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# Infrared Studies of Coordination Compounds Containing Low-Oxidation-State Metals. I. Tris(2,2′-bipyridine) and Tris(1,10-phenanthroline) Complexes

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Infrared spectra of tris(2,2′-bipyridine) complexes of Cr(III), Cr(II), Cr(I), Cr(0), Fe(III), Fe(II), V(II), V(0), Ti(0), Ti(−I), Cu(II), Co(III), Co(II), Co(I), Co(0), Mn(II), Mn(0), and Mn(−I) and of tris(1,10-phenanthroline) complexes of Fe(III), Cu(II), Co(III), Co(II), and Co(I) have been measured in the 4000–100-cm$^{-1}$ region. The Cr–N, Fe–N, and Cu–N stretching bands have been assigned by using the metal isotope technique. Other metal–nitrogen stretching bands have been assigned based on similarity of spectra. The metal–nitrogen stretching bands of the Cr(III), Cr(II), Cr(I), Cr(0), Fe(III), Fe(II), V(II), V(0), Ti(0), Ti(−I), and Co(III) are in the 390–300-cm$^{-1}$ region, whereas those of the Cu(II), Ni(II), Zn(II), Co(II), Co(I), Co(0), Mn(II), Mn(0), and Mn(−I) are in the 290–180-cm$^{-1}$ region. In the former group (A), all the d electrons are in the $t_{2g}$ (bonding) orbitals whereas the $e_g$ (antibonding) orbitals are partially occupied in the latter group (B). In a series of metal complexes in which the metal is the same and the formal oxidation state is varied, the metal–nitrogen stretching frequencies remain fairly constant throughout the series unless the d-electron configuration changes from type A to B. This result seems to suggest that an increasing fraction of the electron population on the metal resides on the ligand orbitals in the low-oxidation-state complexes so that the electron density around the metal remains fairly constant throughout the series. In fact, the ligand spectra of low-oxidation-state complexes in the 1625–1475- and 1000–900-cm$^{-1}$ regions are similar to that of Li(2,2′-bipy) in which the ligand is negatively charged.

## Introduction

There have been relatively few studies dealing with the effect of changing oxidation state on the infrared spectra of transition metal complexes. Furthermore, most of the previous investigations have covered a rather narrow range of oxidation states. For example, Clark[2] noted that the Fe–Cl stretching frequency of the $FeCl_4^-$ ion is 378 cm$^{-1}$ whereas that of the $FeCl_4^{2-}$ ion is 282 cm$^{-1}$. Such a drastic change in the metal–ligand stretching frequency was also observed for the Co–N stretching frequencies of the $[Co(NH_3)_6]^{3+}$ ion (499, 476, 449 cm$^{-1}$) and the $[Co(NH_3)_6]^{2+}$ ion (327 cm$^{-1}$).[3] However, only two oxidation states have been studied in these previous investigations.

It is well known[4] that 2,2′-bipyridine (abbreviated as bipy) and 1,10-phenanthroline (abbreviated as phen) form metal complexes in which the formal oxidation state of the metal varies over a wide range. For example, it is possible to prepare a series of chromium complexes of the type $[Cr(bipy)_3]^{n+}$ where $n$ is 3, 2, 1, and 0.[5] No infrared studies have yet been made on the effect of changing the oxidation state over such a wide range using a series of complexes of the same structure. In the present paper, we have carried out an extensive study on the infrared spectra of $(bipy)_3$ and $(phen)_3$ complexes of Cr(III), Cr(II), Cr(I), Cr(0), Fe(III), Fe(II), V(II), V(0), Ti(0), Ti(−I), Co(III), Co(II), Co(I), Co(0), Mn(II), M(0), and Mn(−1). Infrared spectra of most of these compounds have not yet been reported previously.

In a series of $(bipy)_3$ and $(phen)_3$ complexes of the same metal, the metal–nitrogen (M–N) stretching frequency serves as a direct measure of the strength of the coordinate bond. It has been extremely difficult, however, to assign these M–N stretching bands on an empirical basis. Thus Inskeep[6] assumed that the highest frequency bands (300–260 cm$^{-1}$) of the $(bipy)_3$ complexes of Co(II), Ni(II), Cu(II), and Zn(II) which are absent in the free ligand are the M–N stretching bands. However, this assumption is not necessarily valid since some ligand vibration which does not appear in the free ligand may be activated by complex formation. On the other hand, Clark and Williams[7] concluded that no bands above 200 cm$^{-1}$ can be assigned to the M–N stretching vibrations. As is shown in our previous paper,[8] it is possible to make clear-cut band assignments of metal–ligand vibrations by using the metal isotope technique.[9] In the present paper, we have applied this technique to the assignments of the Cr–N, Fe–N, and Cu–N stretching modes. It was possible to suggest the assignments of the M–N stretching modes of other metal complexes without metal isotope data since their spectra were similar to those complexes for which metal isotope data are available.

## Experimental Section

**Preparation of Compounds. Chromium Complexes.**—$^{50}Cr(bipy)_3$ and its $^{53}Cr$ analog (black crystals) were prepared by converting the respective isotopic oxides ($Cr_2O_3$ purchased from Oak Ridge National Laboratories) to isotopic $CrCl_3$ by the method described by Angelici.[10] The isotopic $CrCl_3$ was then electrolytically reduced to $Cr_{aq}^{2+}$ in an apparatus similar to that described by Hutchinson.[11] A 3 $N$ solution of HCl was used in the anode compartment. Anhydrous $CrCl_3$ (50 mg) was added to the cathode compartment which contained 3 ml of $H_2O$ and 0.1 ml of 3 $N$ HCl. The reduction under nitrogen was carried out at 4–5 V and 50–100 mA. The $Cr_{aq}^{2+}$ solution obtained was titrated into 3 ml of deaerated $H_2O$ containing *ca.* 2 g of sodium acetate.

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[1] Author to whom correspondence should be addressed.

[2] R. J. H. Clark, *Spectrochim. Acta*, **21**, 955 (1965).

[3] L. Sacconi, A. Sabatini, and P. Gans, *Inorg. Chem.*, **3**, 1772 (1964).

[4] W. R. McWhinnie and J. D. Miller, *Advan. Inorg. Chem. Radiochem.*, **12**, 135 (1969).

[5] S. Herzog and W. Schon, *Z. Anorg. Allg. Chem.*, **297**, 323 (1958); S. Herzog, K. C. Renner, and W. Schon, *Z. Naturforsch. B*, **12**, 809 (1957); F. Hein and S. Herzog, *Z. Anorg. Allg. Chem.*, **267**, 337 (1952).

[6] R. G. Inskeep, *J. Inorg. Nucl. Chem.*, **24**, 763 (1962).

[7] R. J. H. Clark and C. S. Williams, *Spectrochim. Acta, Part A*, **23**, 1055 (1967).

[8] B. Hutchinson, J. Takemoto, and K. Nakamoto, *J. Amer. Chem. Soc.*, **92**, 3335 (1970).

[9] K. Nakamoto, K. Shobatake, and B. Hutchinson, *Chem. Commun.*, 1451 (1969); K. Shobatake and K. Nakamoto, *J. Amer. Chem. Soc.*, **92**, 3332 (1970); K. Shobatake and K. Nakamoto, *ibid.*, **92**, 3339 (1970); K. Nakamoto, C. Udovich, and J. Takemoto, *ibid.*, **92**, 3973 (1970); N. Ohkaku and K. Nakamoto, *Inorg. Chem.*, **10**, 798 (1971).

[10] A. J. Angelici, "Synthesis and Technique in Inorganic Chemistry," W. B. Saunders, Philadelphia, Pa., 1969, p 31.

[11] B. Hutchinson, Ph.D. Dissertation, Illinois Institute of Technology, 1970.

Dark red crystals of $Cr_2(CH_3COO)_4 \cdot 2H_2O$ were obtained upon cooling. To this was added 70 mg of bipy and 3 ml of deaerated $H_2O$ under an inert gas atmosphere. The resulting mixture was treated as described by Brauer.[12]

$[^{50}Cr(bipy)_3](ClO_4)_2$ was prepared by using $^{50}CrCl_3$ which was obtained by the method described above. The anode compartment contained 3 *N* $HClO_4$ and the cathode compartment contained 25 mg of $^{50}CrCl_3$, 3 ml of 0.1 *N* $HClO_4$, and 50 mg of $NaClO_4$. The $Cr_{aq}^{2+}$ solution obtained was titrated into 75 mg of bipy dissolved in 1 ml of deaerated methanol. The resulting black precipitate was then treated as described by Brauer.[12] The purity of the metal isotopes was as follows: $^{50}Cr$, 89.01%; $^{53}Cr$, 96.40%.

