Scheme II summarizes the preparative routes for $Y_n^{PPh_3}$ complexes.

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Registry No. $Rh_2Cl_2(CO)_2[P(C_2H_5)_3]_2$, 41507-98-6; $Rh_2Cl_2(CO)_2[P(CH_3)_3]_2$, 49634-24-4; $Rh_2Cl_2(CO)_2[P(CH_3)_2C_6H_5]_2$, 36713-91-4; $Rh_2Cl_2(CO)_2[P(N(CH_3)_2)_3]_2$, 36713-92-5; $Rh_2Cl_2(CO)_2[P(C_6H_5)_3]_2$, 34676-63-6; $Rh_2Cl_2[P(OCH_3)_3]_4$, 49634-27-7; $Rh_2Cl_2(CO)_2[P(OCH_3)_3]_2$, 41612-78-6; $Rh_2Cl_2(CO)_2[n\text{-}C_3H_7OPF_2]_2$, 49634-30-2; $Rh_2Cl_2[n\text{-}C_3H_7OPF_2]_4$, 49634-31-3; $Rh_2Cl_2(CO)_2(C_8H_{12})$, 49855-72-3; $Rh_2Cl_2(CO)[P(C_6H_5)_3]_3$, 36713-93-6; $Rh_2Cl_2(CO)_3(C_2H_4)$, 49694-03-3; $Rh_2Cl_2(CO)_3[P(C_6H_5)_3]$, 34818-92-3; $Rh_2Cl_2(CO)_2(C_2H_4)_2$, 12306-60-4; $[RhCl(C_8H_{12})]_2$, 12092-47-6; $[RhCl(CO)_2]_2$, 14523-22-9; $n\text{-}C_3H_7OPF_2$, 3964-95-2; $[RhCl(C_2H_4)_2]_2$, 12081-16-2; $Rh_2Cl_2(CO)_3(n\text{-}C_3H_7OPF_2)$, 49634-34-6; $Rh_2Cl_2(CO)_3[P(OCH_3)_3]$, 49634-35-7; $Rh_2Cl_2(CO)(C_2H_4)_3$, 49634-54-0; $Rh_2Cl_2CO(n\text{-}C_3H_7OPF_2)_3$, 49634-36-8; $Rh_2Cl_2(CO)[P(OCH_3)_3]_3$, 49634-37-9.

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Cobalt-, Nickel-, Copper-, and Zinc(II) Nitrate and Nitrite Complexes of 1,2-Dimorpholinoethane and 1,2-Dipiperidinoethane[1]

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The ligands 1,2-dimorpholinoethane (EDM) and 1,2-dipiperidinoethane (EDP) have been shown to react with Co(II), Ni(II), Cu(II), and Zn(II) nitrites and nitrates to give complexes with the general formulation MLX_2 (L = EDM and EDP; X = NO_2 and NO_3). The complexes were characterized by elemental analysis, infrared, visible, and ultraviolet spectroscopy, solution and solid state magnetic susceptibilities, and conductivity measurements. The complexes have a six-coordinate, distorted octahedral geometry with two nitrogens from the EDM or EDP ligand and two bidentate oxygen coordinated NO_2^- or NO_3^- moieties making up the coordination sphere of the central metal atom. The stabilities, solubilities, and coordination geometry of these species are discussed in light of the base strengths and steric requirements of the EDM and EDP ligands.

Introduction

We have previously investigated the complexes formed by the interaction of 1,2-dimorpholinoethane (EDM) and 1,2-dipiperidinoethane (EDP) with divalent first-row transition-metal halides as well as with divalent palladium and platinum halides.[2] Both of these ligands coordinate as though they are tetra-N-substituted ethylenediamines. The EDM ligand has two ether linkages which are potential donor sites but have been shown not to take part in coordination.[3] Both of these ligands have been shown to be extremely sterically demanding due to the spatial requirements of the morpholine and piperidine rings.[3]

In light of these extreme steric requirements, it was of interest to investigate the interaction of these ligands with transition-metal salts containing bulky and/or ambidentate anions. The salts chosen for this study were the nitrates and nitrites of selected divalent first-row transition metals.

