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The Donor Properties of Pyridine-N Oxide

By

G. Franz, J. Fujita, D. J. Phillips, J. V. Quagliano,

S. Y. Tyree, J. A. Walmsley.

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(Contribution from the Departments of Chemistry of the University of North Carolina  
and the Florida State University)

THE DONOR PROPERTIES OF PYRIDINE N-OXIDE

by J. V. Quagliano, J. Fujita, G. Franz,  
D. J. Phillips, J. A. Walmsley, and S. Y. Tyree

ABSTRACT

The coordination chemistry of pyridine N-oxide with a variety of acceptors has been investigated. The new substances  $\text{Co}(\text{ClO}_4)_2 \cdot 6\text{L}$ ,  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{L}$ ,  $\text{CoCl}_2 \cdot 3\text{L}$ ,  $\text{CoCl}_2 \cdot \text{L} \cdot \text{H}_2\text{O}$ ,  $\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{L}$ ,  $\text{NiCl}_2 \cdot \text{L} \cdot \text{H}_2\text{O}$ ,  $\text{NiBr}_2 \cdot 6\text{L}$ ,  $\text{NiI}_2 \cdot 6\text{L}$ ,  $\text{NiBr}_2 \cdot \text{L} \cdot \text{H}_2\text{O}$ ,  $\text{Cu}(\text{ClO}_4)_2 \cdot 4\text{L}$ ,  $\text{Cu}(\text{NO}_3)_2 \cdot 2\text{L}$ ,  $\text{CuCl}_2 \cdot \text{L}$ ,  $\text{CuCl}_2 \cdot 2\text{L}$ ,  $\text{Zn}(\text{ClO}_4)_2 \cdot 6\text{L}$ ,  $\text{ZnCl}_2 \cdot 2\text{L}$ ,  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{L}$ ,  $\text{Fe}(\text{ClO}_4)_2 \cdot 6\text{L}$ ,  $\text{Fe}(\text{ClO}_4)_3 \cdot 6\text{L}$ , and  $\text{SnBr}_4 \cdot 2\text{L}$  (where L = pyridine N-oxide) have been isolated and characterized by molecular conductance measurements in non-aqueous solvents, magnetic susceptibility measurements, and infrared spectra. All of the perchlorates and some of the nitrates and halides have only the pyridine N-oxide in the first coordination sphere. However, in some cases, both nitrates and halides are coordinated to the central ion.

Introduction

As a logical extension of previous work on the donor properties of substituted phosphine<sup>1</sup> and arsine<sup>2</sup> oxides we wish to report now the results

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(1) J. C. Sheldon and S. Y. Tyree, This Journal, 80, 4775 (1958)

(2) D. J. Phillips and S. Y. Tyree, ibid., 83, xxxx (1961)

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of a study of the ability of pyridine N-oxide to behave as a ligand.

We find only three prior pyridine N-oxide adducts, the hydrochloride<sup>3</sup>,

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(3) J. Meisenheimer, Ber. 59, 1848 (1926)

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a 1:1 adduct with  $\text{SO}_3$ <sup>4</sup>, and the hexakis(pyridine N-oxide)cobalt(II) tetra-

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(4) P. Baumgarten and H. Erbe, *ibid.*, 71, 2603 (1938)

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carbonylcobaltate(-1)<sup>5</sup>. However, it is our understanding that two adducts

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(5) G. Franz, Dissertation, Technische Hochschule Munich (1959)

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with zinc chloride have also been prepared.<sup>6</sup>

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(6) Sister M. Ellen Dolores Lynch, C.S.C., Dunbarton College of Holy Cross, Washington, D. C., private communication.

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#### Experimental

Reagents. Reagent or analytical grade chemicals were used without further purification except in the cases noted.

Pyridine N-oxide was prepared once by the method of Ochai<sup>7</sup>. Other

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(7) E. Ochai, J. Org. Chem., 18, 548 (1953)

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samples were obtained from Reilley Chemical and Tar, and K and K Chemical laboratories. All samples were purified by vacuum distillation, collecting the fraction distilling between 125° and 130° at 8 mm.

