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Pyridine Complexes of Cobalt(II) and Nickel(II) Nitrates[1]

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Cobalt(II) and nickel(II) nitrate complexes of pyridine have been prepared by reaction of the anhydrous nitrates with pyridine in nonaqueous solution and characterized as $[Co(py)_3(NO_3)_2]$, $[Co(py)_3(NO_3)_2]\cdot 3py$, $[Ni(py)_3(NO_3)_2]$, and $[Ni(py)_3(NO_3)_2]\cdot 3py$. It has been concluded from thermal, magnetic, conductometric, and spectral data that the tris(pyridine) complexes are octahedral, with both monodentate and bidentate nitrate groups, and that the hexakis(pyridine) complexes should be formulated as the corresponding tris(pyridine) complexes, containing 3 moles of crystal pyridine.

Introduction

Pyridine as a ligand can, with the same metal salt, form a series of complexes of the type $M(py)_xX_2$ (M = metal; x = 2, 4, or 6; X = anion). Specific examples are the complexes of cobalt(II) bromide containing 2, 4, or 6 moles of pyridine[3] and the complexes of nickel(II) chloride with 2 or 4 moles of pyridine. Many of these complexes have been well characterized, but little is available on the pyridine complexes of anhydrous cobalt(II) and nickel(II) nitrates. Rosenthal and Drago have recently reported on the synthesis and structural considerations of $[Ni(py)_3(NO_3)_2]$.[4]

Nitrate groups can function as bidentate ligands,[5] bridging groups,[6] monodentate ligands,[7] and ionic species[8] in various inorganic systems. The functional characteristics appear to be dependent upon the nature and number of molecules of other ligands present. In the pyridine N-oxide complexes the nitrate groups are bidentate in octahedral dinitratobis(pyridine N-oxide)nickel(II), whereas they are not coordinated in octahedral hexakis(pyridine N-oxide)nickel(II) nitrate,[8] conclusions which also applied to the analogous cobalt(II) complexes. Since pyridine can form a series of complexes with the same metal salt, the systems pyridine–cobalt(II) nitrate and pyridine–nickel(II) nitrate were investigated to determine the influence of pyridine upon nitrate coordination.

Experimental Section

Starting Materials.—Reagent grade methanol was dried by distillation from magnesium activated with iodine. Reagent grade pyridine was dried by distillation from potassium hydroxide and stored over barium oxide. Practical grade 2,2-dimethoxypropane was used without further purification. Silver nitrate, cobalt, nickel, and bismuth were dried over sulfuric acid prior to use.

Dinitratotris(pyridine)cobalt(II).—Cobalt (10 g) was added to a solution of 25 g of silver nitrate in 125 ml of methanol. The mixture was shaken continuously for 24 hr. A wine-red solution of cobalt(II) nitrate was obtained, which gave no test for Ag^+. The reaction mixture was filtered and 75 ml of pyridine slowly added to the filtrate. Rose-colored crystals formed immediately and were collected on a sintered-glass filter, washed with ethyl ether, and dried *in vacuo* for 2 hr at room temperature.

Anal. Calcd for $[Co(py)_3(NO_3)_2]$: Co, 14.02; N, 16.66. Found: Co, 14.06; N, 16.60.

The compound was also prepared by dehydrating hexaaquocobalt(II) nitrate with 2,2-dimethoxypropane and adding pyridine to the solution at room temperature.

Dinitratotris(pyridine)cobalt(II)–Tris(pyridine).—A sample of dinitratotris(pyridine)cobalt(II) was placed in a desiccator over pyridine for 15 days at room temperature. The starting material added 3 moles of pyridine, changing to a pink powder.

Anal. Calcd for $[Co(py)_3(NO_3)_2]\cdot 3py$: Co, 8.97. Found: Co, 9.05. A microanalytical determination of nitrogen was not possible because of rapid loss of pyridine.

Dinitratotris(pyridine)nickel(II).—A solution of nickel nitrate in methanol could not be prepared by the method used for cobalt(II) nitrate because of the slowness of the silver nitrate–nickel reaction in methanol. An intermediate reaction between bismuth and silver nitrate was used.[9] Bismuth (15 g) was added to a solution of 34 g of silver nitrate in 200 ml of methanol, and the mixture was allowed to stand for 24 hr with occasional shaking. A clear solution of bismuth(III) nitrate was obtained which gave no test for Ag^+. Suspended solids were removed by filtration, 7 g of nickel was added to the filtrate, and the mixture was refluxed for 7 hr. The resulting nickel(II) nitrate solution gave no test for Bi^{3+}. The warm solution was filtered and 25 ml of pyridine added. Crystallization was induced by adding 100 ml of ethyl ether to the warm solution. Blue crystals slowly formed, and these were recrystallized from methanol–ether. The product was washed with ethyl ether and dried *in vacuo* over Drierite.

