the similarities, *i.e.*, only slightly higher frequencies and force constants in the py compounds, suggests that while pyridine possesses orbitals suitable for π-bonding it does not actually form very strong π-bonds *in these molecules*. (The reason for this will be considered shortly.)

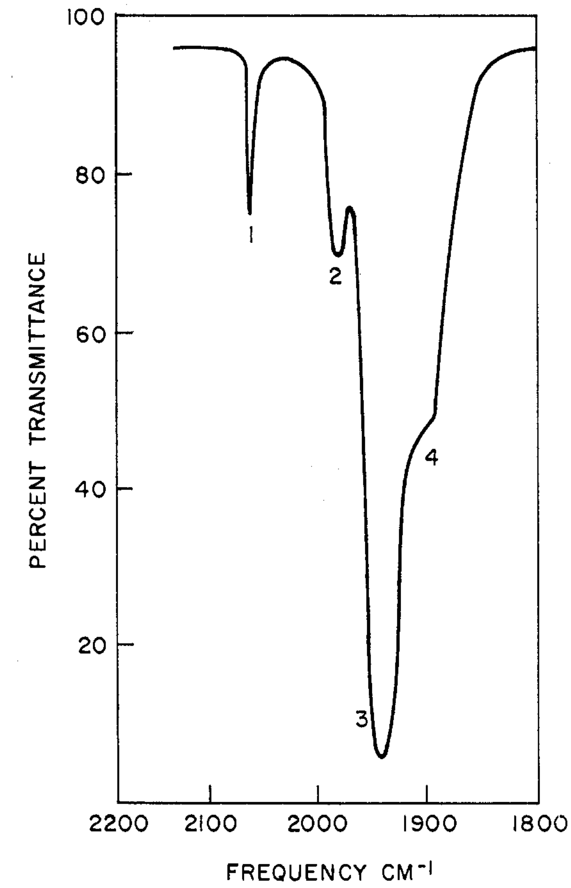

Fig. 3.—The spectrum of $Mo(py)(CO)_5$ in $CHCl_3$, ~7.8 mg./ml.: cell thickness, ~0.1 mm.; fluorite prism. The spectra of the analogous Cr and W compounds are nearly identical.

In order for structure 5b to be acceptable, we would have to conclude from qualitative similarity of the spectra to those of the $M(Am)(CO)_5$ compounds that π-bonding to py is negligible. In view of the anisotropy of any π-interaction which might occur, strong π-bonding would split the degeneracy of the E vibration, but no splitting is observed. Since the force constants do in fact indicate that π-bonding is negligible, structure 5b can be considered consistent with the spectral data.

It therefore appears that py in the $M(py)(CO)_5$ molecules has negligible π-interaction with the metal, and as a consequence the spectra in themselves provide no evidence for preferring one or the other of structures 5a and 5b. Of course 5a is preferable for steric reasons.

For both the *cis*-$M(py)_2(CO)_4$ and $M(dipy)(CO)_4$ compounds, the force constants, k_1 and k_2, are 0.2–0.3 md./Å. higher than for the $M(en)(CO)_4$ compounds. These increases are beyond the level of experimental uncertainty and show that in these disubstituted compounds some experimentally detectable degree of π-bonding does exist.

