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Cobalt(II) Complexes of Pyridine

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Pyridine complexes of cobalt(II) perchlorate, tetrafluoroborate, and nitrate have been prepared and studied by a variety of physical methods in both the solid and solution states. Their behavior is found to be generally similar to that of their nickel(II) analogues.[2] *The tetragonally distorted perchlorate and tetrafluoroborate, $[Copy_4X_2]$, complexes contain coordinated anions in both the solid state and in dichloromethane-pyridine solutions. Both are found to undergo extensive decomposition in nitromethane solutions. Addition of pyridine to such solutions produces species found to be different from that produced in the $[Copy_4(BF_4)_2]$-pyridine system, which is probably $[Copy_6]^{2+}$. The nitrate complex, $[Copy_3(NO_3)_2]$, is thought to be monomeric in the solid state. It is shown to lose one mole of pyridine in dichloromethane and nitromethane solutions, forming $[Copy_2(NO_3)_2]$. In dichloromethane-pyridine and nitromethane-pyridine solutions, the nitrate complex reacts with pyridine to form $[Copy_4(NO_3)_2]$ and $[Copy_5(NO_3)]^+$ (or $[Copy_4(NO_3)]^+$), respectively. No evidence is found for the existence of $[Copy_6]^{2+}$ under these conditions. The tetrafluoroborate complex dissolves in pyridine to produce a species assumed to be $[Copy_6]^{2+}$, for which spectrochemical parameters are calculated.*

Introduction

Although there are many reports in the literature concerning the properties of various $[Mpy_6]^{n+}$ py = pyridine, n = integer species, only a very few of them have been authenticated. Thus only recently have the existences of $[Nipy_6]^{2+}$ (in a nitromethane-pyridine solution)[2] and $[Fepy_6]^{2+}$ (in the solid state)[3] been substantiated. In contrast, however, no completely documented case for the existence of $[Copy_6]^{2+}$ has yet been presented. While most earlier reports on this matter have been at best inconclusive, recent studies have shown that many of them have also been incorrect.

The compound designated as $[Copy_6]Cl_2$[4] has been shown to contain two moles of lattice pyridine in the solid state[5] and to decompose to $[Copy_2Cl_2]$ in a number of pyridine-free solutions.[6] The structure of $[Copy_6]Br_2$, found to be stable only in a pyridine atmosphere,[7] is more than likely analogous to its chloride counterpart. The fact that the $[Nipy_6]X_2$ ($X = Br^-$, I^-) complexes also lose two moles of pyridine when exposed to the atmosphere or washed with ethanol[8] is a further indication that $[Copy_6]Br_2$ is not a definite entity. The report of the existence of $[Copy_6]I_2$ in a nitromethane-pyridine solution[9] has been herein reexamined and is thought to be incorrect. The work of Norbury *et al.*[10] regarding the $[Nipy_6]X_2$ ($X = CNO^-$, CNS^-, $CNSe^-$) complexes has shown that these complexes contain only four molecules of coordinated pyridine both in the solid state and in nitromethane pyridine solutions. These results substantiate an earlier report on the behavior of the cyanate complex,[2] and indicate that the designation of $[Copy_6](CNO)_2$ as a « hexakis » complex solely on the basis of solid state magnetic data[11] is quite likely incorrect. The solution behavior[12,13] of this supposed compound indicates its instability in non-coordinating solvents with respect to the pseudotetrahedral $[Copy_2(NCO)_2]$.

Although the existence of crystalline $[Copy_6](NO_3)_2$ has long been proposed,[4,14-16] recent work by Biagetti and Haendler has shown[17] that both $[Mpy_6](NO_3)_2$ ($M = Co^{II}$, Ni^{II}) compounds in fact contain only three moles of coordinated pyridine, both in the solid state and in chloroform and dichloromethane solutions. Those articles concerning the existence of crystalline $[Copy_6](ClO_4)_2$[4,18,19] offer no evidence as to the nature of the species within the first coordination sphere of the metal ion.

At present there are thus no definitive indications of the presence of $[Copy_6]^{2+}$ in either the solid state or in solution, although $[Co_3py_6(CO)_8]$[20] may be in actuality $[Copy_6][Co_2(CO)_8]$, in analogy to $[Fe_5py_6(CO)_{13}]$, which has already been studied.[3] In light of this situation and as a continuation of studies con-

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cerning nickel-pyridine systems,[2] the synthesis and physical studies of the pyridine complexes of cobalt nitrate, perchlorate, and tetrafluoroborate are presented. Reactions of these salts with pyridine, in an attempt to produce $[Copy_6]^{2+}$, are discussed in detail. While this paper was in preparation, another report[21] describing the solution behavior of the pyridine complex of cobalt perchlorate appeared. Comparisons of pertinent data will be made later.