Anal. Calcd for $[Ni(py)_3(NO_3)_2]$: Ni, 13.98; N, 16.67. Found: Ni, 13.96; N, 16.65.

This compound was also prepared by dehydrating hexaaquonickel(II) nitrate with 2,2-dimethoxypropane and adding pyridine at room temperature.

Dinitratotris(pyridine)nickel(II)–Tris(pyridine).—A sample of dinitratotris(pyridine)nickel(II), placed in a desiccator over pyridine for 16 days at room temperature, added 3 moles of pyridine, changing to a light blue powder.

Anal. Calcd for $[Ni(py)_3(NO_3)_2]\cdot 3py$: Ni, 8.93; N, 17.05. Found: Ni, 8.97; N, 17.01.

This compound was also prepared from hexaaquonickel(II) nitrate by dehydration in methanol with 2,2-dimethoxypropane followed by addition of a large excess of pyridine. The product which crystallized on cooling the solution was washed with cold 7% pyridine in ethyl ether and dried by shaking the compound on coarse filter paper.

Analyses.—Cobalt and nickel were determined by weighing

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(1) Taken in part from the Ph. D. thesis of Richard V. Biagetti.

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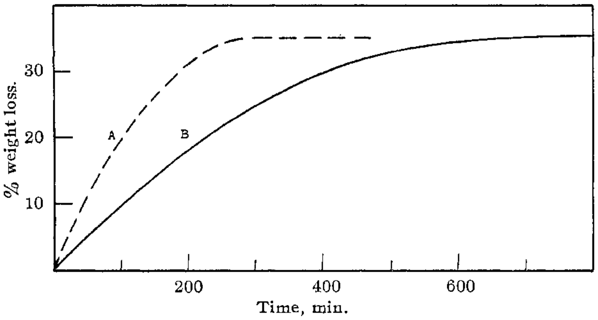

Figure 1.—Isothermal decomposition of (A) $[Co(py)_3(NO_3)]_2 \cdot 3py$ and (B) $[Ni(py)_3(NO_3)_2] \cdot 3py$ at 25°.

as the tetrakis(pyridine) thiocyanates.[10] Nitrogen was determined with the Coleman Model 29 nitrogen analyzer.

Electronic Spectra.—Visible spectra of solutions in chloroform and dichloromethane were obtained with a Perkin-Elmer Model 4000 Spectracord. Reflectance spectra of the solids were obtained with a Cary Model 14 recording spectrophotometer.

Thermogravimetric analyses, conductance measurements at 25.0°, infrared spectra, magnetic susceptibilities at 23.5°, and X-ray powder diffraction photographs were obtained as previously described.[11]

Results

Dinitratotris(pyridine)cobalt(II) and dinitratotris(pyridine)nickel(II) add 3 moles of pyridine at room temperature to yield the corresponding hexakis(pyridine) complexes, thermogravimetric analyses of which are shown in Figure 1. The hexakis(pyridine) complexes undergo weight losses of 35.2 and 35.6%, for cobalt and nickel, respectively, compared to the theoretical losses of 36.0 and 36.1% for formation of the tris(pyridine) complexes. X-Ray diffraction patterns of the products are those of the tris(pyridine) complexes. Addition and removal of pyridine are reversible at room temperature. Thermogravimetry of the tris(pyridine) complexes shows that the cobalt(II) compound decomposes to a violet oil above 85°, and the nickel compound decomposes to a green oil above 90°. The oils, which have not yet been studied further, do not crystallize on cooling.

The metal nitrate–pyridine complexes (Table I) are soluble in many organic solvents but are insoluble in hydrocarbons and ethyl ether. The cobalt(II) complexes form orchid solutions, and the nickel(II) complexes form blue solutions in chloroform and dichloromethane. On standing, the chloroform solutions of the tris(pyridine) complexes, but not those in dichloromethane, slowly deposit precipitates which have not been characterized. Solutions of the hexakis(pyridine) complexes do not react in this manner.