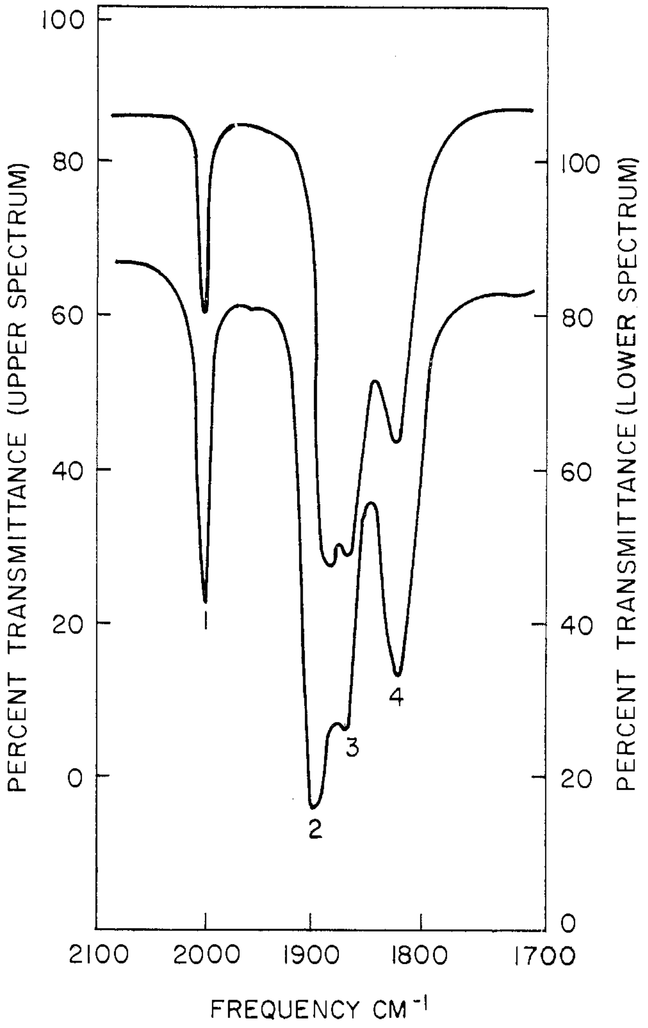

Fig. 4.—The spectra of *cis*-W(py)$_2$(CO)$_4$ (upper curve) and W(dipy)(CO$_4$) (lower curve). Saturated solutions in CHCl$_3$ used in both cases; cell thicknesses 0.087 mm. (upper) and 1.0 mm. (lower); fluorite prism.

For M(dipy)(CO)$_4$ it is necessary to consider the possible consequences of anisotropy in the π-bonding. Let us take the dipy molecule, the metal atom, and the two CO$^{(1)}$ groups to lie in the xy plane, with the CO$^{(2)}$ groups then lying along the z axis. Now the dipy molecule can accept dπ electrons from the d$_{xz}$ and d$_{yz}$ orbitals of the metal only; the CO$^{(2)}$ groups each interact with these two dπ orbitals only whereas the CO$^{(1)}$ groups each interact with one of these and with the d$_{xy}$ orbital. Thus, as a result of the anisotropy of the π-interaction of dipy we might expect that while both k_1 and k_2 should be higher in M(dipy)(CO)$_4$ than in M(en)(CO)$_4$, k_2 should rise the most. This is exactly what is observed in Table IV. For the Cr compounds k_1 rises by 0.23 while k_2 rises by 0.41; for the Mo compound k_1 rises by 0.18 while k_2 rises by 0.28; for the W compound k_1 rises by 0.19 while k_2 rises by 0.37. On the average, then, k_2 rises by 1.5–2.0 times as much as does k_1. It is true that the differences in these pairs of numbers, averaging 0.15, are near the borderline of the reliability of the numbers, and data for only a single compound would not be very persuasive. However, the occurence of about the same result in all cases makes it seem likely that the differences are real.

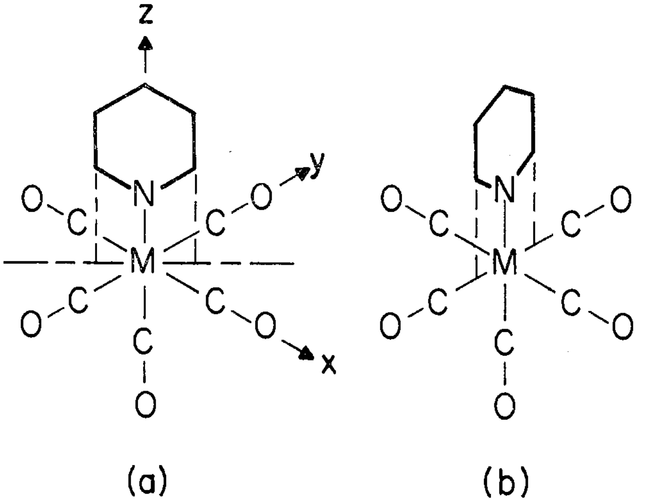

Fig. 5.—The two symmetrical orientations of the pyridine ring in M(py)(CO)$_5$: in (a) the plane of the ring includes an OC–M–CO axis; in (b) the plane of the ring bisects opposite OC–M–OC angles. Both forms have C$_{2v}$ symmetry, however.