Experimental Section

Reagents. Reagent grade ether was used without further purification. Spectral reagent grade dichloromethane (Merck) and nitromethane (Eastman) were stored over Linde 4-A molecular sieves before use. Reagent grade pyridine was dried over barium oxide, distilled (b.p. 113-4°), and stored over molecular sieves. Hydrated cobalt(II) perchlorate (G. F. Smith) was used as obtained. Practical grade 2,2-dimethoxypropane (DMP) (Eastman) was used with no further purification. All other reagents were used as obtained.

Synthesis. Bis(perchlorato)tetrakis(pyridine)cobalt(II). The pale pink compound was obtained by the some procedure used for the analogous nickel(II) complex,[2] with hydrated cobalt(II) perchlorate and DMP used as starting materials. *Anal.* Calcd. for $[Copy_4(ClO_4)_2]$: C, 41.8; H, 3.48; N, 9.75. Found: C, 41.7; H, 3.45; N, 10.0.

Bis(tetrafluoroborato)tetrakis(pyridine)cobalt(II). To 50 ml of a 40% aqueous solution of fluoroboric acid was added 10.8 g of cobalt(II) carbonate. After the bubbling ended, the black cobalt oxide was removed by filtration, and the solution volume reduced by heating. After cooling, the red crystals of hexaquocobalt(II) tetrafluoroborate were removed by filtration and air-dried overnight.

To a solution of 90 ml of DMP and 10 ml of anhydrous methanol was added 12 g of the tetrafluoroborate compound. After the mixture was stirred for four hours, twenty-five ml of pyridine was added to the red solution, producing a red oil which became crystalline after fifteen minutes of stirring. The pink crystals were filtered and washed repeatedly with small portions of ether. They were then suspended in ether, re-filtered, rewashed, and dried for 12 hours *in vacuo* at 25°C. The pale pink crystals are more hygroscopic than those of the corresponding perchlorate compound. *Anal.* Calcd. for $[Copy_4(BF_4)_2]$: C, 43.7; H, 3.74; N, 10.2. Found: C, 43.1; H, 4.16; N, 10.2.

Dinitratotris(pyridine)cobalt(II). The deep pink compound was prepared by the same method described for the nickel(II) nitrate compound,[2] starting with hydrated cobalt(II) nitrate and DMP. *Anal.* Calcd. for $[Copy_3(NO_3)_2]$: C, 42.9; H, 3.57; N, 16.7. Found: C, 42.1; H, 3.54; N, 16.7.

The preparation of diiodobis(pyridine)cobalt(II) has been described previously.[22]

Spectral measurements. Solution electronic spectra were obtained on Beckman DK-2 and Cary 14 M recording spectrophotometers. For these systems in which excess pyridine was added to the solution, an equivalent amount of pyridine was used in the reference cell. Mull electronic spectra were obtained on the Cary by using a glass plate as a holder for the Nujol-mulled sample and Nujol-soaked filter paper as a reference. Infrared spectra of Nujol-mulled solids were obtained on a Perkin-Elmer 521 spectrophotometer (using potassium bromide plates) and a Beckman IR5A spectrophotometer (using cesium bromide plates). Solution spectra were obtained on the Beckman instrument using cesium bromide cells.

Conductance measurements were obtained as previously described.[2] Magnetic data were obtained by the Guoy method, using $Hg[Co(NCS)_4]$[23] and $K_3[Fe(C_2O_4)_3] . 3H_2O$ [24] as standards. Diamagnetic corrections were estimated from Pascal's constants.[25,26]

Results

Electronic spectral data for the compounds are reported in Table I for both the solid compounds and their dichloromethane, nitromethane, and pyridine solutions. Magnetic data for the solid compounds and conductance values for their dichloromethane and nitromethane solutions are reported in Tables II and III, respectively.