N,N-dimethylformamide (DMF) was purified by a modification of Method I of Rochow<sup>8</sup>.

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(8) A. B. Thomas and E. G. Rochow, This Journal, 79, 1843 (1957)

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The specific conductance of the purified solvent was found to be  $3.49 \times 10^{-7} \text{ ohm}^{-1} \text{ cm.}^{-1}$ .

Tin(IV) bromide was obtained from student preparations and redistilled. B. p.  $208^{\circ}$  at 750 mm. Literature value<sup>9</sup> =  $207^{\circ}$ .

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(9) L. L. Quill, Ed., "The Chemistry and Metallurgy of Miscellaneous Materials," McGraw-Hill Book Company, 1950, p. 205.

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Nickel(II) bromide and nickel(II) iodide were prepared by dehydrating  $\text{NiBr}_2 \cdot 6\text{H}_2\text{O}$  and  $\text{NiI}_2 \cdot 6\text{H}_2\text{O}$  over  $\text{P}_2\text{O}_5$  in vacuo.

Zinc nitrate was prepared by dehydrating  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  over  $\text{P}_2\text{O}_5$  in Vacuo. Analyses. Nitrogen analyses were done by the Dumas method on a semimicro scale. Halogen analyses were done by direct titration of the aqueous solutions of some complexes. In some cases gravimetric determinations as  $\text{AgCl}$  were made. Metal analyses were done as outlined previously<sup>2</sup> or by electroplating techniques.<sup>10</sup> Carbon and hydrogen analyses were performed

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(10) W. F. Hillebrand and G. E. Lundell, "Applied Inorganic Analysis", Second Edition, John Wiley and Sons, Inc., New York, New York (1953)

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by the Schwarzkopf Microanalytical Laboratory, Woodside, New York and Weiler and Strauss, Oxford, England.

Preparation of the Complexes. Ethanol solutions of anhydrous metal halides or of the metal salt hydrates were added to ethanol



solutions of pyridine N-oxide. In some cases immediate crystallization ensued. In other cases it was necessary to place the solutions in the refrigerator overnight to obtain crystals. In still other cases acetone was added until a cloudiness or slight precipitation was observed, when the mixture was placed in the refrigerator. In some few cases it was necessary to evaporate the solutions almost to dryness to get incipient crystallization. In all cases the crystals were filtered, washed with ethanol and either acetone or ether, and finally dried in vacuo over  $P_2O_5$  or  $CaCl_2$ . Some of the complexes were obtained by two or more techniques. In general, the complexes are more soluble in methanol than in ethanol. Consequently, some of the less soluble complexes were recrystallized from the former solvent. The detailed preparations which follow are typical.

Hexakis(pyridine N-oxide)cobalt(II) perchlorate. A solution of 1.0 g. (2.7 mmols) of  $Co(ClO_4)_2 \cdot 6H_2O$  in 50 ml. of ethanol was added to one of 1.3 g. (14 mmols) of the ligand in 50 ml. of ethanol. The pale pink, finely divided precipitate which formed was washed and dried as described above. Mixing of the reactants in mole ratios of more or less than 1:6 gave only the same product. Anal. Calc. for  $[Co(C_5H_5NO)_6](ClO_4)_2$ : Co, 7.11; C, 43.49; H, 3.65. Found: Co, 7.05; C, 43.30; H, 3.90.

Hexakis(pyridine N-oxide)cobalt(II) nitrate. The complex was prepared by the same method used for the preceding complex, using  $Co(NO_3)_2 \cdot 6H_2O$  as starting material. The product was large, dark red crystals. Anal. Calc. for  $[Co(C_5H_5NO)_6](NO_3)_2$ : Co, 7.82; C, 47.81; H, 4.01. Found: Co, 7.97; C, 48.07; H, 4.31.