$[Cr(bipy)_3](ClO_4)_3$ (yellow crystals) was prepared by the oxidation of $[Cr(bipy)_3](ClO_4)_2$ as described by Baker and Dev Mehta.[13] $[Cr(bipy)_3](ClO_4)$ (indigo blue crystals) was prepared by shaking $[Cr(bipy)_3](ClO_4)_2$ with magnesium powder in water under nitrogen.[12]

**Iron Complexes.**—$[Fe(bipy)_3](ClO_4)_2$ and $[Fe(phen)_3](ClO_4)_2$ were prepared by the method of Burstall and Nyholm.[14] $[Fe(bipy)_3](ClO_4)_3$ and $[Fe(phen)_3](ClO_4)_3$ were prepared by the oxidation of an ice-cold solution of $[Fe(bipy)_3]SO_4$ or $[Fe(phen)_3]SO_4$ with chlorine gas followed by warming the solution to room temperature and adding $NaClO_4$. The Fe(II) complexes are red whereas the Fe(III) complexes are blue-green.

$[^{54}Fe(phen)_3](ClO_4)_3$ and its $^{57}Fe$ analog were prepared by using metallic $^{54}Fe$ and $^{57}Fe$, respectively, which were reduced[8] under hydrogen from respective isotopic $Fe_2O_3$ purchased from Oak Ridge National Laboratory. Metallic $^{54}Fe$ (or $^{57}Fe$) was dissolved in dilute $H_2SO_4$ under nitrogen and treated with the stoichiometric amount of phen. The resulting red solution was cooled in an ice bath and saturated with chlorine gas and treated as described previously. The purity of the metal isotopes was as follows: $^{54}Fe$, 98.19%; $^{57}Fe$, 90.73%.

**Vanadium Complexes.**—$[V(bipy)_3]I_2$ was prepared by the method of Herzog.[15] The electrolytic reduction of $VOSO_4$ to $VSO_4$ was carried out in an apparatus similar to that described by Hutchinson.[11] The cathode compartment contained $VOSO_4 \cdot 3H_2O$ dissolved in 3% $H_2SO_4$. The anode compartment contained 3% $H_2SO_4$. Reduction was accomplished at *ca.* 4–5 V and 100 mA. The resulting violet solution was added to a slight excess of bipy and KI dissolved in 30% air-free methanol. The solution turned green, and, after a few minutes, crystallization commenced. After standing overnight, black crystals were isolated under nitrogen, washed with a small amount of cold air-free water, and dried *in vacuo* over $P_2O_5$.

$V(bipy)_3$ was prepared by the method of Herzog.[15] $[V(bipy)_3]I_2$ was dissolved in 50% air-free methanol and magnesium powder was added. The resulting mixture was shaken until the supernatant became nearly colorless. It was then filtered through a fine frit under nitrogen. After washing with air-free water and methanol and drying over $P_2O_5$, black crystals of $V(bipy)_3$ were separated from entrapped magnesium powder by extraction with benzene in an apparatus similar to that described by Herzog.[15] The spectrum of $V(bipy)_3$ thus obtained is in good agreement with that reported by Pappalardo.[16]

**Titanium Complexes.**—$Ti(bipy)_3 \cdot n THF$ was prepared by the method of Herzog and Taube.[17] A THF solution of $Li_2(bipy)$ (2 mol) was added to a THF solution of $TiCl_4$ (1 mol) and bipy (2 mol) in a dry nitrogen atmosphere. The black-blue precipitate was filtered from the dark blue solution and washed with THF.

$Li[Ti(bipy)_3] \cdot n THF$ was prepared by the method of Herzog and Taube.[17] $TiCl_4$ (1 mol) was reduced to $TiCl_3$ in a THF solution by adding metallic mercury. To this was added a THF solution of bipy (2 mol) and $Li_2(bipy)$ (3 mol) under nitrogen. The black-violet precipitate was filtered and washed with THF.

**Lithium Complex.**—$Li(bipy) \cdot n THF$ was prepared by the method of Herzog and Taube.[18] bipy (1.562 g, 0.01 mol) was dissolved in 50 ml of air-free and dry THF, to which 0.069 g (0.01 g-atom) of metallic lithium was added. After stirring the mixture for 2 hr, dark red crystals were obtained. Excess THF was removed under vacuum.

**Copper Complexes.**—Copper complexes of the types $[Cu(bipy)_3]X_2 \cdot nH_2O$ (X = Cl, Br, I, $ClO_4$) and $[Cu(phen)_3]X_2$ (X = Br, I, $ClO_4$) were prepared by the literature methods.[19,20] The color of these complexes is blue. $[^{63}Cu(bipy)_3]Cl_2 \cdot 7H_2O$ and its $^{65}Cu$ analog were prepared by using isotopic $CuCl_2 \cdot 2H_2O$ which was prepared by dissolving isotopic CuO (purchased from Oak Ridge National Laboratory) in concentrated HCl. The isotopic pairs of the bromide and iodide were prepared by adding KBr and KI, respectively, to the solutions of the isotopic $[Cu(bipy)_3]Cl_2 \cdot 7H_2O$. $[^{63}Cu(phen)_3](ClO_4)_2$ and its $^{65}Cu$ analog were prepared by a method similar to that used for isotopic $[Cu(bipy)_3](ClO_4)_2$. The purity of the metal isotopes was as follows: $^{63}Cu$, 99.73%; $^{65}Cu$, 99.70%.

**Cobalt Complexes.**—$[Co(bipy)_3]X_2$ and $[Co(phen)_3]X_2$ (X = Cl, Br, I, $ClO_4$) were prepared by the literature methods,[14,21] purified by recrystallization from water, and dried over $P_2O_5$ *in vacuo* overnight. $[Co(bipy)_3](ClO_4)_3$ and $[Co(phen)_3](ClO_4)_3$ were prepared by the methods of Burstall and Nyholm[14] and Lee, *et al.*,[22] respectively. The color of these complexes is brownish yellow. $[Co(bipy)_3]X$ (X = Cl, Br, I, $ClO_4$) and $[Co(phen)_3]X$ (X = Br, I, $ClO_4$) were prepared by the methods described previously.[23,24] $Co(bipy)_3$ was prepared by the method of Herzog, *et al.*[25] The color of these Co(I) and Co(0) complexes is almost black.

**Manganese Complexes.**—$[Mn(bipy)_3]X_2$ (X = $ClO_4$, Br, I) was prepared by the method of Burstall and Nyholm.[14] These complexes are yellow and can be purified by the recrystallization from water. $Mn(bipy)_3$ and $Li[Mn(bipy)_3] \cdot n THF$ were prepared by the methods of Herzog.[26,27] In both cases, $[Mn(bipy)_3]Br_2$ was reduced to $Mn(bipy)_3$ or $Li[Mn(bipy)_3]$ by $Li_2(bipy)$ in a THF solution under nitrogen.

**Infrared Spectra.**—The infrared spectra were obtained on a Beckmann IR-12 (4000–300 $cm^{-1}$) and a Hitachi Perkin-Elmer FIS-3 (400–100 $cm^{-1}$) spectrophotometer. All spectra were obtained as Nujol mulls. The mulls were prepared in a drybox, the atmosphere of which was equilibrated with a sodium-potassium alloy. No decomposition was observed when the mulls were placed between well-polished and securely fastened CsI plates. The far-infrared spectra were obtained on polyethylene plates. The mulls were protected from oxygen by a thin sheet of polyethylene securely fastened over the surface of the mull. The far-infrared spectra of metal isotope compounds were recorded with a scanning speed of 2 $cm^{-1}$/min and the reproducibility of frequency reading was checked by multiple scans of several samples over the desired frequency range. The average error in frequency reading was 0.5 $cm^{-1}$.

## Results and Discussion

**Chromium Complexes.**—Figure 1 illustrates the far-infrared spectra of $[Cr(bipy)_3](ClO_4)_3$, $[Cr(bipy)_3](ClO_4)_2$, $[Cr(bipy)_3](ClO_4)$, and $Cr(bipy)_3$. In order to assign the Cr–N stretching modes, we have carried out metal isotope experiments on the Cr(0) and Cr(II) complexes. As is seen in Figure 1, two bands at 385.0 and 312.0 $cm^{-1}$ of $^{50}Cr(bipy)_3$ are shifted to lower frequencies (by 3.5 and 5.5 $cm^{-1}$, respectively) by the $^{50}Cr$–$^{53}Cr$ substitution while all other bands show shifts of less than 0.5 $cm^{-1}$. Thus, these two bands must be assigned to the Cr(0)–N stretching modes. Figure 1 shows that the spectra of the Cr(I) and Cr(III) complexes are similar to that of the Cr(0) complex; all these complexes exhibit only two distinct bands between 400 and 300 $cm^{-1}$. Therefore, two bands at *ca.*

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[12] G. Brauer, "Handbook of Preparative Inorganic Chemistry," Vol. II, 2nd ed, Academic Press, New York, N. Y., 1965, pp 1361–1363.

[13] B. R. Baker and B. Dev Mehta, *Inorg. Chem.*, **4**, 848 (1965).