Infrared spectral data on the crystalline complexes indicate that all pyridine molecules and anions present are coordinated to the metal. All complexes possess a pyridine infrared absorption at 427 cm^{-1}. The shift of this absorption from its free ligand value of 403 cm^{-1} has previously been noted in analogous nickel(II) complexes.[2] The absorptions assignable to the perchlorate and tetrafluoroborate anions in the 1100 cm^{-1} region are similar to others in which coordinated anions have been found.[2] The nitrate absorptions are shifted from their values in ionic nitrates, and the observed absorptions are in good agreement with those previously reported for $[Copy_3(NO_3)_2]$.[17] When the nitrate complex is dissolved in either nitromethane or dichloromethane, Beer's law studies on the infrared band at 403 cm^{-1} (assignable to free pyridine) indicate that one mole of pyridine is lost per cobalt ion:

$$[Copy_3(NO_3)_2] \xrightarrow{CH_3NO_2 \text{ or } CH_2Cl_2} [Copy_2(NO_3)_2] + py \quad (1)$$

Similar behavior has been noted for the nickel complex[2] and also for both the cobalt and nickel complexes in chloroform.[17]

The electronic transitions (Table I) observed for the perchlorate and tetrafluoroborate complexes have been assigned utilizing the energy level diagram for a six-coordinate d^7 system. The splittings of the $\nu_1(^4T_{1g}(F) \rightarrow {}^4T_{2g})$ and $\nu_3(^4T_{1g}(F) \rightarrow {}^4T_{1g}(P))$ transitions seen in some instances are due to tetragonal distortions in the ligand field. These transitions are then from the ground state to the $^4B_{2g}$ and ^4E_g (ν_1) and $^4A_{2g}$ and ^4E_g (ν_3)

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Table I. Electronic Spectral Data for Cobalt(II) Complexes

Complex	Solvent	λ_{max} (mμ)	ν (cm^{-1})	Transition[a]
$Copy_4(ClO_4)_2$	mull	442	22625	—
		[516, 544][b]	[19380, 18382]	ν_3
		[1125, 1190 (sh)[c]]	[8889, 8403]	ν_1
$Copy_4(BF_4)_2$	mull	440	22727	—
		[505, 540]	[19801, 18518]	ν_3
		1100	9091	ν_1
$Copy_4(ClO_4)_2$	CH_2Cl_2	450 (9)[d]	22222	—
		525 (17)	19047	ν_3
		1100 (5)	9091	ν_1
$Copy_4(BF_4)_2$	CH_2Cl_2	460 (8)	21739	—
		[515 (14), 535 (12)]	[19417, 18691]	ν_3
		1095 (3)	9132	ν_1
$Copy_4(ClO_4)_2$	CH_2Cl_2+py	470 (9)	21276	—
		515 (16)	19417	ν_3
		1105 (4)	9050	ν_1
$Copy_4(BF_4)_2$	CH_2Cl_2+py	460 (7)	21739	—
		[520 (12), 537 (10)]	[19230, 18621]	ν_3
		1100 (3)	9091	ν_1
$Copy_4(ClO_4)_2$	CH_3NO_2+py	[505 (65), 518 (59)]	[19801, 19305]	ν_3
		540 (sh)	18518	ν_2
		1131 (9)	8842	ν_1
$Copy_4(BF_4)_2$	CH_3NO_2+py	[505 (63), 520 (60)]	[19801, 19230]	ν_3
		545 (sh)	18348	ν_2
		1132 (8)	8834	ν_1
$Copy_4(BF_4)_2$	py	475 (sh)	21052	—
		505 (30)	19801	ν_3
		540 (sh)	18518	ν_2
		1110 (6)	9010	ν_1
$Copy_3(NO_3)_2$	mull	475	21052	
		520	19230	ν_1
		625	16000	ν_2
		[e]		
$Copy_3(NO_3)_2$	CH_2Cl_2	530[f]	18867	—
		[1085, 1250]	[9217, 8000]	—
$Copy_3(NO_3)_2$	CH_2Cl_2+py	475 (sh)	21052	—
		516 (39)	19379	ν_3
		620 (4)	1619	ν_2
		1395 (4)	7169	ν_1
$Copy_3(NO_3)_2$	CH_3NO_2	530[f]	18867	—
		[1085, 1260]	[9217, 7937]	—
$Copy_3(NO_3)_2$	CH_3NO_2+py	475 (sh)	21052	—
		508 (50)	19685	ν_3
		620 (sh)	16129	ν_2
		[e]		

[a] ν_1, ν_2, and ν_3 refer, respectively, to the $^4T_{1g}(F) \rightarrow {}^4T_{2g}$, $^4T_{1g}(F) \rightarrow {}^4A_{2g}$, and $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ allowed transitions for six-coordinate cobalt(II) complexes. The doublets are due to transitions to the separate components of the triplet levels, which in several cases are split by the tetragonal distortions in the ligand field. [b] Brackets denote doublet character for the observed peaks. [c] sh = shoulder. [d] Molar absorptivity at λ_{max}. [e] No ν_1 transition obtained. [f] Values of molar absorptivity vary with concentration of complex. See text.