Both nitrate and nitrite can coordinate to a central transition-metal ion in several different ways. Nitrate can coordinate either as a monodentate or bidentate ligand bonding through one or two of the oxygens. Being a relatively weak ligand, it can also act as a noncoordinating anion. Nitrite being a much stronger ligand never acts as a noncoordinating or ionic ligand in coordination compounds. It can bond through the nitrogen to give the well-known nitro complexes or through one of the oxygens to give the less common nitrito species. It can also act as a bridging ligand bonding through the nitrogen and one of the oxygens.[4] A fourth mode of coordination is also known with the nitrite acting as a bidentate ligand coordinating through the two oxygens.[5]

Herein we report the preparation and characterization of the divalent cobalt, nickel, copper, and zinc nitrate and nitrite complexes of EDM and EDP.

Experimental Section

All reagents were commercially available and were used as obtained except for the following. Both of the ligands, EDM and EDP, were prepared according to the literature by the condensation of the appropriate amine with 1,2-dichloroethane in refluxing benzene.[6] EDM was recrystallized from absolute ethanol, mp 73–74° (lit. 73–74°), and confirmed by mass spectrum, parent = 200, and nmr.[7] EDP was purified by vacuum distillation through a 10-cm Vigreaux column at 55–57° at 10^{-3} mm of pressure and confirmed by mass spectrum, parent = 196, and nmr. Acetonitrile was distilled from CaH_2. Acetone was dried over anhydrous $MgSO_4$, and benzene was distilled over sodium prior to use.

Physical Measurements. Infrared spectra were recorded on a Beckman Instruments Model I.R.-10 recording spectrophotometer in the range 4000–600 cm^{-1} as KBr disks or Nujol mulls. Near-infrared, visible, and ultraviolet spectra were recorded on a Beckman Instruments Model DK-1 recording spectrophotometer in the range 40.0 to 4.0 kK with 1.0-cm matched quartz cells as methylene chloride or chloroform solutions. Conductivities were measured on an Industrial Instruments Model RC-16B-2 conductivity bridge. The conductivity cell was equipped with bright platinum electrodes and calibrated with a standard aqueous potassium chloride solution. Magnetic susceptibilities were determined in solution by the method of Evans on a Varian Associates Model T-60 spectrometer.[8] The sweep width was calibrated against the splitting of the methyl doublet of

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(1) A preliminary account of part of this work has appeared in A. L. Lott II, *J. Amer. Chem. Soc.*, 93, 5313 (1971).

(2) A. L. Lott II and P. G. Rasmussen, *J. Inorg. Nucl. Chem.*, 32, 101 (1970); A. L. Lott II and P. G. Rasmussen, *J. Amer. Chem. Soc.*, 91, 6502 (1969).

(3) W. R. Scheidt, J. C. Hanson, and P. G. Rasmussen, *Inorg. Chem.*, 8, 2398 (1969).

(4) J. Chatt, L. A. Duncanson, B. M. Gatehouse, J. Lewis, R. S. Nyholm, M. L. Tobe, P. F. Todd, and L. M. Venanzi, *J. Chem. Soc.*, 4073 (1959); K. Nakamoto, J. Fujita, and H. Murata, *J. Amer. Chem. Soc.*, 80, 4817 (1958).

(5) D. M. L. Goodgame and M. A. Hitchman, *Inorg. Chem.*, 4, 721 (1965).

(6) A. Gero, *J. Amer. Chem. Soc.*, 76, 5158 (1954).

(7) S. M. Ali, F. M. Brewer, J. Chadwick, and G. Garton, *J. Inorg. Nucl. Chem.*, 9, 124 (1959).

(8) D. F. Evans, *J. Chem. Soc.*, 2003 (1959).

acetaldehyde ($J = 2.85$ Hz).[9] Solid state susceptibilities were determined by the Faraday method on a quartz spring balance that has been described elsewhere.[10] The balance was calibrated with $NiSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$ and $Hg[Co(SCN)_4]$.[11] Elemental analyses for carbon, hydrogen, and nitrogen as well as molecular weights were determined by Spang Microanalytical Laboratory, Ann Arbor, Mich., and Galbraith Laboratories, Inc., Knoxville, Tenn.