[14] F. M. Burstall and R. S. Nyholm, *J. Chem. Soc.*, 3570 (1952).

[15] S. Herzog, *Z. Anorg. Allg. Chem.*, **294**, 155 (1958).

[16] R. Pappalardo, *Inorg. Chim. Acta*, **2**, 209 (1968).

[17] S. Herzog and R. Taube, *Z. Anorg. Allg. Chem.*, **306**, 159 (1960).

[18] S. Herzog and R. Taube, *Z. Chem.*, **2**, 208 (1962).

[19] F. N. Jaeger and J. A. Van Dijk, *Z. Anorg. Allg. Chem.*, **25**, 37 (1963).

[20] S. K. Dhar and F. Basolo, *J. Inorg. Nucl. Chem.*, **25**, 37 (1963).

[21] F. Blau, *Monatsh. Chem.*, **10**, 372 (1889).

[22] C. S. Lee, E. M. Gorton, H. M. Neuman, and H. R. Hunt, *Inorg. Chem.*, **5**, 1397 (1966).

[23] R. J. Fitzgerald, B. Hutchinson and K. Nakamoto, *ibid.*, **9**, 2618 (1970).

[24] N. Maki and M. Yamaguchi, *J. Amer. Chem. Soc.*, **86**, 514 (1964).

[25] S. Herzog, R. Klausch, and J. Lantos, *Z. Chem.*, **4**, 150 (1964).

[26] S. Herzog, *ibid.*, **2**, 24 (1962).

[27] S. Herzog, *ibid.*, **3**, 392 (1963).

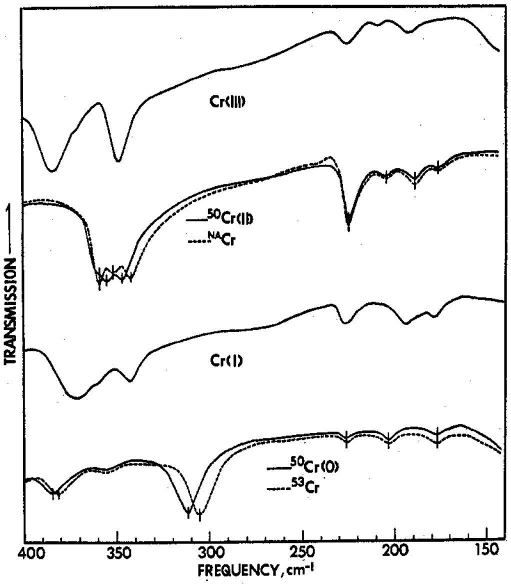

Figure 1.—Far-infrared spectra of the $[Cr(bipy)_3](ClO_4)_n$ series.

385 and 349 cm$^{-1}$ of the Cr(III) complex and two bands at *ca.* 371 and 343 cm$^{-1}$ of the Cr(I) complex have been assigned to the Cr–N stretching modes. However, the spectrum of the Cr(II) complex is different from those of others, in that it shows two or three bands which are closely located between 360 and 340 cm$^{-1}$. In order to assign the Cr(II)–N stretching modes, we have compared the spectra of $[^{50}Cr(bipy)_3](ClO_4)_2$ and $[Cr(bipy)_3](ClO_4)_2$ [Cr(natural abundance) contains *ca.* 84% of $^{52}Cr$ and small percentages of $^{53}Cr$, $^{50}Cr$, and $^{54}Cr$]. Figure 1 shows that two bands at 355.0 and 347 cm$^{-1}$ of the $^{50}Cr$ complex are shifted to lower frequencies (by 4.0 cm$^{-1}$) while all other bands give almost no shifts when $^{50}Cr$ is substituted by Cr. Thus these two bands must be assigned to the Cr(II)–N stretching modes. According to the present results, the Cr–N stretching frequencies of all four complexes are at 385–350 and 350–308 cm$^{-1}$ regardless of the formal oxidation state of the central metal.

Table I lists the observed frequencies of the $[Cr(bipy)_3]^{n+}$ series. In addition to two Cr–N stretching bands, these complexes exhibit at least four ligand vibrations B, D, E, and F which are commonly found in other $(bipy)_3$ complexes.[8]

TABLE I

FAR-INFRARED SPECTRA OF THE $[Cr(bipy)_3](ClO_4)_n$ SERIES (CM$^{-1}$)

| $[Cr(bipy)_3]^{3+}$ | $[Cr(bipy)_3]^{2+}$ | $[Cr(bipy)_3]^{+}$ | $[Cr(bipy)_3]^{0}$ | Assignment |
|---|---|---|---|---|
| 385 (m) | 351 (s) | 371 (m) | 382 (m) | Cr–N str |
| (Hidden) | 359 (m) | 352 (w) | 357 (vw) | Ligand B |
| 349 (m) | 343 (m) | 343 (m) | 308 (s) | Cr–N str |
| 226 (w) | 225 (m) | 228 (w) | 227 (w) | Ligand D |
| 193 (vw) | 205 (w) | | | |
| | 189 (w) | 195 (w) | 203 (s) | Ligand E |
| 177 (w) | 175 (vw) | 179 (w) | 178 (w) | Ligand F |

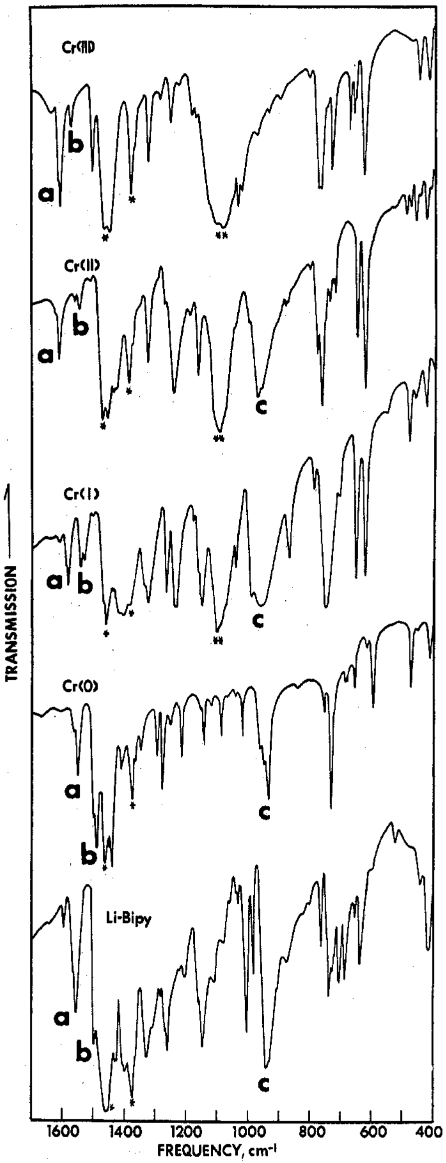

Figure 2.—Infrared spectra of the $[Cr(bipy)_3](ClO_4)_n$ series and Li(bipy) in the high-frequency region: *, Nujol band; **, perchlorate band.

Figure 2 shows the infrared spectra of the $[Cr(bipy)_3]^{n+}$ series in the 2000–400-cm$^{-1}$ region. The bands observed in this region are due to the bipy ligand. In general, these spectra are too complicated to give detailed assignments. It is possible, however, to discuss two regions of the spectra on an empirical basis. One is at 1000–900 cm$^{-1}$ where ring deformation modes of the bipy ligand are expected. As is seen in Figure 2 and Table II, the Cr(III) complex shows almost no absorption in this region. However, the Cr(II), Cr(I), and Cr(0) complexes exhibit strong bands near 955 cm$^{-1}$ (labeled as c in Figure 2 and Table II). It is interesting to note that Li(bipy) in which the bipy ligand is negatively charged also exhibits a strong band at 944 cm$^{-1}$. Thus, the appearance of a strong band in this region may indicate that the bipy ligand is negatively charged in the complex.

Another region of interest is in the 1625–1475-cm$^{-1}$ region where the C=C and C=N stretching bands of the bipy ligand are expected. As is seen in Figure 2 and Table II, two bands labeled as a and b are sensitive to the change in oxidation state: both bands are shifted to lower frequencies as the oxidation state is lowered. Again, the spectra of low-oxidation-state complexes such as Cr(0) and V(0) (discussed later) resemble the spectrum of Li(bipy) in this region.