Table II. Magnetic Properties of the Complexes

Complex	$10^6\chi_m$	$10^6\chi'_m$	T(°C)	μ_{eff} (B.M.)
$Co(C_5H_5N)_4(ClO_4)_2$	11036	11192[a]	298	5.20[b]
$Co(C_5H_5N)_4(BF_4)_2$	10754	10924	298	5.11
$Co(C_5H_5N)_3(NO_3)_2$	8600	8709	300	4.56[c]

[a] The diamagnetic corrections are estimated to be 156×10^{-6} units for the perchlorate complex, 170×10^{-6} units for the tetrafluoroborate complex, and 109×10^{-6} units for the nitrate complex. [b] Jones and Bull (Ref. 21) report $\mu = 5.25$ B.M. [c] Biagetti and Haendler (Ref. 17) report $\mu = 4.60$ B.M.

levels. In some cases only the splitting between the components of the $^4T_{1g}(P)$ level is large enough to be seen.

The transitions at >20,000 cm^{-1} are assumed to be due to spin-orbit coupling of the $^4T_{1g}(P)$ (or in the case of splitting, the ^4E_g) level, although the possibility of an intensity-enhanced quartet-doublet transition has been raised.[27] The ν_2 transition, seen as a low-energy shoulder on the ν_3 transition, was observed in only a few instances. This assignment is based on the prediction that ν_2 for six-cordinate cobalt(II) complexes is approximately twice as high in energy as the ν_1 transition.[27]

For the tetrafluoroborate complex dissolved in pyridine, the infrared absorption is assigned as the ν_1 transition, and the main absorption in the visible region is assigned as ν_3. The high energy shoulder on the ν_3 peak is assumed to be due to spin-orbit coupling,[27] and the low energy shoulder is assigned as the ν_2 transition. The equations used to calculated Dq and B′ for the $[Copy_4(BF_4)_2]$–py system (the one most likely to contain $[Copy_6]^{2+}$) are those used by Eilbeck *et al.*[28]

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Table III. Conductance Data for Co^{II} Complexes

Complex	Solvent	Λ molar	Temp. °C	Conc.×10^3 *M*	Type [a]
$Copy_4(ClO_4)_2$	CH_2Cl_2	2.66	22.8	0.251	non
$Copy_4(ClO_4)_2$	CH_2Cl_2+py	14.9	23.8	0.174	non
$Copy_4(ClO_4)_2$	CH_3NO_2	188.	24.4	1.09	2: 1
$Copy_4(ClO_4)_2$	CH_3NO_2+py	140.	25.2	0.954	2: 1
$Copy_4(BF_4)_2$	CH_2Cl_2	2.00	24.6	2.27	non
$Copy_4(BF_4)_2$	CH_2Cl_2+py	9.71	24.6	0.406	non
$Copy_4(BF_4)_2$	CH_3NO_2+py	139.	24.6	2.23	2: 1
$Copy_3(NO_3)_2$	CH_2Cl_2	<0.152	22.4	0.352	non
$Copy_3(NO_3)_2$	CH_2Cl_2+py	2.05	23.8	0.228	non
$Copy_3(NO_3)_2$	CH_3NO_2	6.45	25.2	7.16	non
	CH_3NO_2+py	110.	25.1	0.456	1: 1
$Copy_2Cl_2$	CH_2Cl_2 [a]	<0.226	22.8	0.236	non
$[(C_6H_5)_3AsCH_3]I$	CH_2Cl_2 [a]	33.9	23.5	0.750	elect.
$[(C_6H_5)_3AsCH_3]_2Co(NO_3)_4$	CH_2Cl_2 [a]	43.7	22.8	0.481	elect.
$[(C_6H_5)_3AsCH_3]_2Ni(NO_3)_4$	CH_2Cl_2 [a]	71.1	23.2	0.413	elect.

[a] Due to the poor solvating properties of dichloromethane, extensive ion pairing occurs at all concentrations. Thus only the presence or absence of ionic species (and not their type) are determined from this solvent.