Preparation of $ML(NO_3)_2$ (L = EDM and EDP; M = Cu, Ni, and Zn): All six complexes were prepared by the same general method. In a typical experiment 2 mmol of the hydrated metal nitrate was stirred with 25 ml of 2,2-dimethoxypropane for 35 min to dehydrate the metal salt. Enough absolute ethanol was added to give a clear solution. To the metal nitrate solution was added, with rapid stirring, 4.0 mmol of the appropriate ligand dissolved in 5 ml of absolute ethanol. The product precipitated from solution almost immediately. The reaction mixture was stirred for an additional 20 min and then filtered. The product was washed with 4 × 30 ml portions of anhydrous ether and air dried. The copper complexes were purified by recrystallization from acetonitrile. The nickel and zinc complexes were purified by dissolving in methylene chloride, filtering to remove any insolubles, removing the solvent on a rotary evaporator, and drying under vacuum at room temperature.

Preparation of $CoL(NO_3)_2$ (L = EDM and EDP). Due to the sensitivity of these compounds to the atmosphere, particularly water when in solution or wet, special precautions had to be taken. In a 125-ml erlenmeyer flask equipped with a 24/40 standard taper female neck and a side arm with a stopcock was placed 0.58 g, 2.0 mmol, of $Co(NO_3)_2 \cdot 6H_2O$. A flow of dry nitrogen was started and 50 ml of 2,2-dimethoxypropane was added. The reaction mixture was stirred for 35 min to dehydrate the metal salt. To the clear purple solution was added, under nitrogen, 4.0 mmol of the appropriate ligand dissolved in 5 ml of absolute ethanol. An immediate precipitate formed. The reaction mixture was stirred for an additional 20 min, filtered under nitrogen, washed with 4 × 30 ml portions of anhydrous ether, and dried under vacuum. Purification was accomplished in a manner analogous to the above nickel and zinc nitrate complexes.

Preparation of $M(EDM)(NO_2)_2$ (M = Co, Ni, Cu, and Zn). The same general method of preparation was used for all four complexes. In a typical experiment 2.0 mmol of the hydrated metal nitrate and 0.55 g, 8.0 mmol, of $NaNO_2$ were stirred together with 25 ml of absolute ethanol for 30 min. The reaction mixture was cooled in a CO_2-acetone bath to precipitate the $NaNO_3$ formed as well as the excess $NaNO_2$. The cold solution was filtered into a solution of 2.00 g, 8.0 mmol, of EDM in 20 ml of absolute ethanol. The desired complex was deposited from solution on standing at 0°. The product was collected by filtration, washed with 4 × 30 ml portions of anhydrous ether, and air dried. The copper complex was recrystallized from acetone. The other three were purified by Soxhlet extraction into methylene chloride, removal of the solvent on a rotary evaporator, and drying under vacuum at room temperature.

Preparation of $M(EDP)(NO_2)_2$ (M = Co, Ni, Cu, and Zn). The four complexes were prepared by the same general method. In a typical experiment 2.0 mmol of the hydrated metal nitrate and 0.55 g, 8.0 mmol, of $NaNO_2$ were stirred together with 25 ml of absolute ethanol. The reaction mixture was cooled in a CO_2-acetone bath to precipitate the $NaNO_3$ formed as well as the excess $NaNO_2$. The cold solution was filtered into a solution of 8.0 mmol of EDP, 1.57 g or 1.72 ml, in 20 ml of absolute ethanol. After stirring the resulting reaction mixture for 30 min, the solvent was removed on a rotary evaporator. The resulting slurry was triturated with 5 × 10 ml portions of hexane to remove the excess ligand and dried under vacuum. The copper complex was recrystallized from benzene and the nickel complex from anhydrous ether, while the cobalt and zinc species were purified by Soxhlet extraction into methylene chloride, removal of the solvent, and drying under vacuum.

Results

The analytical data are given in Table I. All of the complexes are soluble in organic solvents such as methylene chloride and chloroform to give air-stable solutions except for the cobalt nitrate species whose solutions must be handled under a nitrogen atmosphere. Even then, solutions of these species slowly decompose over a period of 24 hr depositing a brown residue. In the solid state these cobalt complexes are also unstable, even when stored under vacuum, with some decomposition being noted after 2 to 3 weeks. As a consequence these compounds were always prepared just prior to use and all handling and reactions were done in a nitrogen atmosphere. The magnetic moments in the solid state and in methylene chloride solution are shown in Table II. They are in the range that would be expected for the respective metals in the 2+ oxidation state. Molecular weight and conductivity data, Tables I and II, indicate that all the complexes are undissociated monomers in acetone and methylene chloride solutions, although there is some evidence for slight solvation of the cobalt and zinc nitrate complexes in acetone solution. The electronic spectral data are shown in Table III.