Two regions of spectra mentioned above may be used

TABLE II

CHARACTERISTIC LIGAND VIBRATIONS OF $(bipy)_3$ COMPLEXES ($cm^{-1}$)

| | Cr(III)[a] | Cr(II)[a] | Cr(I)[a] | Cr(0) | Fe(III)[a] | Fe(II)[a] | V(II)[b] | V(0) | Ti(0) |
|---|---|---|---|---|---|---|---|---|---|
| *a* | 1605 (s) | 1603 (m) | 1582 (m) | 1552 (s) | 1609 (m) | 1609 (m) | 1598 (m) | 1570 (s) | 1574 (s) |
| *b* | 1570 (w) | 1553 (w) | 1540 (m) | 1502 (sh) | 1570 (w) | 1570 (w) | 1582 (w) | 1508 (s) | 1506 (s) |
| | | 1437 (w) | 1528 (m) | 1490 (s) | | | 1560 (w) | | |
| *c* | | 965 (vs)[e] | 955 (vs)[e] | 947 (s) | | | | 930 (vs) | 940 (vs) |
| | Normal | Intermed | Intermed | Low | Normal | Normal | Intermed | Low | Low |

| | Ti(−I)[c] | Cu(II)[d] | Co(III)[a] | Co(II)[a] | Co(I)[a] | Co(0) | Mn(II)[b] | Mn(0) | Mn(−I)[c] |
|---|---|---|---|---|---|---|---|---|---|
| *a* | 1573 (s) | 1605 (m) | 1610 (s) | 1600 (m) | 1590 (m) | 1575 (m) | 1598 (s) | 1600 (m) | 1565 (m) |
| *b* | 1504 (m) | 1580 (m) | 1575 (m) | 1575 (w) | 1565 (w) | 1506 (m) | 1585 (sh) | 1573 (m) | 1535 (w) |
| | 1490 (m) | | | | | | 1580 (sh) | | |
| | | | | | | | 1568 (sh) | | |
| *c* | 930 (vs) | | | | 970 (s)[e] | 975 (vs) | | 958 (vs) | 944 (vs) |
| | Low | Normal | Normal | Normal | Intermed | Low | Normal | Intermed | Low |

[a] Perchlorate. [b] Iodide. [c] Lithium salt. [d] Chloride. [e] This band is not due to the $ClO_4^-$ ion since the corresponding halide complex exhibits the same band.

to classify $(bipy)_3$ complexes roughly into three groups: "normal"-, "intermediate"-, and "low"-oxidation-state complexes. A complex belongs to the "normal" oxidation state if it has no strong absorption between 1000 and 900 $cm^{-1}$ and exhibits a relatively strong band in the 1610–1600-$cm^{-1}$ region. A complex belongs to the "low" oxidation state if it exhibits a strong absorption in the 1000–900-$cm^{-1}$ region and several strong–medium-intensity bands in the 1575–1490-$cm^{-1}$ region. Generally, the color of these low-oxidation-state complexes is black or nearly black. As stated above, our infrared study suggests that the bipy ligand in low-oxidation-state complexes is negatively charged as that of Li(bipy). This result is in good agreement with those of Koenig and Herzog[28] and Hanazaki and Nagakura,[29] who studied the electronic transitions of these complexes. A complex may be classified as "intermediate" if it exhibits bands characteristic of both "normal"- and "low"-oxidation-state complexes. Table II summarizes the observed frequencies and the resulting classifications of all the $(bipy)_3$ complexes studied.

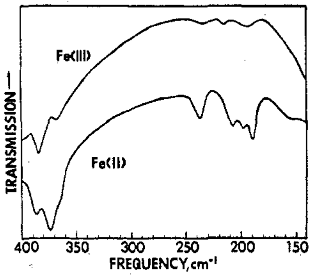

Figure 3.—Far-infrared spectra of the $[Fe(bipy)_3](ClO_4)_n$ series.

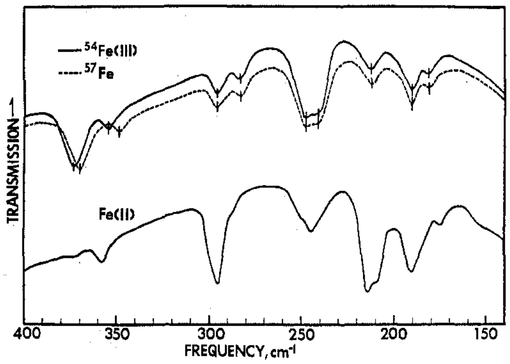

Figure 4.—Far-infrared spectra of the $[Fe(phen)_3](ClO_4)_n$ series.

TABLE III

FAR-INFRARED SPECTRA OF $[Fe(bipy)_3](ClO_4])_n$ AND $[Fe(phen)_3](ClO_4)_n$ ($n = 2, 3$)

| $[Fe(bipy)_3]^{3+}$ (Fe) | $[Fe(bipy)_3]^{2+}$ ($^{54}Fe$)[a] | $[Fe(bipy)_3]^{2+}$ $\Delta\tilde{\nu}$,[b] $cm^{-1}$ | Assignment |
|---|---|---|---|
| 384 (m) | 386.0 (m) | 6.0 | Fe–N str |
| 367 (w) | 376.2 (m) | 5.2 | Fe–N str |
| (Hidden) | 365 (sh) | 0 | Ligand B |
| 229 (vw) | 238.2 (w) | −0.6 | Ligand D |
| 207 (vw) | 203 (w) | *c* | Ligand E |
| 194 (vw) | 190 (w) | 0.0 | |
| | 163 (vw) | *c* | Ligand F |

| $[Fe(phen)_3]^{3+}$ ($^{54}Fe$) | $[Fe(phen)_3]^{3+}$ $\Delta\tilde{\nu}$,[b] $cm^{-1}$ | $[Fe(phen)_3]^{2+}$ (Fe)[a] | Assignment |
|---|---|---|---|
| 374.0 (s) | 374 (w) | 4.4 | Fe–N str |
| 354.1 (w) | 359 (w) | 6.3 | Fe–N str |
| 296.0 (w) | 296 (s) | 0.0 | Ligand B |
| 282.4 (w) | 289 (sh) | −0.6 | |
| 247 (m, br) | 250 (sh) | 0 | Ligand C |
| 242 (m, sh) | 244 (sh) | 0 | |
| 212.2 (w) | 216 (s) | 0.2 | N–Fe–N bend |
| | 212 (sh) | | |
| 190.3 (w) | 192 (m) | 0.1 | Ligand D |
| 180.5 (vw) | 176 (w) | 0 | |

[a] Taken from ref 8. [b] $\tilde{\nu}(^{54}Fe) - \tilde{\nu}(^{57}Fe)$. [c] Too weak to be observed with a milligram-scale sample. The frequencies observed for the Fe(natural abundance) complex are given for these bands.

**Iron Complexes.**—Figures 3 and 4 illustrate the far-infrared spectra of $[Fe(bipy)_3](ClO_4)_n$ ($n = 2, 3$) and $[Fe(phen)_3](ClO_4)_n$ ($n = 2, 3$), respectively. Table III summarizes the observed frequencies, isotopic shifts, and band assignments. In our previous paper,[8] the Fe(II)–N stretching bands of $[Fe(bipy)_3](ClO_4)_2$ have been assigned at *ca.* 381 and 374 $cm^{-1}$ based on the isotopic shifts due to the $^{54}Fe$–$^{57}Fe$ substitution. As is seen in Figure 3, the spectrum of $[Fe(bipy)_3](ClO_4)_3$ is similar to that of $[Fe(bipy)_3](ClO_4)_2$. Therefore, it is reasonable to assign two bands at 384 and 367 $cm^{-1}$ of the former to the Fe(III)–N stretching modes. Previously, two bands at 374 and 359 $cm^{-1}$ of the $[Fe(phen)_3](ClO_4)_2$ have been assigned to the Fe(II)–N stretching modes. As seen in Figure 4, the spectrum of $[Fe(phen)_3](ClO_4)_3$ is also very similar to that of $[Fe(phen)_3](ClO_4)_2$. Therefore, it is reasonable to assign two bands at *ca.* 374 and 354 $cm^{-1}$ of the former to the Fe(III)–N stretching modes. In order to confirm

(28) E. Koenig and S. Herzog, *J. Inorg. Nucl. Chem.*, **32**, 585 (1970).

(29) I. Hanazaki and S. Nagakura, *Bull. Chem. Soc. Jap.*, **44**, 2312 (1971).

these assignments, we have measured the isotopic shifts of $[Fe(phen)_3](ClO_4)_3$ due to the $^{54}Fe$–$^{57}Fe$ substitution. As is seen in Table III and Figure 3, only two bands at *ca.* 374 and 354 $cm^{-1}$ give large shifts relative to others. These results show that the Fe–N stretching frequencies of $(bipy)_3$ or $(phen)_3$ complexes do not change appreciably when the oxidation state is changed from Fe(II) to Fe(III).

Although the spectra of the Fe(II) and Fe(III) complexes are similar in the low-frequency region, they are distinctly different in the high-frequency region. For example, $[Fe(bipy)_3](ClO_4)_2$ exhibits a strong band at 845 $cm^{-1}$ where $[Fe(bipy)_3](ClO_4)_3$ has no absorption. Instead, the latter shows a strong band at 773 $cm^{-1}$. Both Fe(II) and Fe(III) complexes exhibit bands at 1609 $cm^{-1}$ and do not show any absorption between 1000 and 900 $cm^{-1}$ (Table II). Thus, the spectra of these complexes are typical of "normal"-oxidation-state complexes.