Thus, the occurence of some significant amount of metal–substituent π-bonding in the M(dipy)(CO)$_4$ compounds is indicated not alone by the higher values of k_1 and k_2 in these molecules as compared to the force constants in the M(en)(CO)$_4$ molecules, but also by the fact that k_1 and k_2 are affected somewhat differently in just the way one would predict from the electronic structure of the ligand.

In the *cis*-M(py)$_2$(CO)$_4$ compounds, on the other hand, both of the force constants rise by the same amount (within the uncertainties) in each compound compared with the analogous M(en)(CO)$_4$ compound. Thus, from Table IV, we see that the rises, for k_1 and k_2, respectively, are 0.37 and 0.34 for Cr(py)$_2$(CO)$_4$, 0.31 and 0.27 for Mo(py)$_2$(CO)$_4$, and 0.24 and 0.24 for W(py)$_2$(CO)$_4$. Let us again define the x and y axes as those passing through the CO$^{(1)}$ and the z axis as that passing through the CO$^{(2)}$. Models indicate that for steric reasons the planes of the pyridine rings will be the [1,0,1] and [0,1,1] planes[9] (or an equivalent pair). It then follows that the py on the x axis will have its π-interaction with d$_{xz}$ and d$_{xy}$ while that on the y axis can interact only with the d$_{yz}$ and d$_{xy}$ orbitals. Now a CO$^{(1)}$ interacts with one dπ orbital which it shares with two other CO groups and a py and with another dπ orbital which it shares with one other CO and two py groups. On the other hand both of the dπ orbitals which can interact with a CO$^{(2)}$ are shared also by two CO groups and a py. Thus in this case one also would expect some difference in the effect of π-bonding to the py upon the π-bonding to CO$^{(1)}$ and CO$^{(2)}$ groups, but because of the sterically required twisting of the two py groups out of coplanarity, the effect should be much less pronounced. This is in agreement with the data discussed above.

Finally, it is necessary to comment on the fact that in

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(9) The notation for the planes is the standard one explained in most books on elementary crystallography.

TABLE V

PREPARATION AND PROPERTIES OF SOME AMINE-SUBSTITUTED METAL CARBONYLS

Compounds	$M(CO)_6$ used, g.	Yield, g.	M.p., °C.	C		H		N	
				Calcd.	Found	Calcd.	Found	Calcd.	Found
$Cr(C_6H_{11}NH_2)(CO)_5$	1.10	0.14	107 d	45.36	45.5	4.50	4.55	...	...
$Mo(C_6H_{11}NH_2)(CO)_5$	1.32	.29	102 d	39.42	39.7	3.91	4.15	4.18	4.36
$W(C_6H_{11}NH_2)(CO)_5$	1.76	.57	125 d	31.23	31.2	3.10	3.42	3.31	3.45
$Cr(C_5H_5N)_2(CO)_4$	1.0	1.0	172 d	52.18	51.3	3.13	3.07	8.70	8.39
$Mo(C_5H_5N)_2(CO)_4$	1.0	1.1	163 d	46.04	45.9	2.76	2.68	7.67	7.99