Even though the nature of the nitrate complex changes upon dissolution and also as pyridine is added to its dichloromethane and nitromethane solutions, the transitions observed for the solid complex and in solvent-pyridine systems are easily assigned using an octahedral model. Since the stereochemistry for $[Copy_2(NO_3)_2]$ can be considered to be that of either a distorted tetrahedron or a distorted octahedron,[29] the transitions for this species were not assigned.

While the magnetic data (Table II) for the perchlorate and tetrafluoroborate complexes are similar to those of other six-coordinated cobalt(II) complexes, the data for the nitrate complex are similar to those cobalt(II) complexes in which a tetrahedral or pseudotetrahedral ligand field is present. This field is, however, a rhombically distorted octahedral one, and fortunately the results can easily be interpreted in this light. Thus, as in the case of some tetragonally distorted cobalt(II) complexes of substituted pyridine N-oxides,[30,31] the large reduction of spin-orbit coupling from that seen in most $[Co(ligand)_6]^{2+}$ complexes is due to a reduction in the orbital degeneracy of the ground state, caused by the rhombic ligand field. While the magnetic moments for the complex in dichloromethane and nitromethane solutions were not obtained, they would be expected to be in the range (μ = 4.5-4.6) reported for other $[CoL_2(NO_3)_2]$ complexes.[29]

The conductance data (Table III) indicate that anion displacement occurs for all complexes dissolved in pyridine-nitromethane solutions and for the perchlorate and tetrafluoroborate complexes dissolved in nitromethane. The solution species formed in the perchlorate and tetrafluoroborate cases are 2: 1 electrolytes, while that formed in the nitrate case is a 1: 1 electrolyte. Only very small amounts of dissociation occur in dichloromethane or dichloromethane-pyridine solutions, the largest being in the case of the perchlorate complex. These results are analogous to those previously reported.[2,17]

Discussion

Structures of the Crystalline Complexes. As in the case of the Ni^{II} complexes,[2] the infrared mull spectra of the perchlorate and tetrafluoroborate complexes indicate that all the pyridine molecules and both of the anions are coordinated, giving rise to six coordinate, tetragonal complexes. The magnetic moments of the complexes are also typical of those previously reported for six-coordinate cobalt(II) complexes.

The electronic mull spectra of these complexes are similar to those reported for $[Copy_2(acetate)_2]$[27] and $[Co(H_2O)_4(NH_3)_2]^{2+}$,[32] in which the splitting of the ν_3 transition is assumed to be due to the tetragonal splitting of the $^4T_{1g}(P)$ level. Thus the electronic data-coupled with the infrared and magnetic data-indicate the crystalline species to be $[Copy_4X_2]$ ($X = ClO_4^-$, BF_4^-).

The infrared mull spectrum of the nitrate complex indicates, as in the case of Ni^{II},[2,17] that all the pyridine molecules and both the nitrate ions are coordinated. Although the complex loses one mole of pyridine upon dissolution, it can be crystallized unchanged from dichloromethane. The magnetic moment is within the range of those values reported for strongly distorted six coordinated cobalt(II) complexes.[30,31]

From stoichiometric considerations the nitrate complex could be formulated either as a monomer or as an ion pair in which two different cobalt(II) environments are present. Such behavior has been noted for the $[Co(DMSO)_3X_2]$[33] and $[Co(pyNO)_3X_2]$[34] (DMSO = dimethylsulfoxide; pyNO = pyridine N-oxide; X = halide, NCS^-) complexes, in which $[CoL_6]^{2+}$ and $[CoX]^{2-}$ species are present. The complex corresponding to the anion in such an ion pair, $[Co(NO_3)_4]^{2-}$, is known to have an absorption of 540 mμ.[35] Since this absorption is absent, the combination of spectral and magnetic data indicate that $[Copy_3(NO_3)_2]$ is analogous to the nickel(II) complex, which has previously[2,17] been found to be monomeric.

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Structure of the Complexes in Solution. Dichloromethane. When either the perchlorate or tetrafluoroborate complex is dissolved in dichloromethane solution, electronic spctra are obtained which are essentially identical to the respective mull electronic spectra. Addition of large excesses of pyridine has little effect on the electronic spectra. Since conductance measurements indicate that at most only relatively small amounts of ionic species are present, the species in solution are formulated as [$\mathrm{Copy_4(ClO_4)_2}$] and [$\mathrm{Copy_4(BF_4)_2}$], respectively. Such behavior is consistent with the low solvating power of dichloromethane.