Table I. Analytical Data

Compd	% C		% H		% N	
	Calcd	Found	Calcd	Found	Calcd	Found
$Co(EDM)(NO_2)_2$[a]	34.19	34.10	5.74	5.73	15.95	15.88
$Co(EDP)(NO_2)_2$	41.50	41.35	6.95	6.88	16.13	16.00
$Co(EDM)(NO_3)_2$	31.34	31.69	5.26	5.56	14.62	14.25
$Co(EDP)(NO_3)_2$	38.03	37.91	6.38	6.42	14.78	14.72
$Ni(EDM)(NO_2)_2$	34.21	34.23	5.74	5.71	15.95	16.03
$Ni(EDP)(NO_2)_2$	41.53	41.50	6.97	7.06	16.16	16.14
$Ni(EDM)(NO_3)_2$	31.36	31.45	5.26	5.32	14.63	14.56
$Ni(EDP)(NO_3)_2$[b]	38.03	38.27	6.38	6.48	14.78	14.75
$Cu(EDM)(NO_2)_2$[c]	33.75	33.66	5.67	5.53	15.74	15.66
$Cu(EDP)(NO_2)_2$	41.00	41.19	6.88	7.00	15.92	15.89
$Cu(EDM)(NO_3)_2$	30.97	31.01	5.20	5.12	14.45	14.44
$Cu(EDP)(NO_3)_2$[d]	37.55	37.61	6.30	6.41	14.59	14.56
$Zn(EDM)(NO_2)_2$	33.58	33.25	5.63	5.62	15.66	15.73
$Zn(EDP)(NO_2)_2$	40.74	40.50	6.83	6.78	15.84	15.89
$Zn(EDM)(NO_3)_2$	30.82	30.65	5.14	5.10	14.38	14.45
$Zn(EDP)(NO_3)_2$	37.36	37.34	6.27	6.48	14.52	14.59

[a] Molecular weight = 353 ± 5 by vapor pressure osmometry in CH_2Cl_2; calcd, 351. [b] Molecular weight = 377 ± 5 by vapor pressure osmometry in CH_2Cl_2; calcd, 379. [c] Molecular weight = 358 ± 5 by vapor pressure osmometry in CH_2Cl_2; calcd, 351. [d] Molecular weight = 380 ± 5 by vapor pressure osmometry in CH_2Cl_2; calcd, 383.

Discussion

Within a given series, nitrite or nitrate, the cobalt, nickel, and zinc complexes are isomorphous as shown by their X-ray powder patterns and thus are assumed to have the same structure. The copper compounds of the same series are isomorphous but their powder patterns differ significantly from those of the corresponding nickel series.

Nickel Complexes. The electronic spectra of the four complexes are very similar. There are three absorption maxima at about 9.2, 15.4, and 25.5 kK. These can be readily interpreted on the basis of an octahedral model with the bands being assigned to the ${}^3A_{2g} \rightarrow {}^3T_{2g}(\nu_1)$, ${}^3A_{2g} \rightarrow {}^3T_{1g}(F)(\nu_2)$, and ${}^3A_{2g} \rightarrow {}^3T_{1g}(P)(\nu_3)$ transitions, respectively.[12] In addition there is a weak transition or shoulder on the low-energy side of the ν_2 transition. This is probably due to the spin-forbidden transition ${}^3A_{2g} \rightarrow {}^1E_g(D)$ which gains measurable intensity *via* spin-orbit coupling to the nearby triplet state.[13] The magnetic moments of the complexes are all the same, within experimental error, both in the solid state and in solution. The average value of 3.25 BM is normal for

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(9) P. L. Corio, "Structure of High Resolution N.M.R. Spectra," Academic Press, New York, N. Y., 1966, p 137.

(10) C. R. Quade, W. H. Brummage, and C. C. Lin, *J. Chem. Phys.*, 37, 1368 (1962).

(11) V. E. Simmons, Ph.D. Dissertation, Boston University, 1963.

(12) B. N. Figgis, "Introduction to Ligand Field Theory," Interscience, New York, N. Y., 1966, p 220.

(13) T. M. Dunn, D. S. McClure, and R. G. Pearson, "Some Aspects of Crystal Field Theory," Harper and Row, New York, N. Y., 1965, p 47.