The green complex formed by  $\text{CoCl}_2$ . A dark green powder precipitated when ethanol solutions of  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  and the ligand were mixed in mole ratios of 1 to 3. The same result is obtained using anhydrous  $\text{CoCl}_2$  as the starting material. Anal. Calc. for  $\text{Co}(\text{C}_5\text{H}_5\text{NO})_3\text{Cl}_2$  : Co, 14.20; C, 43.39; H, 3.64; N, 10.36; Cl, 17.08. Found: Co, 13.97; C, 43.15; H, 3.76; N, 9.64; Cl, 17.72.

The violet  $\text{CoCl}_2$  complex. One g. (2.4 mmoles) of the preceding preparation was dissolved in a minimum quantity of ice-cold water. The green solution turned red quickly. A large quantity of 95% ethanol was added to the red solution. A light violet powdered product formed overnight in the refrigerator.

The same product was obtained directly by the mixing of methanol solutions of  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  and the ligand in a mole ratio of 1:1. It was necessary to add acetone to the methanol solution and store in the refrigerator overnight to obtain the violet crystals. Recrystallization from methanol was accomplished by the addition of acetone.

An identical product can be obtained from ethanol upon mixing the reagents in a mole ratio of 1:1. Anal. Calc. for  $\text{Co}(\text{C}_5\text{H}_5\text{NO})\text{Cl}_2 \cdot \text{H}_2\text{O}$  : Co, 24.36; C, 24.71; H, 2.91; Cl, 29.19; N, 5.77. Found: Co, 24.03; C, 25.45; H, 3.06; Cl, 28.92; N, 5.58.

Hexakis(pyridine N-oxide)nickel(II) perchlorate. The finely divided greenish-yellow crystals were prepared in the manner used for the corresponding Co(II) compound, starting with  $\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ . It was found that the same product was obtained regardless of the mole ratio in which solutions of the reactants were mixed. Anal. Calc. for  $[\text{Ni}(\text{C}_5\text{H}_5\text{NO})_6](\text{ClO}_4)_2$  : Ni, 7.09; C, 43.50; H, 3.65. Found: Ni, 7.17; C, 43.30; H, 3.71.

The yellow  $\text{NiCl}_2$  complex. Ethanol solutions of  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  and the ligand were mixed in the mole ratio of 1:1. A light yellow powdery precipitate separated upon the addition of acetone. The product was recrystallized from methanol by the addition of acetone. Anal. Calc. for  $\text{Ni}(\text{C}_5\text{H}_5\text{NO})\text{Cl}_2 \cdot \text{H}_2\text{O}$  : Ni, 24.18; C, 24.74; H, 2.91. Found: Ni, 24.11; C, 25.21; H, 3.07.

Hexakis(pyridine N-oxide)nickel(II) bromide. An ethanol solution of 2.7 g. (29 mmoles) of the ligand was added to an ethanol solution of 1 g. (4.6 mmoles) of  $\text{NiBr}_2$ . The resulting solution was evaporated under vacuum at about  $50^\circ$  to incipient crystallization. A crop of light green crystals was obtained at room temperature. Anal. Calc. for  $[\text{Ni}(\text{C}_5\text{H}_5\text{NO})_6]\text{Br}_2$  : Ni, 7.44; C, 45.66; H, 3.83. Found: Ni, 7.39; C, 45.45; H, 4.13.

Hexakis(pyridine N-oxide)nickel(II) iodide. The complex was prepared in the manner described for the preceding complex, starting with  $\text{NiI}_2$ . Anal. Calc. for  $[\text{Ni}(\text{C}_5\text{H}_5\text{NO})_6]\text{I}_2$  : Ni, 6.65; C, 40.80; H, 3.42. Found: Ni, 6.98; C, 41.04; H, 3.44.