**Vanadium Complexes.**—Table IV summarizes the observed frequencies and band assignments of $[V(bipy)_3]I$ and $V(bipy)_3$. The spectra of the V(II) and V(0) complexes are very similar to that of the Cr(I) complex (Figure 1) in the 400–300-$cm^{-1}$ region. Therefore, two bands at *ca.* 370 and 340 $cm^{-1}$ of these vanadium complexes have been assigned to the V–N stretching modes. Although the far-infrared spectra of these two vanadium complexes are similar to each other, their high-frequency spectra are different; a strong sharp band of the V(II) complex at 775 $cm^{-1}$, for example, disappears completely and a new band appears at 750 $cm^{-1}$ when V(II) is reduced to V(0). Although the V(II) complex shows almost no absorption in the 1000–900-$cm^{-1}$ region, the V(0) complex exhibits a strong band at 930 $cm^{-1}$. Furthermore, the V(II) complex absorbs at 1598–1560 $cm^{-1}$ whereas the V(0) complex absorbs at 1570–1508 $cm^{-1}$ (Table II). Thus, V(II) is classified as an "intermediate", whereas V(0) is classified as a "low"-oxidation-state complex.

TABLE IV

FAR-INFRARED SPECTRA OF $[V(bipy)_3]^{n+}$ AND $[Ti(bipy)_3]^{n+}$ SERIES ($CM^{-1}$)

| $[V(bipy)_3]I_2$ | $V(bipy)_3$ | $Ti(bipy)_3 \cdot nTHF$ | $Li[Ti(bipy)_3] \cdot nTHF$ | Assignment |
|---|---|---|---|---|
| | | | 388 (sh) | Ligand A[a] |
| 374 (m) | 371 (m) | 374 (m)[b] | 365 (w)[b] | M–N str |
| 362 (sh) | 360 (sh) | 374 (m)[b] | 365 (w)[b] | Ligand B |
| 335 (m) | 343 (m) | 339 (m) | 322 (m) | M–N str |
| | | 294 (m) | 288 (m) | THF band |
| 245 (w) | 249 (w) | 248 (w) | 247 (w) | Ligand D |
| 211 (vw) | 215 (w) | 214 (m) | 219 (m) | Ligand E |
| 170 (w) | 160 (sh) | 165 (m) | 164 (m) | Ligand F |
| 137 (s) | 142 (m) | | | ? |

[a] A main band of the ligand A vibration is at 415 $cm^{-1}$. [b] Overlapped band.

**Titanium Complexes.**—The far-infrared spectra of $Ti(bipy)_3 \cdot nTHF$ and $Li[Ti(bipy)_3] \cdot nTHF$ are similar to those of the vanadium complexes except that both Ti complexes exhibit one extra band near 290 $cm^{-1}$. Thus, the band assignments listed in Table IV have been proposed. Again, the effect of changing the oxidation state on far-infrared spectra is not appreciable. In the high-frequency region, however, the spectra of these two complexes are distinctly different. For example, two sharp bands at 749 and 738 $cm^{-1}$ of the Ti(0) complex disappear and a new band appears at 723 $cm^{-1}$ when Ti(0) is reduced to Ti(−I). Both complexes absorb at *ca.* 935 and 1575–1490 $cm^{-1}$ and may be classified as "low"-oxidation-state complexes.

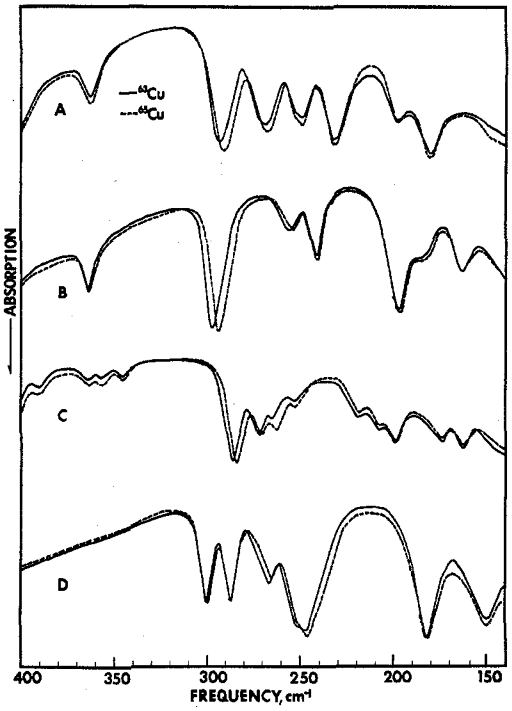

Figure 5.—Far-infrared spectra of $[Cu(bipy)_3]Cl_2$ (A), $[Cu(bipy)_3]Br_2$ (B), $[Cu(bipy)_3](ClO_4)_2$ (C), and $[Cu(phen)_3](ClO_4)_2$ (D).

**Copper Complexes.**—Figure 5 shows the far-infrared spectra of the chloride, bromide, and perchlorate salts of the $[Cu(bipy)_3]^{2+}$ ion and $[Cu(phen)_3](ClO_4)_2$, and Table V lists the observed frequencies, isotopic shifts due to the $^{63}Cu$–$^{65}Cu$ substitution, and the band assignments of these and related complexes. Two bands at 291.2 and 268.0 $cm^{-1}$ of $[^{63}Cu(bipy)_3]Cl_2 \cdot 7H_2O$ show large shifts (3.5 and 3.0 $cm^{-1}$, respectively) relative to others when $^{63}Cu$ is substituted by $^{65}Cu$. Therefore, these two bands have been assigned to the Cu–N stretching modes. Similar results have been obtained for $[^{63}Cu(bipy)_3]Br_2$ which exhibits two metal isotope sensitive bands at 297.2 and 255.4 $cm^{-1}$. As seen in Figure 5, the spectrum of the perchlorate is more complicated than those of the chloride and bromide. It exhibits three isotope-sensitive bands at *ca.* 287, 272, and 265 $cm^{-1}$. A similar phenomenon was noted previously for $[Ni(bipy)_3](ClO_4)_2$.[8] This band splitting may result from the lowering of site symmetry which occurs only in the case of the perchlorate salts. The band near 197 $cm^{-1}$ of the $[Cu(bipy)_3]^{2+}$ ion gives a metal isotope shift of *ca.* 0.8 $cm^{-1}$ and has been assigned to the N–Cu–N bending mode. All other bands show little sensitivity to the $^{63}Cu$–$^{65}Cu$ substitution and have been assigned to various types of ligand vibrations.[8] In the high-frequency region, the $[Cu(bipy)_3]^{2+}$ ion shows a spectrum typical of "normal"-oxidation-state complexes; it exhibits no strong bands at *ca.* 970 $cm^{-1}$ and a medium-intensity band at 1605 $cm^{-1}$ (Table II).

Figure 5D shows the spectrum of $[Cu(phen)_3](ClO_4)_2$. Two bands at 267.5 and 248 $cm^{-1}$ give large shifts relative to others when $^{63}Cu$ is substituted by $^{65}Cu$.

Therefore, these two bands have been assigned to the Cu–N stretching modes. The spectra of the bromide and iodide are very similar to that of the perchlorate. Table V lists the observed frequencies, metal isotope shifts, and band assignments of the $[Cu(phen)_3]^{2+}$ ion. Ligand vibrations have been assigned according to our previous paper.[8]

TABLE V

FAR-INFRARED SPECTRA OF $[Cu(bipy)_3]X_2$ AND $[Cu(phen)_3]X_2$ (CM$^{-1}$)

| $[Cu(bipy)_3]Cl_2 \cdot 7H_2O$ |  | $[Cu(bipy)_3]Br_2$ |  | $[Cu(bipy)_3](ClO_4)_2 \cdot 2H_2O$ |  | Assignment |
|---|---|---|---|---|---|---|
| $^{63}$Cu | $\Delta\tilde{\nu}^a$ | $^{63}$Cu | $\Delta\tilde{\nu}^a$ | $^{63}$Cu | $\Delta\tilde{\nu}^a$ |  |
| 362.0 (w) | 0.2 | 363.8 (w) | 0.7 | 363.5 (vw) | 0.2 |  |
|  |  |  |  | 356.0 (vw) | 0.1 | Ligand B |
|  |  |  |  | 345.4 (vw) | 0.2 |  |
| 291.2 (s) | 3.5 | 297.2 (vs) | 3.5 | 286.8 (vs) | 2.7 | Cu–N str |
| 268.0 (m) | 3.0 | 255.4 (w) | 2.4 | 271.9 (s) | 1.3 | Cu–N str |
|  |  |  |  | 265.0 (sh) | 2.0 |  |
| 250.0 (m) | 0.4 | 241.3 (m) | 0.3 | 253.3 (sh) | 0.0 | Ligand D |
| 231.5 (m) | 0.3 | *b* |  | 218.0 (sh) | 0.0 | Ligand E |
|  |  |  |  | 207.0 (sh) | 0.0 |  |
| 196.4 (sh) | 0.7 | 197.0 (s) | 0.8 | 199.6 (s) | 0.8 | N–Cu–N bend |
| 179.5 (s) | 0.0 | 185 (sh) | *c* | 175.0 (m) | 0.0 | Ligand F |
| 165 (m, br) | *c* | 163.1 (m) | 0.0 | 163.0 (m) | 0.0 |  |