Table II. Magnetic and Conductivity Data

Compd	μ eff solid[a,b]	μ eff soln[b,c]	$\Lambda^{d,e}$	Λ^f
$\mathrm{Co(EDM)(NO_2)_2}$	4.69	4.67	2.4	0.03
$\mathrm{Co(EDP)(NO_2)_2}$	4.71	4.74	1.5	0.16
$\mathrm{Co(EDM)(NO_3)_2}$	4.73	4.70	6.2	0.03
$\mathrm{Co(EDP)(NO_3)_2}$	4.67	4.70	6.0	0.15
$\mathrm{Ni(EDM)(NO_2)_2}$	3.24	3.26	0.5	0.03
$\mathrm{Ni(EDP)(NO_2)_2}$	3.23	3.29	0.6	0.09
$\mathrm{Ni(EDM)(NO_3)_2}$	3.24	3.26	2.4	0.04
$\mathrm{Ni(EDP)(NO_3)_2}$	3.24	3.23	2.2	0.11
$\mathrm{Cu(EDM)(NO_2)_2}$	1.99	1.95	1.1	0.04
$\mathrm{Cu(EDP)(NO_2)_2}$	2.03	1.98	1.0	0.16
$\mathrm{Cu(EDM)(NO_3)_2}$	2.02	1.96	2.0	0.04
$\mathrm{Cu(EDP)(NO_3)_2}$	1.98	2.03	2.0	0.16
$\mathrm{Zn(EDM)(NO_2)_2}$	Diamag	Diamag	1.8	0.03
$\mathrm{Zn(EDP)(NO_2)_2}$	Diamag	Diamag	1.6	0.05
$\mathrm{Zn(EDM)(NO_3)_2}$	Diamag	Diamag	7.1	0.04
$\mathrm{Zn(EDP)(NO_3)_2}$	Diamag	Diamag	6.7	0.14

[a] At 25°. [b] All values in Bohr Magnetons; all values ±0.06 BM. [c] $\mathrm{CH_2Cl_2}$ solution at 37°. [d] $\mathrm{Ohms^{-1}\ cm^2\ mol^{-1}}$. [e] 1×10^{-3} *M* solution in acetone at 24°. Typical values for 1:1 electrolytes = 120. [f] 1×10^{-3} *M* solution in $\mathrm{CH_2Cl_2}$ at 24°. Typical values for 1:1 electrolytes = 20.

Table III. Spectral Data[a-c]

Compd	Absorption max[d]
$\mathrm{Co(EDM)(NO_2)_2}$	8.35 (7.5); 18.25 (81); 20.2 (65).
$\mathrm{Co(EDP)(NO_2)_2}$	8.70 (10); 18.52 (93); 20.39 (74).
$\mathrm{Co(EDM)(NO_3)_2}$	8.35 (9.5); 18.35 (55); 20.2 (40).
$\mathrm{Co(EDP)(NO_3)_2}$	8.57 (18); 19.0 (102); 20.63 (82).
$\mathrm{Ni(EDM)(NO_2)_2}$	9.25 (7.5); 12.5 (sh); 15.15 (14); 25.0 (42).
$\mathrm{Ni(EDP)(NO_2)_2}$	9.76 (14); 13.0 (sh); 15.75 (23); 25.98 (66).
$\mathrm{Ni(EDM)(NO_3)_2}$	9.03 (13); 12.5 (sh); 15.25 (23); 25.4 (38).
$\mathrm{Ni(EDP)(NO_3)_2}$	9.71 (12); 12.66 (sh); 15.75 (39); 25.85 (70).
$\mathrm{Cu(EDM)(NO_2)_2}$	14.3 (197); 11.0 (sh)
$\mathrm{Cu(EDP)(NO_2)_2}$	15.04 (233); 11.1 (sh)
$\mathrm{Cu(EDM)(NO_3)_2}$	14.4 (150); 11.05 (sh)
$\mathrm{Cu(EDP)(NO_3)_2}$	14.87 (200); 10.8 (sh)

[a] All values in kilokaysers. [b] $\mathrm{CH_2Cl_2}$ solutions. [c] The zinc complexes show no absorptions in the range 43 to 4.0 kK except for ligand overtone bands at 4.1, 4.4, and 4.8 kK. [d] Values in parentheses are molar extinction coefficients; sh = shoulder.

nickel(II) complexes in an octahedral environment.

