

With the exception of the insoluble  $\text{Cd}(\text{bipyO}_2)\text{Cl}_2$  compound, all the other investigated  $\text{bipyO}_2$  complexes behave in solution as strong electrolytes. The values of the molar conductivities,  $\Lambda_m$ , in DMF (Table I) are in good agreement with those reported for similar complex salts of pyridine N-oxide under the same conditions<sup>1</sup>: from  $85 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}$  downward for uni-univalent salts, in the range  $140\text{--}170 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}$  for di-univalent salts, and in the range  $200\text{--}260 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}$  for tri-univalent salts. The molar conductivities in water (Table I) are also in good agreement with the values reported for simple<sup>15</sup> and complex<sup>16</sup> salts:  $\Lambda_m = 250 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}$  (at  $0.920 \text{ mmole l.}^{-1}$ ) in water at  $25^\circ$ , for a di-divalent electrolyte such as  $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{C}_2\text{O}_4$ ;  $\Lambda_m = 516 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}$  at  $25^\circ$  for the tri-divalent salt

(15) "International Critical Tables," Vol. VI, McGraw-Hill Book Company, Inc., New York, N. Y., 1929, p. 229.

(16) N. Dhar, *Z. anorg. allgem. Chem.*, **80**, 43 (1913).

$\text{Y}_2(\text{SO}_4)_3$ ; and  $\Lambda_m = 768 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}$  at  $25^\circ$  for  $\text{Cr}_2(\text{SO}_4)_3$ .

The values of the magnetic moments  $\mu_{\text{eff}}$  (Table II) show that the  $\text{bipyO}_2$ -metal complex cations have the same number of unpaired electrons as the "free" metal ions. The tris-chelate cations of the elements from Mn(II) to Zn(II) therefore may be considered to have an octahedral structure utilizing  $4s4p^34d^2$  hybrid orbitals, similar to other transition metal complexes of oxygen donor ligands.<sup>13</sup> The Mn(III) complex ion,  $[\text{Mn}(\text{bipyO}_2)_3]^{3+}$ , recently reported by Nyholm and Turco, also was found to be of the spin-free type.<sup>17</sup>

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(17) R. S. Nyholm and A. Turco, *J. Chem. Soc.*, 1121 (1962) (on p. 1121 ref. 4 should read 3).

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## Infrared Studies of 2,2'-Bipyridine N,N'-Dioxide and its Metal Complexes in the 3–38 $\mu$ Region

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The infrared spectra of 2,2'-bipyridine N,N'-dioxide ( $\text{bipyO}_2$ ) and of eighteen of its metal complexes were measured in the range  $4000\text{--}260 \text{ cm}^{-1}$ . The band appearing in the cesium bromide region of the spectra of the complexes but not in that of free  $\text{bipyO}_2$  was assigned to the metal-to-oxygen stretching vibration. The trend of the frequency values of this band for the various metal complexes is similar to that observed for the complexes of pyridine N-oxide, and is in qualitative agreement with the Irving and Williams stability series. In the spectra of the complexes the bands corresponding, respectively, to the metal-to-oxygen and oxygen-to-nitrogen stretching vibrations were found to be correlated.

In the preceding paper<sup>1</sup> the preparation and properties of 2,2'-bipyridine N,N'-dioxide ( $\text{bipyO}_2$ ) and of a number of its metal complexes were described. The present paper deals with the infrared spectra of  $\text{bipyO}_2$  and of eighteen of its metal complexes (Table I), and assignments are made for the most significant absorption bands. In most cases these assignments are based on a comparative study of the spectra of  $\text{bipyO}_2$  and of related molecules such as pyridine,<sup>2</sup> pyridine N-oxide,<sup>3–6</sup> and biphenyl.<sup>7</sup> Reference is also made to the theoretical<sup>8</sup> and experimental work<sup>9</sup> on *o*-disubstituted benzene type molecules.

(1) P. G. Simpson, A. Vinciguerra, and J. V. Quagliano, *Inorg. Chem.*, **2**, 282 (1963).

(2) L. Corrsin, B. J. Fax, and R. C. Lord, *J. Chem. Phys.*, **21**, 1170 (1953).

(3) H. Shindo, *Pharm. Bull.* (Tokyo), **4**, 460 (1956).