The brownish-yellow  $\text{NiBr}_2$  complex. The product was obtained by the method used to obtain the yellow  $\text{NiCl}_2$  complex, using  $\text{NiBr}_2 \cdot 6\text{H}_2\text{O}$  as the starting material. Anal. Calc. for  $\text{Ni}(\text{C}_5\text{H}_5\text{NO})\text{Br}_2 \cdot \text{H}_2\text{O}$  : Ni, 17.70; C, 18.11; H, 2.13. Found: Ni, 17.73; C, 18.57; H, 2.25.

Tetrakis(pyridine N-oxide)copper(II) perchlorate. Ethanol solutions of  $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  and the ligand reacted to give the same dark green crystalline product regardless of the mole ratio of reactants. Anal. Calc. for  $[\text{Cu}(\text{C}_5\text{H}_5\text{NO})_4](\text{ClO}_4)_2$  : Cu, 9.88; C, 37.37; H, 3.14. Found: Cu, 9.87; C, 37.27; H, 3.06.

The blue-green  $\text{Cu}(\text{NO}_3)_2$  complex. Ethanol solutions of  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  and the ligand were mixed. The resulting blue-green solution yielded crystals upon standing at room temperature for several days. Anal. Calc. for  $\text{Cu}(\text{C}_5\text{H}_5\text{NO})_2(\text{NO}_3)_2$  : Cu, 16.82; N, 14.83. Found: Cu, 16.65; N, 14.94.

The chartreuse  $\text{CuCl}_2$  complex. The product precipitated immediately upon mixing ethanol solutions of  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  and the ligand in a mole ratio of 1:1. Anal. Calc. for  $\text{Cu}(\text{C}_5\text{H}_5\text{NO})\text{Cl}_2$  : Cu, 27.68; C, 26.16; H, 2.20; Cl, 30.89; N, 6.10. Found: Cu, 28.39; C, 26.52; H, 2.30; Cl, 30.65; N, 6.00.

The yellow  $\text{CuCl}_2$  complex. The product precipitated immediately upon mixing ethanol solutions of  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  and the ligand in a mole ratio of 1:2. Anal. Calc. for  $\text{Cu}(\text{C}_5\text{H}_5\text{NO})_2\text{Cl}_2$  : Cu, 19.57; C, 36.99; H, 3.10. Found: Cu, 19.05; C, 37.20; H, 3.44.

Bis(pyridine N-oxide)dichlorozinc. The complex formed immediately when ethanol solutions of  $\text{ZnCl}_2$  and the ligand were mixed in the mole ratio of 1:2. The same white complex was obtained when excess ligand was used. Anal. Calc. for  $[\text{Zn}(\text{C}_5\text{H}_5\text{NO})_2\text{Cl}_2]$  : Zn, 20.03; C, 36.79; H, 3.09. Found: Zn, 19.51; C, 36.95; H, 3.19.

Hexakis(pyridine N-oxide)zinc perchlorate. Two g. (5.5 mmoles) of  $\text{Zn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  in 50 ml. of methanol were added to 2 g. (2.15 mmoles) of the ligand in 30 ml. of methanol. White crystals formed slowly. Recrystallization was effected by dissolving the crystals in a minimum of water, clarifying the solution with activated charcoal, and adding acetone. Although the reactants were mixed in a mole ratio of 1:4, a six-coordinate complex was obtained. The same product was prepared by mixing the reactants in a mole ratio of 1:6. Anal. Calc. for  $[\text{Zn}(\text{C}_5\text{H}_5\text{NO})_6](\text{ClO}_4)_2$  : C, 43.16; Zn, 7.83; H, 3.62. Found: C, 43.56; Zn, 8.24; H, 3.81.

Hexakis(pyridine N-oxide)zinc nitrate. An ethanol solution of 1 gm (5.3 mmoles) of  $\text{Zn}(\text{NO}_3)_2$  was added to an ethanol solution of 2.1 g (22 mmoles) of the ligand. Evaporation under vacuum at  $50^\circ$  almost to dryness was necessary to obtain the white crystals. Anal. Calc. for  $[\text{Zn}(\text{C}_5\text{H}_5\text{NO})_6](\text{NO}_3)_2$ : Zn, 8.60; C, 47.48; H, 3.98. Found: Zn, 8.42; C, 47.46; H, 3.74.