Infrared absorptions due to the nitrite and nitrate moieties were determined by comparison of the spectra with those obtained from the corresponding halo complexes.[2] In the nitrite complexes there are absorptions at 1300, 1175, and 850 $\mathrm{cm^{-1}}$. The free ion (ionic) values are 1335, 1250, and 830 $\mathrm{cm^{-1}}$.[14] The only mode of coordination that is compatible with these shifts from the free ion values is bidentate coordination through the two oxygens.[5] In nitro complexes both the 1335- and 1250-$\mathrm{cm^{-1}}$ bands are increased in energy, while in nitrito complexes the 1335-$\mathrm{cm^{-1}}$ band is increased in energy and the 1250-$\mathrm{cm^{-1}}$ band is decreased in energy. Also, only in the case of bidentate coordination is the 830-$\mathrm{cm^{-1}}$ band increased in energy. In all other modes it remains at approximately the free ion value. The case of the nitrite acting as a bridging ligand is ruled out because the complexes are monomeric. The nitrate complexes have absorption bands at 1545, 1520, 1260, and 810 $\mathrm{cm^{-1}}$. In addition there are combination bands at 1770 and 1715 $\mathrm{cm^{-1}}$. In this case it is much more difficult to differentiate between bidentate and monodentate coordination. The shifts and splittings of the various absorptions upon going from ionic to either monodentate or bidentate coordination are the same. However, Curtis and Curtis have prepared an extensive series of nickel(II) complexes containing ionic, monodentate, and bidentate nitrate.[15] They found that it is possible to differentiate among the various forms of coordination. The doubly degenerate 1400-$\mathrm{cm^{-1}}$ band in ionic nitrate is split to a greater extent and the 830-$\mathrm{cm^{-1}}$ band appears at lower energy in bidentate *vs.* monodentate coordination. Our results are in substantial agreement with those of Curtis and Curtis for bidentate coordination except that the 1400-$\mathrm{cm^{-1}}$ band is split to a greater extent than that found by the above authors. Lever and coworkers have found that in nickel(II) and cobalt(II) complexes containing bidentate nitrate moieties there is a splitting of the $(\nu_1 + \nu_4)$ combination mode in the range of 38-56 $\mathrm{cm^{-1}}$. Monodentate nitrate coordination, with the same metals, gives a splitting of 15-26 $\mathrm{cm^{-1}}$.[16] In the complexes under consideration the splitting is 55 $\mathrm{cm^{-1}}$. Thus, it can be concluded that all of the nickel complexes are six coordinate with an octahedral coordination geometry.

Cobalt Complexes. The electronic spectra of the four complexes all exhibit the same general features. There are absorption maxima at approximately 8.4, 18.5, and 20.3 kK. The spectra are interpretable on the basis of an octahedral model with the bands being assigned to the $^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)(\nu_1)$, $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)(\nu_2)$, and $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)(\nu_3)$ transitions, respectively.[17] It is interesting to note that the molar extinction coefficients are much higher than those normally observed for octahedral cobalt(II) complexes. This behavior, while not common, has been observed for a few other cobalt(II) complexes in an octahedral environment.[18] The magnetic moments of the four compounds are all the same both in solution and in the solid state, the average being 4.70 BM. These values are somewhat low for cobalt(II) in an octahedral environment. Values for octahedral cobalt(II) generally run from 4.8 to 5.1 BM.[19] Several authors, however, have observed magnetic moments lower than 4.8 BM so that the observed values are not in contradiction with an octahedral coordination geometry.[20]

The infrared spectra of the cobalt complexes are virtually identical with those of the corresponding nickel complexes indicating that the nitrite and nitrate anions are likewise in a bidentate environment in these species.

Copper Complexes. The near-infrared and visible spectra of the four compounds all show one major absorption of approximately 14.5 kK. This band is very asymmetric to lower energies with a barely discernible shoulder at about 11.0 kK. The magnetic moments, solid state and solution, are the same within experimental error. The average value is 2.0 BM. This is normal for copper(II) complexes where there are no magnetic interactions between neighboring ions.