When the deep pink nitrate complex is dissolved in dichloromethane, a pink solution is obtained. Far infrared measurements indicate that, upon dissolution, one mole of pyridine is lost per molecule. The visible electronic spectrum of this new species, [$\mathrm{Copy_2(NO_3)_2}$], consists of a single, intense unstructured absorption at 530 mμ, while a conductance measurement indicates that no ionic species are present.

There is, however, a definite indication of some type of solvent-solute interaction. Thus while no change in the position of the visible transition is noted over a molar concentration range of 0.004-0.08, the magnitude of the molar absorptivity decreases from 178 to 104. This range includes previously reported[17] values for the complex in dichloromethane and chloroform, which may also interact in some way with the solute. Similar behavior has been noted for [$\mathrm{Co(HMPA)_2X_2}$] (HMPA = hexamethylphosphoramide) complexes in dichloromethane (X = Cl) and chloroform (X = Cl, Br, I),[36] although in these cases the molar absorptivities *increased* with an increase in solute concentration. Since infrared studies[36] of the C—H stretching frequencies in chloroform indicate the presence of a hydrogen-bonding interaction between solvent proton and coordinated halide in the HMPA complexes, it is likely that a similar interaction is occurring here.

The addition of excess pyridine to dichloromethane solutions of the complex causes an increase in the energy of and a decrease in the intensity of the ν_3 transition, producing an electronic spectrum more typical of six-cordinate cobalt(II) complexes, but different from that of crystalline [$\mathrm{Copy_3(NO_3)_2}$]. Since conductance measurements indicate that no ionic species are present, the most probable species in solution is [$\mathrm{Copy_4(NO_3)_2}$], as shown in equation (2):

$$[\mathrm{Copy_3(NO_3)_2}] \xrightarrow{\mathrm{CH_2Cl_2}} [\mathrm{Copy_2(NO_3)_2}] + \mathrm{py} \xrightarrow{\text{excess py}} [\mathrm{Copy_4(NO_3)_2}] \qquad (2)$$

An earlier report[17] of the solution spectrum of the tetrakis-complex is probably that of a mixture of the bis-and tetrakis-pyridine complexes, since the reported values of ν_3 and ε are intermediate between those ascribed herein to the individual species.

Nitromethane. When either the perchlorate or tetrafluoroborate complex is dissolved in nitromethane, the initial pink color quickly changes to a brown one[21] which upon dilution becomes gold. The electronic spectra for these systems contain no apparent absorption bends in the visible or near infrared regions, but do contain an intense absorption just below the solvent cutoff at 380 mμ. Conductance measurements indicate that anion displacement has occurred. These results indicate that some radical type of decomposition, probably also involving some displacement of pyridine molecules, has taken place. Although some type of decomposition occurs when the analogous nickel(II) complexes are dissolved in nitromethane,[2] the species formed therein give the normal elctronic spectra expected of six-coordinated nickel(II) complexes.

Addition of excess pyridine to these nitromethane solutions reproduces pink-colored solutions, whose electronic spectra resemble those of known six-coordinate cobalt(II) complexes. Conductance measurements again indicate the absence of coordinated anions. Although it is tempting to describe the spectra in terms of the production of [$\mathrm{Copy_6}$]$^{2+}$, the definite decompostion of the complexes in pyridine-free nitromethane solutions, the splitting of the ν_3 peak, and the magnitude of the molar absorptivities are probable indications that the cobalt(II) species present contain(s) some nitromethane and/or decomposition products within the coordination sphere(s).

When the nitrate complex is dissolved in nitromethane, the resulting species loses one mole of pyridine, as indicated from far infrared studies. Since conductance measurements indicate that no ionic species are present, and since the electronic is identical to that of [$\mathrm{Copy_3(NO_3)_2}$] dissolved in dichloromethane, the species present must be [$\mathrm{Copy_2(NO_3)_2}$]. The molar absorptivity of the visible peak of this complex in nitromethane varies in a way similar to that found in dichloromethane, even though the mode of solvent-solute interaction is quite probably different in the two cases. Over a molar concentration range of 0.006-0.08, the molar absorptivity for the peak at 530 mμ decreases from 183 to 115. While such behavior has previously been noted for [$\mathrm{Co(TMNO)_4}$]($\mathrm{ClO_4}$)$_2$ (TMNO = trimethylamine N-oxide), in that case the molar absorptivity increased with an *increase* in solute concentration.[37,38]