Hexakis(pyridine N-oxide)iron(II) perchlorate. A methanol solution of the ligand was added to a methanol solution of  $\text{Fe}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  in the mole ratio of 1:6. The dark red crystals separated upon standing overnight in the refrigerator. Anal. Calc. for  $[\text{Fe}(\text{C}_5\text{H}_5\text{NO})_6](\text{ClO}_4)_2$ : C, 43.65; H, 3.66. Found: C, 43.91; H, 3.76.

Hexakis(pyridine N-oxide)iron(III) perchlorate. The yellow crystals were prepared by a method similar to that used for the preceding compound, starting with the corresponding iron(III) salts. Anal. Calc. for  $[\text{Fe}(\text{C}_5\text{H}_5\text{NO})_6](\text{ClO}_4)_3$ : C, 38.96; H, 3.27; N, 9.02. Found: C, 39.34; H, 3.56; N, 8.88.

Bis(pyridine N-oxide)tetrabromotin(IV). Ethanol solutions of tin(IV) bromide and the ligand were mixed in several ratios. In each case the white complex precipitated immediately. Anal. Calc. for  $[\text{SnBr}_4(\text{C}_5\text{H}_5\text{NO})_2]$ : Sn, 18.88; N, 4.46; Found: Sn, 17.37; N, 4.38.

Conductance and Magnetic Susceptibility measurements have been described in the previous paper<sup>2</sup>. It was found that most of the above substances were insufficiently soluble in either nitrobenzene or nitromethane to use either as the solvent for the conductivity measurements. All were sufficiently soluble in DMF to give approximately M/1000 solutions.

Absorption Measurements. Infrared spectra of all substances were taken with a Perkin-Elmer Model 221 recording spectrophotometer equipped with a sodium chloride prism. Spectra of the solid complexes were obtained by means of the potassium bromide disk technique and checked by measurements in Nujol mulls.

### Results

The new complexes are listed in Table I together with some of their physical properties. Only the NO stretch frequencies are listed from the infrared spectra, the detailed assignment of all absorption bands together with the necessary spectra will be the subject of a later communication. The molar conductances are for approximately M/1000 solutions, the exact concentration for each measurement being tabulated in the last column of Table I. Some of the variation in molar conductances within electrolyte types can be accounted for by the fact that some of the values are for concentrations as low as  $0.80 \times 10^{-3}$  M. while others are for solutions as concentrated as  $2.0 \times 10^{-3}$  M. Sears and co-workers<sup>11</sup> measured the conductances of a number of 1:1 electrolytes in DMF at 25° over a range of concentrations.

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(11) P. G. Sears et al., J. Phys. Chem., 59, 373 (1955)

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We determined the equivalent conductance of tetramethylammonium bromide in DMF at 25°C. and at a concentration of  $1.12 \times 10^{-3}$  M to be  $84.4 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ . The corresponding value obtained by Sears et al, estimated from figure 1 of their paper, is 85. Molar conductances of the zinc perchlorate adduct were measured at three concentrations to estimate the effect of concentration upon the values reported in Table I. In addition, molar conductances of one other 2:1 complex and one other 3:1 complex were measured. The results are tabulated in Table II.