The infrared spectra of the nitrite complexes are quite different from those of the nickel nitrite species. There are nitrite absorptions at 1375, 1350, 1290, 1175, 860, and 830 $\mathrm{cm^{-1}}$. The bands at 1290, 1175, and 860 $\mathrm{cm^{-1}}$ are roughly the same as those found in the nickel species and are indicative of bidentate coordination. The appearance of nitrite absorptions at 1375, 1350, and 830 $\mathrm{cm^{-1}}$ would seem to indicate that nitrite is functioning in a manner other than as a bi-

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(14) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," Wiley, New York, N. Y., 1963, p 151-155.

(15) N. F. Curtis and Y. M. Curtis, *Inorg. Chem.*, 4, 108 (1965).

(16) A. B. P. Lever, E. Mantovani, and B. S. Ramaswamy, *Can. J. Chem.*, 49, 1957 (1971).

(17) B. N. Figgis, "Introduction to Ligand Field Theory," Interscience, New York, N. Y., 1966, p 223.

(18) F. A. Cotton, D. M. L. Goodgame, and R. H. Soderberg, *Inorg. Chem.*, 2, 1162 (1963); R. E. Weston and T. F. Broadsky, *J. Chem. Phys.*, 27, 683 (1957).

(19) B. N. Figgis and J. Lewis, *Progr. Inorg. Chem.*, 6, 287 (1964).

(20) J. A. Walmsby and S. Y. Tyree, *J. Amer. Chem. Soc.*, 83, 3770 (1961); B. N. Figgis and R. S. Nyholm, *J. Chem. Soc.*, 338 (1959); E. Bannister and F. A. Cotton, *ibid.*, 2276 (1960).

dentate ligand in these complexes. These band positions are most compatible with the nitrite behaving as a monodentate ligand bonding through nitrogen.[5] This would then make the complexes five coordinate.

A crystal structure analysis was undertaken on the Cu(NO_2)$_2$EDM complex to verify the exact nature of the coordination polyhedron.[21] The structure is based on a very distorted octahedron with the two EDM nitrogens and the four nitrite oxygens making up the coordination sphere. The two EDM nitrogens and one oxygen from each nitrite form an approximate square plane about the copper atom: Cu-N = 2.01 (2) Å; Cu-O = 1.99 (2) Å. The fifth and sixth positions are occupied by the other two nitrite oxygens at a distance of 2.39 (2) Å. The trans O-Cu-O angle which is normally 180° in octahedral compounds is decreased to 112° in order that the internal O-N-O angle of the nitrite moieties remains within reasonable bounds. This difference in Cu-O bond lengths in nitrite complexes has been observed in other nitrite complexes.[22] Even with the structure in hand we are still at a loss to explain the anomalous infrared absorptions.

The infrared spectra of the nitrates present the same complexities and problems as do the nitrite spectra. There are strong, broad absorptions covering the ranges 1430-1500 and 1260-1320 cm^{-1}. In addition there is a weak absorption at 810 cm^{-1} and combination bands at 1760 and 1730 cm^{-1}. Within each of the major absorption envelopes several maxima are observable. In the 1430-1500-cm^{-1} envelope part of the absorption is contributed by the C-H absorptions of the organic ligands.

The complexity and breadth of the major nitrate absorptions preclude obtaining any useful information other than that the anions are not in an ionic environment. The ($\nu_1 + \nu_4$) combination band region in these complexes is uncluttered and therefore is more amenable to interpretation. The splitting of the combination band is 30 cm^{-1}. This is smaller than is normally found for bidentate groups (38-56 cm^{-1}) but larger than that found for monodentate species (15-21 cm^{-1}).[16] X-Ray analysis of dinitratobis-2-picolinecopper(II) has shown that each nitrite moiety has one long and one short metal-oxygen bond.[23] The splitting of the combination band in this complex is intermediate between that found for monodentate and bidentate nitrate groups. This information coupled with the results of the crystal structure of the Cu(EDM)(NO_2)$_2$ complex makes it reasonable to assign the copper nitrate complexes a distorted octahedral coordination geometry with two long and two short copper-oxygen bonds.

Zinc Complexes. The infrared spectra of the zinc compounds are virtually identical with corresponding nickel and cobalt complexes with which they are isomorphous. They are diamagnetic and exhibit no absorptions in the visible and near-infrared regions of the spectrum except for ligand overtone bands at 4.1, 4.4, and 5.8 kK. Thus, they can also be assigned to an octahedral coordination geometry along with the rest of the EDM and EDP complexes.