the $M(py)(CO)_5$ compounds π-bonding to py is too slight to have any detectable effect on the CO stretching constants although in the *cis*-$M(py)_2(CO)_4$ and $M(dipy)(CO)_4$ compounds π-bonding to the substituents makes small but real changes in the k values. The situation would appear to be comparable to that previously observed and discussed for certain isonitrile complexes.[10] Pyridine, like an isonitrile, is capable of functioning as a simple σ donor; it is possible for σ py $\rightarrow$ M bonds to exist without any help from py $\leftarrow$ M π-bonding. On the other hand, it is apparently necessary that CO-to-metal bonding be synergic if it is to exist at all. Thus, in the $M(py)(CO)_5$ compounds the five CO groups draw off essentially all of the dπ electrons to themselves, as they do in the $M(Am)(CO)_5$ compounds. In the $M(py)_2(CO)_4$ and $M(dipy)(CO)_4$ cases, where there are more dπ electrons available per CO group and the ratio of competing substituents to CO groups is 2.5 times greater than in the monosubstituted compounds, the CO groups take a detectably less complete command of the dπ electrons than they do in the $M(en)(CO)_4$ compounds where they have no competition at all from the substituents. This sort of explanation would lead to the prediction that on continued replacement of CO groups by py or dipy, these ligands would continue to increase their degree of acceptance of metal dπ electrons. In the limit one might expect then that compounds of the sort $M(dipy)_3$ might be obtained and such compounds are of course known.[11]

Experimental

Reagents.—Molybdenum and tungsten carbonyls, purchased from Climax Molybdenum Co., and chromium carbonyl, donated by the Diamond Alkali Company, were used as received. Liquid aliphatic amines were dried over KOH flakes and fractionally distilled. Pyridine was refluxed over and then distilled from barium oxide. α,α-Dipyridyl was used as received from Eastman. Diethylene glycol dimethyl ether (diglyme) was distilled from sodium. Dried amines and solvents were stored under nitrogen until used.

General Methods.—While all of the compounds prepared seemed stable as solids, most of them were sensitive to air when in solution. Hence all reactions were performed in a nitrogen atmosphere and the cyclohexylamine and monopyridine complexes also were recrystallized in a nitrogen atmosphere. Metal carbonyl generally sublimed from the reaction vessels into the reflux condensers in the course of the reactions; it was returned mechanically. The volume of liberated carbon monoxide was measured by displacement of water.

Cyclohexylamine Pentacarbonyls.—In each case about 5 mmoles of carbonyl was heated with 5 ml. of cyclohexylamine for 30 to 60 min. Decomposition (to unidentified products) always was evident and the quantities of CO evolved varied from 70–100% of the theoretically expected amount. Excess amine then was removed in a stream of nitrogen at room temperature (or by washing with water in the Cr case) and the residue extracted with pentane or hexane. These solutions were evaporated, yielding crude products from which residual hexacarbonyl was removed by sublimation at room temperature. The crude products were then recrystallized under nitrogen from hexane in the presence of activated charcoal. The products precipitated as yellow needles. Analyses, etc., are collected in Table V.

Ethylenediamine Chromium Tetracarbonyl.—$Cr(CO)_6$ (1.0 g.) and 5 ml. of ethylenediamine were heated at 120° for 1 hr. About 75% of the theoretical volume of CO was evolved. Ethanol was added to the cool reaction mixture which then was filtered to remove 0.30 g. of unreacted $Cr(CO)_6$. Addition of 50 ml. of water to the filtrate gave a yellow precipitate which was collected, washed several times with water, and dried under vacuum. Remaining traces of $Cr(CO)_6$ were removed by sublimation under vacuum at room temperature to leave 0.35 g. of product as a yellow, microcrystalline powder which begins to decompose at ~280° but does not melt up to 305°.

Anal. Calcd. for $C_6H_8CrN_2O_4$: C, 31.15; H, 3.60; N, 12.50. Found: C, 32.3; H, 3.79; N, 12.4.

Ethylenediamine Molybdenum Tetracarbonyl.—$Mo(CO)_6$ (5.78 g.), ethylenediamine (1.20 g.), and diglyme (25 ml.) were heated together at 130° for 0.25 hr. during which time the theoretical amount of CO (based on amine) was evolved. Solvent and excess $Mo(CO)_6$ were removed on the steam bath under vacuum. The residual yellow solid was washed with chloroform, methanol, benzene, and hexane, leaving 2.10 g. of product. The compound is nearly insoluble in most organic media and only slightly soluble in alcohols, nitromethane, and pyridine. Recrystallization was carried out using an acetone–ethanol–water mixture. The compound melted at 294° with decomposition and gas evolution.