Table I

| Compound                                   | NO frequency<br>$\text{cm}^{-1}$ | $\mu_{\text{eff}}$ | $\frac{\Lambda}{\text{ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}}$ | Conc.<br>$\text{mmole l}^{-1}$ |
|--------------------------------------------|----------------------------------|--------------------|-----------------------------------------------------------------|--------------------------------|
| $\text{C}_5\text{H}_5\text{NO} = \text{L}$ | 1243                             | ----               | ---                                                             | ---                            |
| $[\text{CoL}_6](\text{ClO}_4)_2$           | 1219                             | 4.69               | 144                                                             | 1.12                           |
| $[\text{CoL}_6](\text{NO}_3)_2$            | 1220                             | 4.77               | 151                                                             | 0.97                           |
| $\text{CoL}_3\text{Cl}_2$                  | 1220                             | 4.75               | 30.2                                                            | 0.97                           |
| $\text{CoLCl}_2 \cdot \text{H}_2\text{O}$  | 1202                             | 4.75               | 28.7                                                            | 1.03                           |
| $[\text{NiL}_6](\text{ClO}_4)_2$           | 1219                             | 3.30               | 175                                                             | 0.83                           |
| $\text{NiLCl}_2 \cdot \text{H}_2\text{O}$  | 1208                             | 3.21               | 42.9                                                            | 1.21                           |
| $[\text{NiL}_6]\text{Br}_2$                | 1220<br>1212                     | 3.28               | 116                                                             | 1.31                           |
| $[\text{NiL}_6]\text{I}_2$                 | 1218                             | ----               | 138                                                             | 1.73                           |
| $\text{NiLBr}_2 \cdot \text{H}_2\text{O}$  | 1202                             | 3.16               | 132                                                             | 0.94                           |
| $[\text{CuL}_4](\text{ClO}_4)_2$           | 1215<br>1205                     | 1.62               | 155                                                             | 1.21                           |
| $\text{CuL}_2(\text{NO}_3)_2$              | 1205                             | 1.89               | 133                                                             | 0.98                           |
| $\text{CuL}_2\text{Cl}_2$                  | 1223<br>1206                     | 0.63               | 15.9                                                            | 2.02                           |
| $\text{CuLCl}_2$                           | 1203                             | 0.85               | 25.4                                                            | 0.94                           |
| $[\text{ZnL}_2\text{Cl}_2]$                | 1209<br>1205                     | ----               | 7.0                                                             | 2.91                           |
| $[\text{ZnL}_6](\text{ClO}_4)_2$           | 1221                             | ----               | 166                                                             | 0.28                           |
| $[\text{ZnL}_6](\text{NO}_3)_2$            | 1224                             | ----               | ---                                                             | ---                            |
| $[\text{FeL}_6](\text{ClO}_4)_2$           | 1218                             | 5.40               | 166                                                             | 0.94                           |
| $[\text{FeL}_6](\text{ClO}_4)_3$           | 1209                             | 5.90               | 249                                                             | 0.92                           |
| $[\text{SnBr}_4 \cdot 2\text{L}]$          | 1192                             | ----               | 23.9                                                            | 0.99                           |

Table II

| <u>Comp.</u>                                                                         | <u>Conc., M x 10<sup>3</sup></u> | <u><math>\Delta \kappa</math><br/>ohm<sup>-1</sup> cm.<sup>2</sup> mol.<sup>-1</sup></u> |
|--------------------------------------------------------------------------------------|----------------------------------|------------------------------------------------------------------------------------------|
| [Zn(C <sub>9</sub> H <sub>5</sub> NO) <sub>6</sub> ](ClO <sub>4</sub> ) <sub>2</sub> | 0.28                             | 166                                                                                      |
| [Zn(C <sub>9</sub> H <sub>5</sub> NO) <sub>6</sub> ](ClO <sub>4</sub> ) <sub>2</sub> | 0.92                             | 161                                                                                      |
| [Zn(C <sub>9</sub> H <sub>5</sub> NO) <sub>6</sub> ](ClO <sub>4</sub> ) <sub>2</sub> | 1.42                             | 149                                                                                      |
| [Co(Φ <sub>3</sub> AsO) <sub>4</sub> ](ClO <sub>4</sub> ) <sub>2</sub>               | 0.51                             | 165                                                                                      |
| [Fe(Φ <sub>3</sub> AsO) <sub>4</sub> ](ClO <sub>4</sub> ) <sub>3</sub>               | 0.58                             | 255                                                                                      |

We conclude that 1:1 complexes exhibit conductances in DMF at 25° downward from 85, those of 2:1 complexes are in the range 140-170, and those 3:1 complexes are in the range 200-260.