Conclusions

The stabilities of the various complexes can be compared with respect to their resistance to decomposition in the solid state and in solution. Within each series, nitrite or nitrate, the EDP species are more stable than those containing EDM. This is to be expected since piperidine has a k_b about 10^3 times that of morpholine.[24] In the coupled species, EDM and EDP, the same trend should hold true making EDP a much stronger base than EDM. Since the bonding of amines to transition metals is primarily σ in nature, the stronger the base the stronger will be the metal-amine bond providing such things as steric factors do not change. Space filling models show that the two ligands have virtually identical steric requirements and therefore base strengths should be the predominating factor in determining the stabilities of the EDM and EDP complexes. Within any series the order of stability follows the order: $Ni > Cu \cong Zn \gg Co$. For a given metal the nitrites are much more stable than nitrates. There are two explanations for this. The nitrite anion lies much higher in the spectrochemical series than does nitrate and therefore has a greater coordinating ability.[25] Steric requirements also probably play a major role. The nitrate anion, being larger than the nitrite moiety, will have larger steric requirements. Since the steric requirements of the EDM and EDP ligands are, in themselves, as great or greater than any bidentate diamine that has been studied, the added steric encumbrances of nitrate *vs.* nitrite should lead to lower stability.[2] A combination of both factors undoubtedly is operative but it is impossible to sort them out and determine which is the most important.

It is interesting to note that the EDP complexes are much more soluble than the corresponding EDM species. For example, the EDP nitrite complexes are sufficiently soluble in ether and benzene to permit their recrystallization from these solvents whereas the corresponding EDM species can be Soxhlet extracted with these solvents for several days with no solubility being noted. Also in solvents like chloroform, methylene chloride, or acetonitrile, where the solubility of both the EDP and EDM complexes is appreciable, the EDP species are by far the most soluble. The only difference between the two ligands is the replacement of two methylene groups in the para positions of the rings with ether linkages. This should increase the affinity of the EDM complexes for polar solvents, especially ethers; however the opposite seems to be the case. This would imply that in the crystalline state there are interactions involving the ether linkages. However, crystal structures that have been determined for EDM complexes show that there are no intermolecular distances which are short enough to constitute any significant or discernible interactions, hydrogen bonding or otherwise.[3,21]

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Registry No. Co(EDM)(NO_2)$_2$, 34110-71-9; Co(EDP)(NO_2)$_2$, 49626-85-9; Co(EDM)(NO_3)$_2$, 49626-86-0; Co(EDP)(NO_3)$_2$, 49626-87-1; Ni(EDM)(NO_2)$_2$, 49626-88-2; Ni(EDP)(NO_2)$_2$, 49626-89-3; Ni(EDM)(NO_3)$_2$, 49626-90-6; Ni(EDP)(NO_3)$_2$, 49626-91-7; Cu(EDM)(NO_2)$_2$, 49626-92-8; Cu(EDP)(NO_2)$_2$, 49626-93-9; Cu(EDM)(NO_3)$_2$, 49626-94-0; Cu(EDP)(NO_3)$_2$, 49626-95-1; Zn(EDM)(NO_2)$_2$, 49626-96-2; Zn(EDP)(NO_2)$_2$, 49626-97-3; Zn(EDM)(NO_3)$_2$, 49626-98-4; Zn(EDP)(NO_3)$_2$, 49626-99-5.

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(21) A. L. Lott II, unpublished results. The structure refinement converged at a conventional *r* factor of 13.8%. Severe crystal decomposition was noted during data collection. A new set of data is being collected with the crystal mounted in a capillary so that the refinement can be continued to a more reasonable value.

(22) F. S. Stevens, *J. Chem. Soc. A*, 2081 (1969).

(23) A. F. Cameron, R. H. Nuttall, and D. W. Taylor, *J. Chem. Soc. D*, 865 (1970).

(24) $K_b = 2 \times 10^{-3}$ *for piperidine*, R. T. Morrison and R. N. Boyd, "Organic Chemistry," Allyn and Bacon, Boston, Mass., 1959, p 850; $K_b = 2.44 \times 10^{-6}$ for morpholine, "The Chemistry of Heterocyclic Compounds," Vol. 17, R. H. Wiley, Ed., Interscience, New York, N. Y., 1962, p 379.

(25) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 3rd ed, Interscience, New York, N. Y., 1972, pp 577-578.