With the addition of pyridine to a nitromethane solution of the complex, the visible transition becomes higher in energy and less intense, with the spectrum becoming more typical of six-coordinate cobalt(II) complexes. Since the conductance value for this system indicates that one nitrate ion remains coordinated, the resulting species is then either [$\mathrm{Copy_5(NO_3)}$]$^+$ (with a monodentate nitrate) or [$\mathrm{Copy_4(NO_3)}$]$^+$ (with a bidentate or bridging nitrate), although the former appears more likely. This behavior is shown in equation (3):

$$[\mathrm{Copy_3(NO_3)_2}] \xrightarrow{\mathrm{CH_3NO_2}} [\mathrm{Copy_2(NO_3)_2}] + \mathrm{py} \xrightarrow{\text{excess py}} [\mathrm{Copy_{4\ or\ 5}NO_3}]^+ + \mathrm{NO_3}^- \qquad (3)$$

Although no evidence is thus found for the existence of [$\mathrm{Copy_6}$]($\mathrm{NO_3}$)$_2$ in either nitromethane-pyridine solutions (the compound is insoluble in pyridine itself) or in the solid state,[17] a report concerned with the electronic spectrum of such a purported species

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(36) M. R. Rosenthal, Ph. D. Thesis, University of Illinois, 1965.

(37) D. W. Herlocker, *J. Inorg. Nucl. Chem.*, 30, 2197 (1968).

(38) D. W. Herlocker and R. S. Drago, *Inorg. Chem.*, 7, 1479 (1968).

has appeared.[9] The compound in question was prepared by recrystallizing hydrated cobalt nitrate from pyridine;[16] unfortunately no analytical data have been reported.[9,16] An attempt to duplicate this synthesis[16] resulted in the preparation of $[Copy_3(NO_3)_2]$. Since this latter compound is pyridine-insoluble, and since the «$[Copy_6](NO_3)_2$» species[9] is pyridine-soluble, it is obvious that the two comounds prepared must be different . In addition the electronic spectrum of the pyridine-soluble species[9] is decidedly different from that thought to be due to $[Copy_6]^{2+}$ (see next section, and it is thus likely to be due to a mixed pyridine-water complex.

The proton and N^{14} nmr spectra of «$[Copy_6](NO_3)_2$» have been recently reported.[15,39] From the method of preparation,[15] it is probable that the crystalline complex prepared is in reality $[Copy_3(NO_3)_2 . 3py]$.[17] The isotropic shift data are reported in a nitromethane-pyridine solution, in which $[Copy_6]^{2+}$ is definitely not formed. Although no solution electronic spectra are reported, the solution species present is likely to be $[Copy_5(NO_3)]^+$. The linearity of plots of chemical shifts of protons in « complexed » ligand *vs.* mole fraction of «complexed» ligand (taken as proof of the existence of $[Copy_6]^{2+}$) can be explained by assuming that $[Copy_5(NO_3)]^+$ is the only complex observed over the range studied. While the linearity of such plots has been used in helping to establish the existence of certain complexes of trimethylamine N-oxide[37,38] and substituted pyridine N-oxides,[40,41] it is a necessary but not sufficient criterion for complex identification, to be used only in conjunction with other evidence.

Since the electronic spectrum of the purported «$[Copy_6](NO_3)_2$» species is said to be identical to that for «$[Copy_6]I_2$» (prepared by dissolving $[Copy_2I_2]$ in a nitromethane-pyridine solution),[9] a sample of the pseudotetrahedral iodide complex[22] was dissolved in several different nitromethane-pyridine solutions. Under these conditions, however, at least two cobalt(II) species are found, neither of which corresponds to «$[Copy_6]I_2$». Since one of the species exhibited transitions in the 650-680 mμ range in systems containing pyridine/complex ratios of 154/1 and 1110/1 (although its concentration in the second system was very small), it is undoubtedly unreacted $[Copy_2I_2]$. The remaining species (one or more) exhibited a broad, intense absorption slowly rising into the ultraviolet region. Although this type of absorption is generally indicative of iodide coordination, it is obvious that whatever species might be present, the species assigned as «$[Copy_6]I_2$» is not. Since the reported[9] conductance value for $[Copy_2I_2]$ in a nitromethane-pyridine solution indicates that the iodides are not coordinate, the species observed[9] is again probably a mixed pyridine-water complex.