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(5) Y. Kakiuti, S. Kida, and J. V. Quagliano, *ibid.*, in press.

(6) H. Shindo, Ph.D. Dissertation, Tokyo University, 1959; *Kagaku no Ryōhiki, Zokan*, **28**, 163 (1958).

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The infrared spectrum of  $\text{bipyO}_2$  resembles that of pyridine N-oxide (pyO) and the assignments made in the former are based largely on our study of the latter.<sup>4,5</sup> The frequency shifts and the intensity variations observed when comparing the spectra of  $\text{bipyO}_2$  metal complexes with the spectrum of the free  $\text{bipyO}_2$  also are similar to those reported for pyO metal complexes and free pyO.<sup>4,5</sup>

### Experimental

The infrared spectra were obtained as described previously.<sup>10</sup> Figures 1 and 2 show two typical spectra in the sodium chloride ( $1700\text{--}650 \text{ cm}^{-1}$ ) and in the cesium bromide ( $650\text{--}260 \text{ cm}^{-1}$ ) regions. Table I lists the compounds investigated, together with the values of the NO stretching, NO bending, and MO stretching frequencies.

**Preparation of  $[\text{Cu}(\text{bipyO}_2)_2][\text{PtCl}_4] \cdot 4\text{D}_2\text{O}$ .**—Finely powdered anhydrous  $[\text{Cu}(\text{bipyO}_2)_2][\text{PtCl}_4]$  was introduced in a vacuum desiccator together with  $\text{D}_2\text{O}$ , and the system was immediately

*Nippon Kagaku Zasshi*, **77**, 1572 (1956); Y. Kakiuti, *ibid.*, **80**, 28 (1959).

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TABLE I  
OBSERVED FREQUENCIES (CM.<sup>-1</sup>) OF 2,2'-BIPYRIDINE N,N'-DIOXIDE AND ITS METAL COMPLEXES