Anal. Calcd. for $C_6H_8MoN_2O_4$: C, 22.88; H, 3.00; N, 10.45. Found: C, 22.2; H, 3.23; N, 10.3.

Ethylenediamine Tungsten Tetracarbonyl.—$W(CO)_6$ (1.76 g.) and 5 ml. of ethylenediamine were heated together at 120° for 2 hr., when the theoretical volume of CO had been evolved. Addition of water (50 ml.) and alcohol (50 ml.) gave a yellow precipitate which was collected, washed well with water, and dried under vacuum (~0.05 mm.) at room temperature. Traces of unreacted $W(CO)_6$ were removed by continued pumping, leaving 1.10 g. of product. The compound is insoluble in most organic solvents but slightly soluble in alcohol and nitromethane. It begins to decompose at ~300° and does not melt at any temperature up to 310°.

Anal. Calcd. for $C_6H_8N_2O_4W$: C, 20.24; H, 2.26. Found: C, 20.6; H, 2.60.

Diethylenetriamine Complexes.—The Cr and W compounds were prepared by direct reaction of the amine with the hexacarbonyls as previously described.[5] The previously reported preparation[5] of the Mo compound involves reaction of the amine with cycloheptatrienyl molybdenum tricarbonyl. In this work the Mo compound also was prepared directly from the hexacarbonyl. $Mo(CO)_6$ (1.32 g.) and diethylenetriamine (3 ml.) were heated together at 150° for 0.25 hr., when the theoretical quantity of CO had been evolved. Ethanol (30 ml.) was added

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(10) F. A. Cotton and F. Zingales, *J. Am. Chem. Soc.*, **83**, 351 (1961).

(11) S. Herzog, *J. Inorg. Nucl. Chem.*, **8**, 557 (1958).

to the cooled reaction mixture and the yellow crystalline solid was collected by filtration. After thorough washing with ethanol and pentane the solid was dried under vacuum affording 1.30 g. of product, which is insoluble in nearly all common solvents and only slightly soluble in pyridine and nitromethane. It begins to decompose above 300° but no melting point was observed up to 350°.

Anal. Calcd. for $C_7H_{13}MoN_3O_3$: C, 29.69; H, 4.63; N, 14.84. Found: C, 29.9; H, 4.75; N, 14.7.

Pyridine Complexes.—$Cr(py)(CO)_5$ and $W(py)(CO)_5$ were prepared by refluxing a mixture of the hexacarbonyl with pyridine until approximately one equivalent of CO had been evolved. The separation and purification procedures were those reported by Strohmeier and Gerlach.[12] $Mo(py)(CO_5)$ was also prepared by direct reaction, but was recrystallized from hexane at −80°. The preparation of this compound does not seem to have been reported previously.

Anal. Calcd. for $C_{10}H_5MoNO_5$: C, 38.12; H, 1.60. Found: C, 38.3; H, 1.78.

Strohmeier has reported photochemical reaction of $W(CO)_6$ with pyridine to give $W(py)_2(CO)_4$. We have prepared this and its Cr and Mo analogs by direct thermal reaction. A mixture of the metal carbonyl (1 g.) with 2.5 ml. of pyridine was refluxed until nearly two equivalents of carbon monoxide were evolved. The deeply colored mixtures were allowed to cool, whereupon an orange-yellow solid separated in each case. Pentane was added and the mixture was stirred and then filtered. The solid was washed well with pentane to remove pyridine metal pentacarbonyl and any residual carbonyl. Recrystallization was effected by dissolution in acetone followed by precipitation by addition of water. The bis-(pyridine) chromium tetracarbonyl complex is very unstable and decomposes readily in air to form pyridine chromium pentacarbonyl (as shown by infrared), free pyridine (odor), and a green solid insoluble in organic media, which may be Cr_2O_3. Yields, analyses, etc., are given in Table V for the Cr and Mo compounds, both of which are yellow-orange in color. The properties of the W compound were as previously reported.[12]

α,α-Dipyridyl Complexes.—These were all prepared by the method used by Abel, Bennett, and Wilkinson[5] for α,α-dipyridyl molybdenum tetracarbonyl.