| $[Cu(phen)_3]Br_2$ Cu | $[Cu(phen)_3]I_2$ Cu | $[Cu(phen)_3](ClO_4)_2$ $^{63}$Cu | $\Delta\tilde{\nu}^a$ | Assignment |
|---|---|---|---|---|
| 301 (m) | 300 (m) | 300.5 (m) | 0.5 | Ligand B |
| 295 (sh) | 285 (m) | 286.5 (m) | 0.2 |  |
| 268 (m) | 265 (w) | 267.5 (w) | 1.5 | Cu–N str |
| *d* | *d* | 251 (sh) | *c* | Ligand C |
| 240 (s) | 239 (s) | 248 (s) | 2.0 | Cu–N str |
| 190 (m) | 189 (s) | 182.3 (s) | 0.0 | Ligand D |
| 152 (w) | 148 (m) | 150.0 (s) | 0.0 | Ligand E |

[a] $\tilde{\nu}(^{63}Cu) - \tilde{\nu}(^{65}Cu)$. [b] Too weak to be observed. [c] Isotopic shifts cannot be measured accurately due to poor shape of the band. [d] Hidden by neighboring band.

**Cobalt Complexes.**—The infrared spectra of $[Co(bipy)_3]X_2$ (X = Cl, Br, I, $ClO_4$) show a strong band at *ca.* 265 cm$^{-1}$ as represented by $[Co(bipy)_3](ClO_4)_2$ of Figure 6. Since the spectrum of $[Co(bipy)_3](ClO_4)_2$ is very similar to that of $[Ni(bipy)_3]I_2$ for which metal isotope data are available,[8] it is reasonable to assign the strong band at 266 cm$^{-1}$ and a weak band at 246 or 228 cm$^{-1}$ of the former to the Co(II)–N stretching modes.

Figure 6 also compares the spectrum of $[Co(bipy)_3](ClO_4)$ with that of $[Zn(bipy)_3]Cl_2 \cdot 2H_2O$.[30] Previously,[8] two strong bands at 234 and 183 cm$^{-1}$ of the Zn(II) complex have been assigned to the Zn–N stretching modes by the metal isotope technique. Since the far-infrared spectrum of the Co(I) complex is similar to that of the Zn(II) complex, we assign two strong bands at *ca.* 238 and 185 cm$^{-1}$ of the former to the Co(I)–N stretching modes.

As is seen in Figure 6, the spectrum of $Co(bipy)_3$ is different from that of either the Co(II) or the Co(I) complex. It is possible, however, to assign two strong bands at 280 and 257 cm$^{-1}$ to the Co(0)–N stretching modes since the M–N stretching bands thus far observed are generally strong and all other bands can be attributed to various ligand vibrations (Table VI).

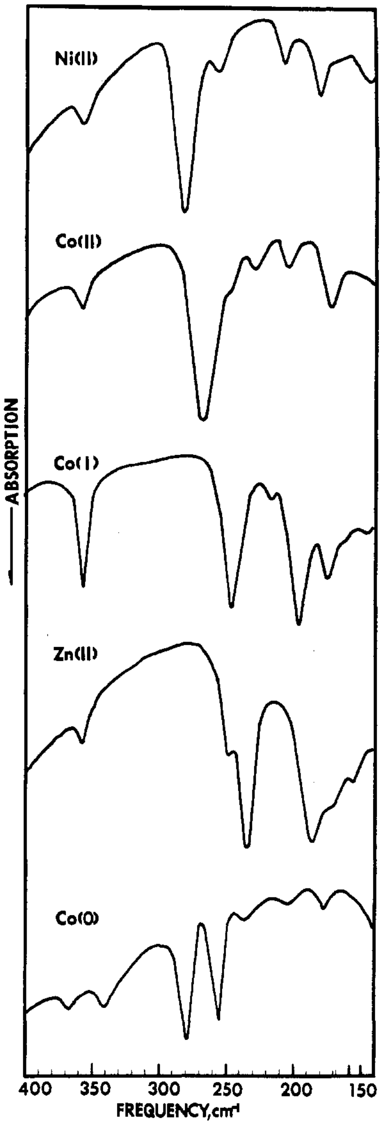

Figure 6.—Far-infrareds pectra of $[Ni(bipy)_3]I_2$, $[Co(bipy)_3](ClO_4)_2$, $[Co(bipy)_3](ClO_4)$, $[Zn(bipy)_3]Cl_2 \cdot 2H_2O$, and $Co(bipy)_3$.

The high-frequency spectra (Table II) show that the Co(III) and Co(II) complexes belong to the "normal," the Co(I) complex belongs to the "intermediate," and the Co(0) complex belongs to the "low" oxidation state.

In order to confirm the Co–N stretching band assignments, the infrared spectra of $(phen)_3$ complexes of Co(I) and Co(II) have also been studied. As is seen in Figure 7, the spectrum of $[Co(phen)_3](ClO_4)$ is very similar to that of $[Zn(phen)_3](ClO_4)_2$. Since the 198- and 175-cm$^{-1}$ bands of the latter have been assigned to the Zn–N stretching modes by the metal isotope method,[8] the corresponding bands at 200 and 175 cm$^{-1}$ of the Co(I) complex can be assigned to the Co(I)–N stretching modes of the phen complex. As is seen in Table VII, other bands can be assigned to the ligand vibrations which are common to all other $(phen)_3$ complexes.

As shown previously, the Co(II)–N stretching frequencies are higher by *ca.* 30 cm$^{-1}$ than the Co(I)–N stretching frequencies in $(bipy)_3$ complexes. If this trend holds in $(phen)_3$ complexes, the Co(II)–N stretching bands of the $(phen)_3$ complex are expected to be

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(30) The strong band at 288 cm$^{-1}$ of $[Zn(bipy)_3]Cl_2 \cdot 7H_2O$ was assigned to ligand C vibration in our previous paper.[8] This band disappears when it is dehydrated to $[Zn(bipy)_3]Cl_2 \cdot 2H_2O$. Thus, this band may be due to a librational mode of crystal water. The bands corresponding to ligand C vibrations were not observed in any $(bipy)_3$ complexes studied in this paper.

TABLE VI

FAR-INFRARED SPECTRA OF THE $[Co(bipy)_3]^{n+}$ SERIES (CM$^{-1}$)

| $[Co(bipy)_3]X_2$ | | | | $[Co(bipy)_3]X$ | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| X = Cl | X = Br | X = I | X = $ClO_4$ | X = Cl | X = Br | X = I | X = $ClO_4$ | $Co(bipy)_3$ | Assignment |
| 356 (w) | 355 (w) | 354 (w) | 357 (w) | 354 (m) | 355 (m) | 354 (m) | 356 (s) | 369 (w)<br>343 (w) | Ligand B |
| 264 (vs) | 264 (vs) | 263 (vs) | 266 (vs) | 238 (s) | 238 (s) | 241 (s)[a] | 244 (s)[a] | 280 (s) | Co–N str |
| 252 (sh) | 250 (sh) | 248 (sh) | 246 (sh) | 244 (sh) | 246 (sh) | 241 (s)[a] | 244 (s)[a] | 236 (w) | Ligand D |
| 228 (sh) | 234 (sh) | 232 (sh) | 228 (w) | 185 (vs) | 186 (vs) | 189 (vs) | 194 (vs) | 257 (s) | Co–N str |
| 202 (w) | 200 (m) | 199 (w) | 203 (w) | 214 (vw) | 214 (vw) | 213 (vw) | 215 (vw) | 204 (w) | Ligand E |
| 174 (m) | 173 (m) | 171 (w) | 170 (w) | 166 (s) | 168 (s) | 170 (m) | 173 (m) | 178 (w) | Ligand F |

[a] Overlapped band.