Compound	NO stretch	NO bend	MO stretch
bipyO <sub>2</sub>	1262 vs 1255 <sup>a</sup> vs	852 s 840 s	...
[Cr(bipyO <sub>2</sub> ) <sub>3</sub> ](ClO <sub>4</sub> ) <sub>3</sub> ·2H <sub>2</sub> O	1215 sh, vw 1210 <sup>a</sup> vs 1199 sh, vw	843 vs 830 sh, vw	434 <sup>a</sup> vs 420 sh, m
[Cr(bipyO <sub>2</sub> ) <sub>2</sub> Cl <sub>2</sub> ] <sub>2</sub> PtCl <sub>4</sub>	1213 <sup>a</sup> vs 1200 sh, vw	847 vs 837 sh, w	418 <sup>a</sup> vs
[Cr(bipyO <sub>2</sub> ) <sub>2</sub> Cl <sub>2</sub> ](ClO <sub>4</sub> )·H <sub>2</sub> O	1207 <sup>a</sup> vs 1195 sh, vw	845 vs 837 sh, vw	417 <sup>a</sup> s 400 sh, m 385 w
[Mn(bipyO <sub>2</sub> ) <sub>3</sub> ](ClO <sub>4</sub> ) <sub>3</sub> ·2H <sub>2</sub> O	1235 sh, vw 1225 sh, vw 1210 <sup>a</sup> vs	847 vs 833 vs	357 <sup>a</sup> s
[Fe(bipyO <sub>2</sub> ) <sub>3</sub> ](ClO <sub>4</sub> ) <sub>3</sub> ·3H <sub>2</sub> O	1125 sh, vw 1213 <sup>a</sup> vs 1200 sh, vw	847 vs 832 vs	408 <sup>a</sup> vs 377 sh, m
[Fe(bipyO <sub>2</sub> ) <sub>3</sub> ] <sub>2</sub> [PtCl <sub>4</sub> ] <sub>3</sub>	1228 sh, vw 1206 <sup>a</sup> vs 1200 sh, vw	845 vs 831 vs	407 <sup>a</sup> vs 375 sh, w
[Co(bipyO <sub>2</sub> ) <sub>3</sub> ](ClO <sub>4</sub> ) <sub>3</sub> ·2H <sub>2</sub> O	1220 <sup>a</sup> vs 1202 <sup>a</sup> vs	848 vs 834 vs	362 <sup>a</sup> s
[Co(bipyO <sub>2</sub> ) <sub>3</sub> ](ClO <sub>4</sub> ) <sub>2</sub> ·2H <sub>2</sub> O	1215 sh, m 1198 <sup>a</sup> vs	844 vs 830 vs	362 <sup>a</sup> s 346 m
[Ni(bipyO <sub>2</sub> ) <sub>3</sub> ](ClO <sub>4</sub> ) <sub>2</sub> ·2H <sub>2</sub> O	1220 <sup>a</sup> vs 1209 sh, m	848 vs 834 vs	370 <sup>a</sup> s 351 sh, w
[Ni(bipyO <sub>2</sub> ) <sub>3</sub> ](ClO <sub>4</sub> ) <sub>2</sub> ·2H <sub>2</sub> O	1212 <sup>a</sup> vs 1200 <sup>a</sup> vs	844 vs 832 vs	370 <sup>a</sup> s 354 m
[Cu(bipyO <sub>2</sub> ) <sub>3</sub> ](ClO <sub>4</sub> ) <sub>2</sub> ·2H <sub>2</sub> O	1250 sh, vvw 1235 sh, w 1210 <sup>a</sup> vs	850 vs 836 vs	392 <sup>a</sup> m
[Cu(bipyO <sub>2</sub> ) <sub>2</sub> ](ClO <sub>4</sub> ) <sub>2</sub> ·2H <sub>2</sub> O	1210 sh, vw 1201 <sup>a</sup> vs	846 vs 835 vs	410 <sup>a</sup> s
[Cu(bipyO <sub>2</sub> ) <sub>2</sub> ](ClO <sub>4</sub> ) <sub>2</sub> ·4H <sub>2</sub> O	1210 sh, vw 1203 <sup>a</sup> vs	844 vs 835 vs	410 sh, m 397 <sup>a</sup> s
[Cu(bipyO <sub>2</sub> ) <sub>2</sub> ](ClO <sub>4</sub> ) <sub>2</sub> ·4D <sub>2</sub> O	1233 m 1217 <sup>a</sup> vs 1208 sh, w	847 vs 837 vs	404 <sup>a</sup> s
[Zn(bipyO <sub>2</sub> ) <sub>3</sub> ](ClO <sub>4</sub> ) <sub>2</sub> ·2H <sub>2</sub> O	1198 vs 1230 vs 1211 <sup>a</sup> vs	835 vs 845 vs	355 <sup>a</sup> m 340 sh, w
[Zn(bipyO <sub>2</sub> ) <sub>3</sub> ](ClO <sub>4</sub> ) <sub>2</sub> ·2H <sub>2</sub> O	1225 sh, vw 1208 <sup>a</sup> vs	845 vs 834 vs	362 <sup>a</sup> m
[Zn(bipyO <sub>2</sub> ) <sub>3</sub> ](ClO <sub>4</sub> ) <sub>2</sub> ·2H <sub>2</sub> O	1230 vs 1211 <sup>a</sup> vs	848 vs 833 vs	348 <sup>a</sup> vs 332 sh, m
[Cd(bipyO <sub>2</sub> ) <sub>3</sub> ](ClO <sub>4</sub> ) <sub>2</sub> ·H <sub>2</sub> O	1227 <sup>a</sup> vs 1215 sh, vw	854 m	294 <sup>a</sup> m
Cd(bipyO <sub>2</sub> )Cl <sub>2</sub>	1205 sh, vvw	832 vs	

<sup>a</sup> Denotes more intense band.

evacuated and allowed to stand at room temperature for 24 hr. The color of the compound changed from the deep olive-green typical of the anhydrous form to the light yellow-green of the tetrahydrate. The Nujol mull of the deuteration product was prepared, and the spectrum recorded, immediately after opening the desiccator.

### Results and Conclusions

The detailed discussion and assignments of the infrared spectra of bipyO<sub>2</sub> and of its metal complexes may be considered to exceed the scope of this paper and are available elsewhere.<sup>11</sup> However, considering the complexity of the spectra in question, we feel that a careful investigation of all bands was required to give validity to the assignment of those bands that are of major interest in the study of the coordination properties of bipyO<sub>2</sub>, in particular the nitrogen-to-oxygen stretching vibration,  $\nu(\text{N}-\text{O})$ , and the metal-to-oxygen stretching vibration,  $\nu(\text{M}-\text{O})$ . It seems convenient to consider and discuss separately the significance of these absorptions and their shifts.