Spectral Measurements.—The infrared spectra in the CO stretching region all were obtained with a Baird spectrophotometer equipped with a lithium fluoride prism. Polystyrene film was used to provide calibration bands which were placed on each spectrum as it was recorded.

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(12) W. Strohmeier and K. Gerlach, *Z. Naturforsch.*, **15b**, 413, 621 (1961).

CONTRIBUTION FROM THE INSTITUTE FOR ATOMIC RESEARCH AND
DEPARTMENT OF CHEMISTRY, IOWA STATE UNIVERSITY, AMES, IOWA

The Preparation and Properties of Niobium(IV) Compounds.
I. Some Niobium(IV) Halides and their Pyridine Adducts[1a]

BY ROBERT E. McCARLEY AND BRUCE A. TORP[1b]

Received September 8, 1962

Reaction of $NbBr_5$ and niobium metal in a sealed tube under a temperature gradient from 410 to 350° gave $NbBr_4$ in good yields. However, an increase in the higher temperature from 410 to 450° was sufficient to eliminate $NbBr_4$ as a product and cause deposition of a lower bromide. The halides $NbCl_4$ and $NbBr_4$ are isomorphous solids of orthorhombic structure and lattice constants $a = 8.12$, $b = 8.88$, $c = 6.84$ Å. and $a = 8.60$, $b = 9.31$, $c = 7.19$ Å., respectively; both solids are diamagnetic over the range −196 to 25°. Formation of the tetrahalodi-(pyridine)-niobium(IV) complexes resulted from the reactions of the pure tetrahalides (Cl, Br, I) with pyridine at room temperature; at elevated temperatures a second form of $NbBr_4(py)_2$ crystallized from pyridine. Evidence bearing on the structure of the pyridine adducts was obtained from conductance, spectral, and magnetic susceptibility measurements. The complexes are paramagnetic and exhibit moments much lower than the spin-only value for one magnetic electron; the spectra of solutions in pyridine show intense bands in the visible region which have been attributed to charge transfer transitions.

Introduction

In contrast to the abundance of literature pertaining to the chemistry and compounds of niobium(V) is the relatively small volume of information which describes and elucidates the chemistry of niobium in its lower oxidation states. In particular, the coördination and solution chemistry of lower valent niobium has suffered most. The latter situation is in large measure a result of the rather limited conditions under which stable solutions of niobium(V) can be obtained in aqueous media. Consequently aqueous solutions of niobium(V) have not served as a particularly fruitful starting point for the preparation of compounds or solutions of the element in the lower oxidation states. Furthermore where the lower valence states have been obtained under these conditions they are characterized by low stability and high reactivity.[2]

In view of the foregoing facts and the great affinity of the highly acidic niobium(V) compounds for oxide it seemed prudent to eliminate the troublesome water (more generally hydroxylic and other oxygenated solvents, and solvents containing acidic hydrogen) and to consider reactions in basic, but (for our purposes) innocuous solvents such as tertiary amines, nitriles, etc. Indeed, it was found that solutions of the niobium(V) halides (chloride, bromide, and iodide) in pyridine actually were reduced by the solvent producing in each instance the dipyridine adduct of the niobium(IV)

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(1) (a) Contribution No. 1224. Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission. (b) This paper is taken in part from the thesis by B. A. Torp to the Iowa State University in partial fulfillment of the requirements for the degree of Master of Science.

(2) V. Cozzi and S. Vivarelli, *Z. anorg. allgem. Chem.*, **279**, 165 (1955).

(3) R. E. McCarley, B. G. Hughes, J. C. Boatman, and B. A. Torp, in "Reactions of Coordinated Ligands and Homogeneous Catalysis," Advances in Chemistry Series, No. 37, American Chemical Society, Washington, D. C., 1963, pp. 243–255.