Pyridine. Both the nitrate and perchlorate complexes are found to be insoluble in pyridine. A recent report,[21] however, has stated that the solubility of $[Copy_4(ClO_4)_2]$ in pyridine is about 0.01 molar. The resulting electronic spectrum was interpreted as being due to $[Copy_6]^{2+}$, with values for Dq and B′ being reported.

Using pyridine purified only by drying over molecular sieves, a solution (0.012 molar) of the perchlorate complex in pyridine was indeed obtained. The electronic spectrum of this solution is quite similar to that reported by Jones and Bull.[21] If, however, the pyridine is purified both by distillation and subsequent drying over molecular sieves, the solubility of $[Copy_4(ClO_4)_2]$ in it is essentially nil.

Similar behavior is noted for the tetrafluoroborate complex. Thus the solubility of $[Copy(BF_4)_2]$ in pyridine is reduced from >0.04 molar to approximately 0.01 molar if the pyridine is distilled. The electronic spectrum of the complex also changes markedly with the type of pyridine used. The spectrum of the species in distilled pyridine is different from those of $[Copy_4(BF_4)_2]$ in either nitromethane-pyridine solutions or in the solid state. Thus the species present is either $[Copy_5BF_4]^+$ or $[Copy_6]^{2+}$. The general similarity of this spectrum to those[32] for $[Co(NH_3)_6]^{2+}$ and $[Coen_3]^{2+}$ would seem to rule out large amounts of the former species, since a noticeable splitting of the ν_3 absorption would be expected. Calculation of spectral parameters[28] yields values of 1017 cm^{-1} for Dq, 797 cm^{-1} for B′, and 0.82 for β. This value for Dq is greater than that reported for the nickel(II) complex,[2,42] and it places pyridine below ethylenediamine (1100 cm^{-1}) and above both ammonia (1010 cm^{-1}) and water (930 cm^{-1}) in the spectrochemical series for six-coordinate cobalt(II) complexes. The difficulty in preparing a $[Copy_6]^{2+}$ species in spite of this high Dq value is probably due to the steric difficulties inherent in placing six pyridine molecules about the metal ion. In the series of compounds $[Nipy_4X_2]$ ($X = ClO_4^-, Br^-, Cl^-$), it has been found[43] that Dq_{xy} for pyridine decreases from 1250 cm^{-1} to 1120 cm^{-1} and finally to 1030 cm^{-1} as the ligand field strength along the z-axis increases ($ClO_4^- < Br^- < Cl^-$), thus increasing the crowding about the metal ion, a situation which culminates in the still lower Dq value of 957 cm^{-1} for $[Nipy_6]^{2+}$ in pyridine.[2,42] While no results have yet been published for tetragonal cobalt(II) complexes, a similar trend would be expected.

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(39) Yu. N. Molin and E. E. Zaev, *J. Struct. Chem.*, *8*, 140 (1967).
(40) D. W. Herlocker, Ph. D. Thesis, Univ. of Illinois, 1966.
(41) D. W. Herlocker, R. S. Drago, and V. I. Meek, *Inorg. Chem.*, *5*, 2009 (1966).

(42) Recently R. S. Drago and R. E. Cramer (*J. Amer. Chem. Soc.*, *92*, 66 (1970)) have shown that the nmr and visible spectra of $[Nipy_6(ClO_4)_2]$ in pyridine-nitromethane and pyridine-propylene carbonate solutions — while similar — are distinctly different. The difference in calculated Dq values (988 cm^{-1} *vs.* 966 cm^{-1}, respectively) and the determination by nmr of a pyridine coordination number of 6.05 ± 0.45 for the pyridine-propylene carbonate solution indicates some small amount of nitromethane coordination. This latter Dq value compares favorably with that of 957 cm^{-1} obtained from $[Nipy_4(BF_4)_2]$ dissolved in pyridine.[2] Dissolution of $[Copy_4(ClO_4)_2]$ and $[Copy_4(BF_4)_2]$ in pyridine-propylene carbonate solutions results, however, in visible electronic spectra which are essentially identical with those obtained in Table I for the pyridine-nitromethane solutions. Thus it seems that the most reliable source of spectrochemical data for both nickel(II) and cobalt(II) systems is to be found in pure pyridine.
(43) D. A. Rowley and R. S. Drago, *Inorg. Chem.*, *6*, 1092 (1967).