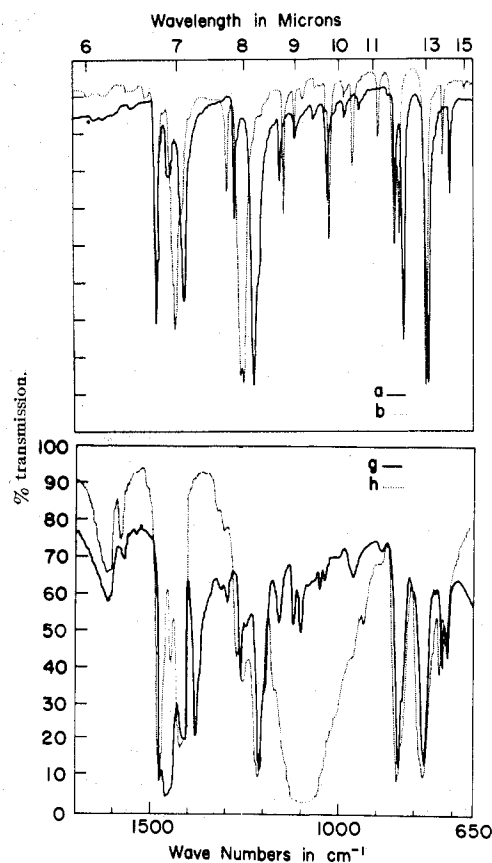


Fig. 1.—a—, Cd(bipyO<sub>2</sub>)Cl<sub>2</sub>; b..., bipyO<sub>2</sub>, 2,2'-bipyridine N,N'-dioxide; g—, [Cr(bipyO<sub>2</sub>)<sub>2</sub>Cl<sub>2</sub>]<sub>2</sub>[PtCl<sub>4</sub>]; h..., [Cr(bipyO<sub>2</sub>)<sub>3</sub>](ClO<sub>4</sub>)<sub>3</sub>·2H<sub>2</sub>O.

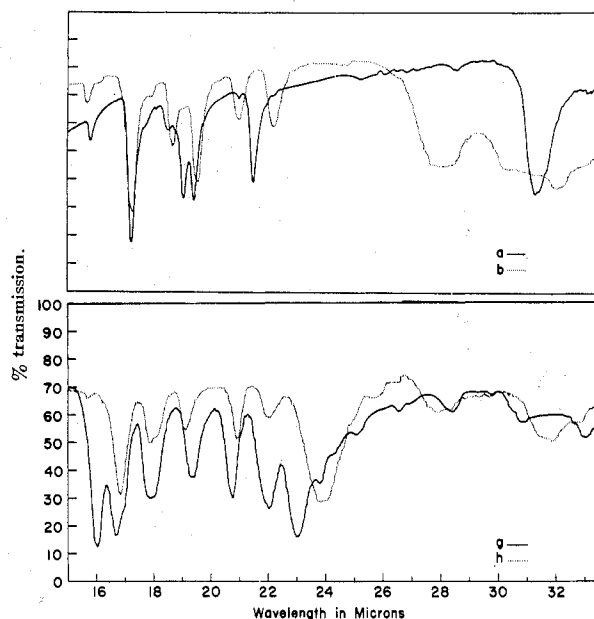


Fig. 2.—a—, bipyO<sub>2</sub>; b..., [Mn(bipyO<sub>2</sub>)<sub>3</sub>][PtCl<sub>4</sub>]; g—, [Cr(bipyO<sub>2</sub>)<sub>3</sub>](ClO<sub>4</sub>)<sub>3</sub>·2H<sub>2</sub>O; h..., [Cr(bipyO<sub>2</sub>)<sub>2</sub>Cl<sub>2</sub>]<sub>2</sub>[PtCl<sub>4</sub>].