### Discussion

The frequencies of the NO band in the several +2 metal complexes appear to fall into two groups, those observed at or near  $1220\text{ cm}^{-1}$  and those observed at or near  $1205\text{ cm}^{-1}$ . These two are 20 and  $35\text{ cm}^{-1}$  lower than  $1243\text{ cm}^{-1}$ , the value we assume due to the NO absorption in the free ligand (in mull) spectra.<sup>12</sup> The population of the group at  $1220\text{ cm}^{-1}$

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(12) G. Sartori, et al., Gazz. Chim. Ital., 85, 1085

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consists exclusively of those complexes in which the pyridine N-oxide is the only ligand in the first coordination sphere of the central ion (some of these show a small splitting of about  $10\text{ cm}^{-1}$ ). The population of the group at  $1205\text{ cm}^{-1}$  consists of complexes in which pyridine N-oxide and another ligand ( $\text{H}_2\text{O}$ , halide, or nitrate) make up the first coordination sphere of the central ion.

Of the nitrate complexes in this report we believe that  $\text{NO}_3^-$  complexing occurs in the copper case only. Very strong bands were observed at  $1292\text{ cm}^{-1}$  and  $1019\text{ cm}^{-1}$  in the infrared spectrum of  $\text{Cu}(\text{C}_5\text{H}_5\text{NO})_2(\text{NO}_3)_2$ , which we feel correspond to the  $\nu_1$  and  $\nu_2$  absorptions respectively of the coordinated nitrate group<sup>13</sup>. In addition, the presence of the  $\nu_4$  absorption

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(13) Gatehouse, et al., J. Chem. Soc., 1960, 613

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is indicated by a high frequency shoulder on the band at  $1470\text{ cm}^{-1}$  which is already broadened by the rough superposition of the pyridine ring deformation upon the background nujol absorption. Ionic  $\text{NO}_3^-$  absorptions only were observed among the other nitrates.

It is clear from the conductivity data that the nitrates and perchlorates all behave as strong electrolytes. In addition, the hexakis (pyridine N-oxide)nickel(II) bromide and iodide dissolve as 2:1 electrolytes. Even the  $\text{Cu}(\text{C}_5\text{H}_5\text{NO})_2(\text{NO}_3)_2$  behaves as a 2:1 electrolyte in DMF, despite the inference from its infrared spectrum that in the solid state the nitrates are coordinated to the copper(II) ion. This result can only mean that DMF solvent molecules are able to displace the nitrate ligands. Such is not the case for the chloride complexes. While the molar conductances of these latter vary from 7.0 for  $\text{Zn}(\text{C}_5\text{H}_5\text{NO})_2\text{Cl}_2$  to 42.9 for  $\text{Ni}(\text{C}_5\text{H}_5\text{NO})\text{Cl}_2 \cdot \text{H}_2\text{O}$ , it is obvious that some chloride coordination persists even at the dilutions used for the conductivity measurements. Rather obviously, the bromide ion is easily displaced by solvent from  $\text{Ni}(\text{C}_5\text{H}_5\text{NO})\text{Br}_2 \cdot \text{H}_2\text{O}$ .

The magnetic moments, each calculated from replicate measurements at one temperature ( $25^\circ$ ), fall well within the range of values usually obtained for the ions concerned, except in the case of Cu(II). The values tabulated for  $\text{Cu}(\text{C}_5\text{H}_5\text{NO})\text{Cl}_2$  and  $\text{Cu}(\text{C}_5\text{H}_5\text{NO})_2\text{Cl}_2$  are obviously low, indicative of insufficient magnetic dilution of individual ions. The values for the other two copper(II) complexes are normal.

Our reluctance to use brackets, [ ], to indicate structural entity for seven of the metal complexes listed in Table I merely indicates that we retain considerable doubt as to several possible, reasonable structures based upon the colors, magnetic properties, and solute behavior.

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