TABLE VII

FAR-INFRARED SPECTRA OF THE $[Co(phen)_3]X_n$ SERIES (CM$^{-1}$)

| Co(III) | Co(II) | | | | Co(I) | | | |
|---|---|---|---|---|---|---|---|---|
| X = $ClO_4$ | X = Cl | X = Br | X = I | X = $ClO_4$ | X = Br | X = I | X = $ClO_4$ | Assignment |
| 305 (vw) | 288 (s) | 287 (s) | 287 (s) | 286 (s) | 318 (w, br)<br>289 (w) | 320 (w, br)<br>287 (w) | 319 (vw)<br>290 (vw) | Ligand B |
| 248 (m)<br>242 (sh) | *b* | *b* | *b* | *b* | 260 (vw)<br>239 (w) | 263 (vw)<br>238 (w) | 262 (vw)<br>238 (w) | Ligand C |
| 378 (s) | 235 (vs) | 237 (vs) | 237 (vs) | 243 (vs) | 197 (vs) | 198 (vs) | 200 (vs) | Co–N str |
| 370 (sh) | 220 (sh) | 221 (sh) | 221 (sh) | 213 (w) | 177 (s)[a] | 175 (s)[a] | 175 (m)[a] | Co–N str |
| 209 (w) | | | | | | | | N–Co–N bend |
| 199 (w) | 168 (w) | 179 (w) | 180 (m) | 185 (m) | 177 (s)[a] | 175 (s)[a] | 175 (m)[a] | Ligand D |
| | 130 (w, br) | 149 (w)<br>125 (vw) | 146 (w)<br>125 (vw) | 152 (m) | 149 (w) | | 148 (w) | Ligand E |

[a] Overlapped band. [b] Hidden by neighboring band.

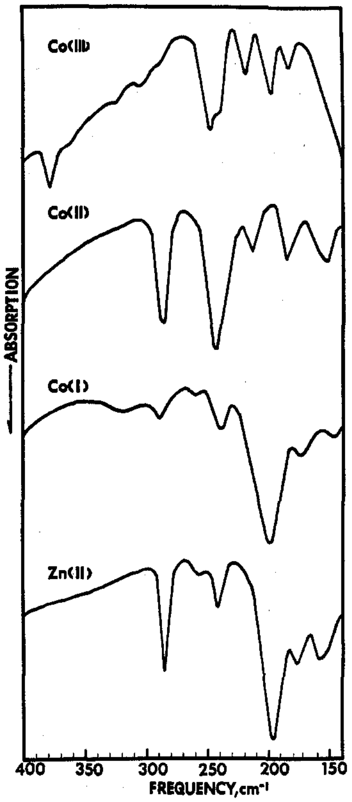

Figure 7.—Far-infrared spectra of the $[Co(phen)_3](ClO_4)_n$ series and $[Zn(phen)_3](ClO_4)_2$.

near 230 and 205 cm$^{-1}$. Thus the bands at 243 (vs) and 213 cm$^{-1}$ (w) of $[Co(phen)_3](ClO_4)_2$ have been assigned to the Co(II)–N stretching bands.

Figure 7 also shows the spectrum of $[Co(phen)_3](ClO_4)_3 \cdot 2H_2O$. Since Co(III) is isoelectronic to Fe(II), its spectrum is similar to that of $[Fe(phen)_3](ClO_4)_2$. The bands at 374 and 359 cm$^{-1}$ of the latter have been assigned to the Fe(II)–N stretchings. Then, it is reasonable to assign two bands at 378 and 370 cm$^{-1}$ (sh) of the former to the Co(III)–N stretching modes. The corresponding bands in $[Co(bipy)_3](ClO_4)_3$ are too weak to be observed. A phenomenon similar to this has long been known for the Co(III)–N stretching bands of the $[Co(NH_3)_6]X_3$. However, the reason for the weakness of these Co(III)–N stretching bands is not obvious.

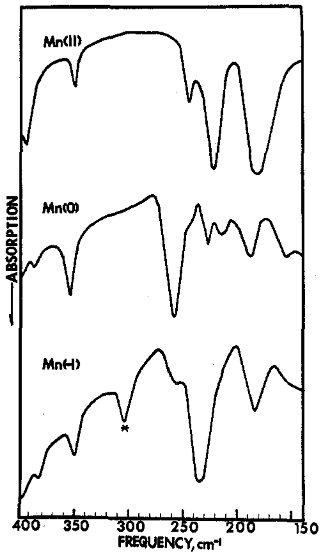

Figure 8.—Far-infrared spectra of $[Mn(bipy)_3]I_2$, $Mn(bipy)_3$, and $Li[Mn(bipy)_3] \cdot n THF$ (* indicates a THF band).

**Manganese Complexes.**—As is shown in Figure 8, the far-infrared spectrum of $[Mn(bipy)_3]I_2$ is very similar to those of $[Zn(bipy)_3]Cl_2 \cdot 2H_2O$ and $[Co(bipy)_3]ClO_4$ shown in Figure 6. Thus, two strong bands at 221 and 182 cm$^{-1}$ can be assigned to the Mn(II)–N stretching modes without metal isotope data. On the other hand, the spectrum of $Mn(bipy)_3$ is similar to that of $[Co(bipy)_3](ClO_4)_2$ of Figure 6. Thus, we have assigned two bands at 258 (s) and 227 cm$^{-1}$ (w) to the Mn(0)–N stretching modes. The spectrum of Li[Mn-

$(bipy)_3]\cdot n$THF is similar to that of $[Zn(bipy)_3]Cl_2\cdot 2H_2O$ except that the former shows an extra band at 305 cm$^{-1}$ which is due to the coordinated THF molecule. Thus, two bands at 235 (strong) and 184 cm$^{-1}$ (m) have been assigned to the Mn(−I)–N stretching modes. In addition to the Mn–N stretching bands, these Mn complexes exhibit ligand bands common to all $(bipy)_3$ complexes. As is shown in Table VIII, however, some of these ligand vibrations are overlapped by strong Mn–N stretching bands.

TABLE VIII

FAR-INFRARED SPECTRA OF THE $[Mn(bipy)_3]^{n+}$ SERIES (CM$^{-1}$)

| $[Mn(bipy)_3]Br_2$ | $[Mn(bipy)_3]I_2$ | $Mn(bipy)_3$ | $Li[Mn(bipy)_3]\cdot n$THF | Assignment |
|---|---|---|---|---|
| 395 (vw, sh) | 395 (w) | 388 (vw) | 383 (vw) | Ligand A′[a] |
| 350 (w) | 350 (w) | 354 (m) | 351 (m) | Ligand B |
| | | | 305 (m) | THF |
| 243 (sh) | 244 (w) | 258 (vs)[b] | 250 (sh) | Ligand D |
| 224 (vs) | 221 (vs) | 258 (vs)[b] | 235 (vs) | Mn–N str |
| 204 (sh) | | 218 (sh) | 218 (sh) | Ligand E |
| | | 227 (w) | | |
| 191 (vs) | 182 (vs) | 188 (m) | 184 (m) | Mn–N str, ligand F |

[a] A weak satellite band of the main peak at *ca.* 415 cm$^{-1}$ (ligand A vibration). [b] Overlapped band.

In the 1000–900-cm$^{-1}$ region, the Mn(II) complex shows no absorption whereas the Mn(0) and Mn(−I) complexes show strong bands near 950 cm$^{-1}$. Thus, the former is typical of "normal" oxidation state whereas the latter are typical of "low"-oxidation-state complexes. However, the Mn(0) complex exhibits two medium-intensity bands at 1600 and 1573 cm$^{-1}$ and was, therefore, classified as an "intermediate" case.

**M–N Stretching Frequencies and Electronic Structure.**—Table IX lists the M–N stretching frequencies of the $[M(bipy)_3]^{n+}$ type complexes for each metal and for each oxidation state. It is seen that all the complexes studied exhibit two M–N stretching bands which are separated by 80–10 cm$^{-1}$ depending upon the metal and its oxidation state. Theoretically, the $[M(bipy)_3]^{n+}$ type complexes belong to the $D_3$ point group and their M–N stretching modes are classified into the $A_1$ (Raman active), $A_2$ (ir active) and 2 E (ir and Raman active) species. It was not possible, however, to determine the symmetry species of the two M–N stretching bands observed in infrared spectra since Raman data are lacking. It was also not possible to discuss the difference in the strength of the M–N bonds between various metals and various oxidation states since force constant calculations were not carried out on these compounds. Thus, our discussions given below are limited to a rather qualitative interpretation of observed spectra.

Table IX also lists the magnetic moments and the d-electron configurations. In terms of a simple MO theory, Cr(III), Cr(II), Cr(I), Cr(0), V(II), V(0), Ti(0), Ti(−I), Fe(III), Fe(II), and Co(III) have filled or partly filled $t_{2g}$ (bonding) orbitals and empty $e_g$ (antibonding) orbitals. It is seen that the M–N stretching frequencies of $(bipy)_3$ complexes of this group (A) are in the 390–300-cm$^{-1}$ region without exception. On the other hand, Co(II), Co(I), Co(0), Mn(II), Mn(0), Mn(−I), Ni(II), Cu(II), and Zn(II) have filled or partly filled $e_g$ (antibonding) orbitals. The M–N stretching frequencies of this group (B) are in the 290–180-cm$^{-1}$ region. Thus, there is a marked difference in the M–N stretching frequencies between these two groups. In the divalent metal series (vertical series), V(II), Cr(II), and Fe(II) belong to group A whereas Mn(II), Co(II), Ni(II), Cu(II), and Zn(II) belong to group B. Although Mn(II) is $d^5$, it gives exceptionally low M–N stretching frequencies since it takes the $(t_{2g})^3(e_g)^2$ configuration (group B). This is also true in the $d^5$ series (horizontal series) in Table IX.