### The Metal-to-Oxygen Stretching Vibration, $\nu(\text{M}-\text{O})$ .

—In the CsBr region, the spectrum of bipyO<sub>2</sub> shows a number of absorptions which are assigned to the various ring skeletal modes. In the spectra of the complexes, these bands appear almost unchanged, except where interference with water or anion bands occurs. In addition to the ligand skeletal bands, the hydrated per-

chlorate complexes have a very strong broad absorption at  $620\text{ cm.}^{-1}$  attributed to the  $\text{ClO}_4^-$  ion and a weak broad absorption below  $500\text{ cm.}^{-1}$ , due to water of hydration,<sup>12</sup> whereas the tetrachloroplatinates have medium or weak absorptions in the ranges  $357\text{--}326$  and  $315\text{--}300\text{ cm.}^{-1}$ , attributed to the  $\text{PtCl}_4^{-2}$  ion. The potassium salt  $\text{K}_2\text{PtCl}_4$  absorbs at  $326\text{ cm.}^{-1}$  (vs) and  $321\text{ cm.}^{-1}$  (sh).<sup>13</sup> In the spectra of the metal complexes no new bands appear in the region of the skeletal vibrations of the free ligand, while a new band (sometimes split) appears between  $434$  and  $340\text{ cm.}^{-1}$ , where the ligand itself has no absorption. In the spectrum of the cadmium(II) chloride complex this new band appears at  $294\text{ cm.}^{-1}$ , that is below the lowest observed skeletal band. The new band appearing in the cesium bromide region of the spectra of the complexes is assigned to the metal-to-oxygen stretching frequency, as supported by the observation that the ligand skeletal bands and the anion bands remain essentially constant for the various metal complexes while the position of the new band depends on the metal atom.

As shown in Table I the frequency values of the  $\nu(\text{M-O})$  stretching vibrations of the complexes of divalent metal ions vary with the metal, M, in the same order as the expected stability constants according to the Irving-Williams series:  $\text{Mn}^{2+} < \text{Co}^{2+} < \text{Ni}^{2+} < \text{Cu}^{2+} > \text{Zn}^{2+}$  and  $\text{Zn}^{2+} > \text{Cd}^{2+}$ . This indicates that the strength of the coordinative bond also varies in the above order and therefore depends mainly on the nature of the coordinating metal. This is in agreement with the results of the reported studies of the infrared spectra of other metal complexes containing oxygen-donor ligands, such as  $\text{pyO}^5$  and acetylacetonate.<sup>14</sup> Also in agreement with the studies on  $\text{pyO}$  and acetylacetonate complexes is the observation that the values of  $\nu(\text{M-O})$  of the investigated trivalent metals ( $\text{Cr}^{3+}$ ,  $\text{Fe}^{3+}$ ) are higher than those of the divalent metals, and that the  $\nu(\text{M-O})$  vibration is higher for  $\text{Cr}^{3+}$  than for  $\text{Fe}^{3+}$ . It is interesting to note that the  $\nu(\text{M-O})$  frequency of the  $[\text{Cr}(\text{bipyO}_2)_3]^{3+}$  cation is higher than that of  $[\text{Cr}(\text{bipyO}_2)_2\text{Cl}_2]^+$  by  $17\text{ cm.}^{-1}$  and that the  $\nu(\text{M-O})$  of  $[\text{Cd}(\text{bipyO}_2)_3]^{2+}$  is also higher, by  $54\text{ cm.}^{-1}$ , than that of the  $\text{Cd}(\text{bipyO}_2)\text{Cl}_2$  complex, in which the chloride ion is likely to be coordinated. This seems to indicate that the  $\nu(\text{M-O})$  stretching frequency, and therefore the strength of the metal-to-oxygen bond, is influenced by the presence in the complex of coordinated anions. It may be noted that the spectra of the  $\text{bipyO}_2$  complexes show only one band, ascribable to the  $\nu(\text{M-O})$  vibration, while two such bands could theoretically be expected for chelates of this type. The failure to observe the expected two  $\nu(\text{M-O})$  bands is, however, not surprising if compared with the similar case of the metal acetylacetonates. For these, Nakamoto<sup>14</sup> calculated both

the  $\nu(\text{M-O})$  stretching frequencies and found that the higher calculated frequency was close to the frequency of the only absorption actually observed in the spectra, while no absorption was observed corresponding to the lower calculated frequency. It is likely that in the case of  $\text{bipyO}_2$  complexes a similar situation occurs, the lower frequency band appearing below the  $\text{CsBr}$  region or being overlaid by other bands.