In a series of $(bipy)_3$ complexes of the same metal and different oxidation state (diagonal series), the M–N stretching frequencies do not change appreciably by changing the oxidation state unless there is a crossover from A to B in electron configuration. Thus, no marked changes in frequencies are seen in the Cr(III)–Cr(0) and Co(II)–Co(0) series, although a dramatic decrease in the Co–N stretching frequencies is seen in going from Co(III) to Co(II). This result is somewhat surprising since a marked effect of changing the oxidation state on infrared spectra was noted previously.[3,4] In these cases, however, the complexes did not involve ligands which can utilize empty $\pi^*$ ligand orbitals for bonding. Thus, the present result can be accounted for if we assume that, as the formal oxidation state is lowered, $\sigma$ bonding becomes weaker and $\pi$ bonding becomes stronger so that the overall M–N bond strength is approximately constant. If this is the case, there will be considerable interaction between the metal $d_\pi$ orbitals and the antibonding ligand $\pi^*$ orbitals so that increasing amounts of electrons of the metal would reside in essentially ligand orbitals as the oxidation state is lowered.[28,29] Thus, the electron distribution in $Cr(bipy)_3$ may be indicated as $Cr^{3\delta+}(bipy^{\delta-})_3$.

Other physical methods have been used to study the nature of bonding in these low-oxidation-state complexes: esr,[31,32] electronic spectra,[28,29,33,34] and nmr contact shifts.[23,35,36] Unfortunately, the results obtained by these methods are conflicting and confusing. For example, Kaizu, *et al.*,[34] concluded from electronic spectra that $Fe(bipy)_3$ is best regarded as an ionic complex. On the other hand, Hall and Reynolds[31a] concluded from esr evidence that $Fe(bipy)_3$ is best regarded as Fe(0) bonded to neutral bipy ligands although they noted the resemblance of electronic spectra between $Fe(bipy)_3$ and $Na^+(bipy^-)$. Mahon and Reynolds[31b] suggested the ionic bonding for $NaFe(bipy)_3$ from its electronic and esr spectra.

Koenig and Herzog[28] and Kaizu, *et al.*,[24] agree that a substantial fraction of the bipy ligands in $Cr(bipy)_3$ has the character of the $bipy^-$ ion. On the other hand, Kaizu, *et al.*,[34] concluded that $V(bipy)_3$ consists of V(0) bonded to neutral bipy ligands. This is in disagreement with Koenig and Herzog,[33] who suggested that $V(bipy)_3$ shows electronic transitions due to the $bipy^-$ ion. Disagreement similar to this is also seen

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(31) (a) F. S. Hall and W. L. Reynolds, *Inorg. Chem.*, **5**, 931 (1966); (b) C. Mahon and W. L. Reynolds, *ibid.*, **6**, 1927 (1967).

(32) G. Abrecht, *Z. Chem.*, **3**, 182 (1963).

(33) E. Koenig and S. Herzog, *J. Inorg. Nucl. Chem.*, **32**, 601, 613 (1970).

(34) Y. Kaizu, T. Yazaki, Y. Torii, and H. Kobayashi, *Bull. Chem. Soc. Jap.*, **43**, 206 (1970).

(35) R. E. DeSimone and R. S. Drago, *J. Amer. Chem. Soc.*, **92**, 2343 (1970).

(36) G. N. La Mar and G. R. Van Hecke, *ibid.*, **91**, 3443 (1969).

TABLE IX

M–N STRETCHING FREQUENCY AND ELECTRONIC STRUCTURE IN THE $[M(bipy)_3]^{n+}$ TYPE COMPOUNDS ($cm^{-1}$)[a]

| | –I | 0 | I | II | III |
|---|---|---|---|---|---|
| $d^3$ | | | | V 374<br>(3.67) 335<br>$(t_{2g})^3$ | Cr 385<br>(3.78) 349<br>$(t_{2g})^3$ |
| $d^4$ | | Ti 374<br>(0) 339<br>$(t_{2g})^4$-ls | | Cr 351<br>(2.9) 343<br>$(t_{2g})^4$-ls | |
| $d^5$ | Ti 365<br>(1.74) 322<br>$(t_{2g})^5$-ls | V 371<br>(1.68) 343<br>$(t_{2g})^5$-ls | Cr 371<br>(2.0) 343<br>$(t_{2g})^5$-ls | Mn 224<br>(5.95) 191<br>$(t_{2g})^3(e_g)^2$-hs | Fe 384<br>(?) 367 |
| $d^6$ | | Cr 382<br>(0) 308<br>$(t_{2g})^6$ | | Fe 386<br>(0) 376<br>$(t_{2g})^6$ | Co 378[b]<br>(0) 370[b]<br>$(t_{2g})^6$ |
| $d^7$ | | Mn 258<br>(4.10) 227<br>$(t_{2g})^5(e_g)^2$ | | Co 266<br>(4.85) 228<br>$(t_{2g})^5(e_g)^2$ | |
| $d^8$ | Mn 235<br>(3.71) 184<br>$(t_{2g})^6(e_g)^2$ | | Co 244<br>(3.3) 194<br>$(t_{2g})^6(e_g)^2$ | Ni 282[c]<br>(3.10) 258<br>$(t_{2g})^6(e_g)^2$ | |
| $d^9$ | | Co 280<br>(2.23) 257<br>$(t_{2g})^6(e_g)^3$ | | Cu 291<br>(?) 268<br>$(t_{2g})^6(e_g)^3$ | |
| $d^{10}$ | | | | Zn 230[c]<br>(0) 184<br>$(t_{2g})^6(e_g)^4$ | |

[a] The numbers at upper right of each group indicate the M–N stretching frequencies ($cm^{-1}$). The number in parentheses gives the observed magnetic moment in units of Bohr magnetons.[4] ls = low spin; hs = high spin. [b] Values for $[Co(phen)_3](ClO_4)_3$. [c] Taken from ref 8.

between these two groups of investigators[33,34] concerning the interpretation of the electronic spectrum of $Ti(bipy)_3$. Our present infrared study suggests that the metal–bipy bonding is predominantly ionic in all these zerovalent complexes.

The degree of $\sigma$ and $\pi$ bonding of the M–N bond has been a subject of the nmr contact shift studies.[28,35,36] Again, some confusion exists concerning the interpretation of the observed nmr contact shifts. It is difficult, however, to deduce such information from vibrational spectra unless a rigorous normal-coordinate analysis is carried out by using a suitable potential field.

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# Metal Complexes of Substituted Dithiophosphinic Acids. VI. Reactions of Difluorodithiophosphinic Acid with Chlorides and Oxychlorides of Chromium, Molybdenum, and Tungsten

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The reaction of difluorodithiophosphinic acid, $F_2PS_2H$, with $O_2CrCl_2$ gave the known $Cr(S_2PF_2)_3$ complex while $OMoCl_4$, $MoCl_5$, $MoCl_4$, $OWCl_4$, and $WCl_6$ gave new difluorodithiophosphinato complexes of the metals in reduced valence states. $WCl_4$, $WCl_4\cdot 2py$, $K_3MoCl_6$, and molybdenum and tungsten metals did not react. The complex $K_3W_2Cl_9$ reacted to give a product which is thought to contain the $[W_2Cl_7S]^{3-}$ anion rather than the difluorodithiophosphinato complex. Aerial oxidation of the $Mo(S_2PF_2)_3$ afforded $OMo(S_2PF_2)_2$. Pyridine reacts with the $OMo(S_2PF_2)_2$ complex to form the complex $OMo(S_2PF_2)_2\cdot 4py$ which does not contain coordinated dithiophosphinato ligands. The complexes $OMo(S_2PF_2)_2$ and $OW(S_2PF_2)_2Cl$ are the first reported oxodifluorothiophosphinato complexes of second- and third-row transition metals.

A series of transition metal salts of the strong acid $F_2PS_2H$[1] prepared by the reactions of the acid with the metal (Cr, Mn, Fe, Co, Ni, Cu), the metal oxide (Ag), or halide (Rh, Pd, Pt, $(C_6H_5)_3PAu$) have recently been reported.[2] The preparations of the $V^{III}$ and $OV^{IV}$ fluoro[3] and other[3-7] substituted dithiophosphinates have

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(1) T. L. Charlton and R. G. Cavell, *Inorg. Chem.*, **8**, 281 (1969); R. W. Mitchell, M. Lustig, F. A. Hartman, J. K. Ruff, and J. A. Merritt, *J. Amer. Chem. Soc.*, **90**, 6329 (1968).

(2) F. N. Tebbe and E. L. Muetterties, *Inorg. Chem.*, **9**, 629 (1970).