**The Nitrogen-to-Oxygen Vibrations.**—The uncoordinated  $\text{bipyO}_2$  molecule in the solid state most likely exists in a staggered conformation, unlike bipyridine, which has been shown to have a planar structure with the nitrogen atoms in *trans* positions.<sup>15,16</sup> In fact  $\text{bipyO}_2$  is an *o*-substituted biphenyl type molecule,<sup>17-19</sup> and various *o*-substituted biphenyls have been shown to have non-planar structures.<sup>20,21</sup> For  $\text{bipyO}_2$  in the solid state a non-symmetrical (non-planar) conformation is strongly supported by the presence in its infrared spectrum of two very strong NO stretching absorptions at  $1262$  and  $1255\text{ cm.}^{-1}$ . In fact, if the molecule were centrosymmetrical with a coplanar *trans* configuration, only one absorption would be expected to result from the NO stretching vibration. In the metal complexes, where  $\text{bipyO}_2$  acts as a chelating ligand, the staggered (*gauche*) configuration becomes the only one possible, as suggested by steric considerations.<sup>1</sup>

The two  $\nu(\text{N-O})$  stretching bands of  $\text{bipyO}_2$  undergo a rather marked change on coordination. In fact, in the spectra of the complexes the  $\nu(\text{N-O})$  stretching vibration generally appears as an intense band with splitting and shoulders. The mid-point of this split band is lower than the mid-point of the two bands of  $\text{bipyO}_2$ , the average shift to lower frequencies for the various complexes being  $45\text{--}55\text{ cm.}^{-1}$ . As discussed in detail for  $\text{pyO}$ -metal complexes,<sup>4,5</sup> this lowering of the  $\nu(\text{N-O})$  stretching frequencies is attributed to a decrease of the N-O double bond character as a result of the oxygen-to-metal coordination. The average magnitude of the shift is in good qualitative agreement with the values reported for the  $\text{pyO}$ -metal complexes. However, in the case of the  $\text{pyO}$ -metal complexes the actual values of the shifts were related to the values of the  $\nu(\text{M-O})$  stretching frequencies, in qualitative agreement with the Irving-Williams rule, while no such trend is observed for  $\text{bipyO}_2$ -metal complexes. This failure to observe a definite influence of the coordinating metal on the  $\nu(\text{N-O})$  stretching absorptions may be ascribed mainly to the influence of water, which is shown by the infrared spectra to be present to some extent in all the complexes and to which the NO stretching vibration of aromatic amine oxides is known to be very sensitive.<sup>22</sup> In addition, other factors such as a change in the confor-

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mation of the ligand as a consequence of chelation, and the influence of different environments in complexes having different coordination numbers and/or containing different anions, may be considered responsible for the more complicated appearance of the  $\nu(\text{N}-\text{O})$  band of the complexes with respect to that of the free  $\text{bipyO}_2$ .

The two very strong absorptions appearing at 852 and 840  $\text{cm}^{-1}$  in the spectrum of  $\text{bipyO}_2$  are tentatively assigned to the NO bending vibrations.<sup>4,5,23</sup> In general, these two absorptions appear with similar intensity but slightly shifted to lower frequencies in the spectra of the metal complexes. Again, the presence of two NO bending bands indicates that the  $\text{bipyO}_2$  molecule, both in the free solid and in the complexes, exists in the *gauche* conformation.

**The Water Absorptions.**—The spectra of the hydrated perchlorate complexes show a medium broad absorption at about 3600–3350  $\text{cm}^{-1}$  (OH stretching) and absorptions of various intensities in the 1600  $\text{cm}^{-1}$  region and below 500  $\text{cm}^{-1}$ , also assigned to the water of hydration.<sup>12</sup> Since the complex cations  $[\text{M}(\text{bipyO}_2)_3]^{+n}$  are coordinatively saturated, the water of hydration is considered to be uncoordinated, in agreement with the observed values of the infrared absorptions. The hydrated compound  $[\text{Cu}(\text{bipyO}_2)_2][\text{PtCl}_4] \cdot 4\text{H}_2\text{O}$  shows the OH stretching vibrations as a medium broad band between 3470 and 3250  $\text{cm}^{-1}$ . In the spectrum of the deuterated compound  $[\text{Cu}(\text{bipyO}_2)_2][\text{PtCl}_4] \cdot 4\text{D}_2\text{O}$  this absorption is absent, whereas a new medium absorption (with splitting) assigned to OD stretching vibration appears at lower frequencies in the range 2625–2350  $\text{cm}^{-1}$ .

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The spectrum of  $[\text{Cu}(\text{bipyO}_2)_2][\text{PtCl}_4] \cdot 4\text{H}_2\text{O}$  shows two strong bands at 1671 and 1619  $\text{cm}^{-1}$ , and that of  $[\text{Cu}(\text{bipyO}_2)_2][\text{PtCl}_4] \cdot 2\text{H}_2\text{O}$  shows two similar medium bands at 1628 and 1587  $\text{cm}^{-1}$ , whereas the anhydrous  $[\text{Cu}(\text{bipyO}_2)_2][\text{PtCl}_4]$  as well as the deuterated  $[\text{Cu}(\text{bipyO}_2)_2][\text{PtCl}_4] \cdot 4\text{D}_2\text{O}$  have no absorption in this range. In the CsBr region  $[\text{Cu}(\text{bipyO}_2)_2][\text{PtCl}_4] \cdot 4\text{H}_2\text{O}$  has a broad, medium absorption in the range 667–612  $\text{cm}^{-1}$ , which becomes weak in the spectrum of  $[\text{Cu}(\text{bipyO}_2)_2][\text{PtCl}_4] \cdot 2\text{H}_2\text{O}$ , and in the spectra of the anhydrous  $[\text{Cu}(\text{bipyO}_2)_2][\text{PtCl}_4]$  and of the deuterated  $[\text{Cu}(\text{bipyO}_2)_2][\text{PtCl}_4] \cdot 4\text{D}_2\text{O}$  disappears, revealing one of the skeletal modes of the ligand at 637  $\text{cm}^{-1}$ . A water absorption in this region has been considered as arising from the rocking mode of coordinated water<sup>24–26</sup> and is consistent with the presence of the two strong bands at 1671 and 1619  $\text{cm}^{-1}$  ( $\text{OH}_2$  bending region) in the spectra of the hydrated copper(II) tetrachloroplatinate(II) complexes. The infrared evidence favors therefore the formulation of these compounds as salts of the cation  $[\text{Cu}(\text{bipyO}_2)_2(\text{H}_2\text{O})_2]^{2+}$ . This formulation is compatible with the coordinative unsaturation of the bis-chelate cation  $[\text{Cu}(\text{bipyO}_2)_2]^{2+}$  with respect to the tris-chelate cation  $[\text{Cu}(\text{bipyO}_2)_3]^{2+}$  present in the perchlorate complex.

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## The Reaction of Nickel with Dioximes

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A series of symmetrically substituted *vicinal* dioximes was investigated with respect to hydrogen ion and Ni(II) ion. The  $\text{p}K_a$  values for eight dioximes were determined. Spectrophotometric data were obtained. Although 3:1 complexes of Ni(II) are well known, they are not well known when the ligand is a dioxime. Species with this stoichiometry are formed with dihydroxyglyoxime in ammoniacal solution and with dimethyl- and di- $\alpha$ -pyridylglyoximes in the presence of oxidizing agents. The  $\text{NiR}_3^-$  and the  $\text{NiR}_3^{-2}$  ions are proposed as the coordinated species existing in solution after the reaction of Ni(II) and dihydroxyglyoxime and Ni(II) and dimethyl- and dipyridylglyoximes under oxidizing conditions, respectively.

### Introduction

In spite of the extensive work on nickel-dioxime systems, certain aspects of their chemistry have not been clearly defined. For example, in the presence of oxidizing agents, Ni(II) ion and dimethylglyoxime

give a red solution<sup>2</sup> rather than a red precipitate. Considerable controversy still exists over the composition of the product. Various workers have reported that the nickel is oxidized to the trivalent,<sup>3a</sup> tetravalent,<sup>2,3b</sup> and even to the pentavalent state.<sup>3b</sup> It also has been

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