The infrared spectra of the solids and of their solutions in chloroform are summarized in Table II. The nitrate absorption frequencies show that the nitrate groups are coordinated in these complexes.[12,13] The infrared spectra of the mulls also show that all pyridines are coordinated in the tris(pyridine) complexes but not in the hexakis(pyridine) complexes. The former show absorption only at 600 cm^{-1}, but the hexakis(pyridine) complexes show absorption at both 630 and 600 cm^{-1}, indicating the presence of both coordinated and uncoordinated pyridine.[14] The intensity of the bands at 600 cm^{-1} suggests they are not due to pyridine liberated during mulling.

TABLE I

SOME PROPERTIES OF THE METAL NITRATE COMPLEXES

Compd	Color	μ_{eff}, BM	Molar conductance in nitromethane,[a] ohm^{-1} cm^2 $mole^{-1}$
$[Co(py)_3(NO_3)_2]$	Rose	4.60	11
$[Co(py)_3(NO_3)_2] \cdot 3py$	Pink	5.13	12
$[Ni(py)_3(NO_3)_2]$	Blue	3.21	12
$[Ni(py)_3(NO_3)_2] \cdot 3py$	Light blue	3.34	20
$[(CH_3)_4]I$	...	...	112

[a] Solution concentrations were 10^{-3} *M*.

The conductance data in nitromethane (Table I) show that the compounds are essentially nonelectrolytes although the values are somewhat larger than expected for true nonelectrolyte behavior. Nitromethane solutions of the cobalt(II) complexes slowly change color from pink to orange on standing. There is no visible change in the nickel(II) solutions, but the conductance of $[Ni(py)_3(NO_3)_2]$ in nitromethane slowly increases with time. These are all indications that the complexes slowly react with the solvent.

The magnetic data reported in Table I suggest octahedral configurations for all of the complexes. The value of 4.60 BM for $[Co(py)_3(NO_3)_2]$ is intermediate between the values expected for either octahedral or tetrahedral cobalt(II),[15] but the value is consistent with those observed for other octahedral nitratocobalt(II) complexes (4.55–4.65 BM).[8,16,17] The hexakis(pyridine) complex has a magnetic moment consistent with an octahedral configuration,[15,18] and the moments for the nickel(II) complexes are also in agreement with octahedral configurations.

The electronic spectra are summarized in Table III. The spectra of the solid cobalt(II) complexes show absorption bands with maxima at 530 mμ and shoulders at 480 mμ. The positions of the maxima are consistent with octahedral configurations for these complexes, and the doublet bands are assignable to a $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ transition. In the spectrum of the tris(pyridine) compound there are three weak bands with maxima at 625, 710, and 890 mμ. One of these is probably due to a $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ transition. The other two may be due to quartet–doublet transitions or may be the results of large deviation from cubic symmetry, as might be expected for an octahedral complex such as $[Co(py)_3(NO_3)_2]$. Another absorption band should be present above 890 mμ, correspond-

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TABLE II

NITRATE ABSORPTION FREQUENCIES FOR METAL NITRATE–PYRIDINE COMPLEXES

Compd	Phase	Frequencies,[a] cm^{-1}, and assignments NO_2 asym str	 NO_2 sym str	 NO str	 Nonplanar def
$[Co(py)_3(NO_3)_2]$	Mull	1482 vs, b	1294 vs, b	1028 m, shp	810 m, shp
	$CHCl_3$[b]	1456 vs, vb[c]	1295 vs, vb		
$[Co(py)_3(NO_3)_2]\cdot 3py$	Mull	1474 s, b	1290 vs, b	1027 s, shp	810 m, shp
	$CHCl_3$	1455 vs, vb[c]	1294 vs, vb		
$[Ni(py)_3(NO_3)_2]$	Mull	1500 s, b	1303 s, b	1028 m, shp	810 803 m, shp
	$CHCl_3$	1440 vs, vb[c]	1294 vs, vb		
$[Ni(py)_3(NO_3)_2]\cdot 3py$	Mull	1429 s, b	1293 s, b	1030 s, shp	810 m, shp
	$CHCl_3$	1435 vs, vb[c]	1292 vs, vb		

[a] s, strong; m, medium; b, broad; shp, sharp; v, very. [b] Because of absorption due to $CHCl_3$, only the NO_2 stretching frequencies were assigned to the spectra in this solvent. [c] Bands are very broad and contain several shoulders due to pyridine absorption.

TABLE III

ELECTRONIC SPECTRA OF THE METAL NITRATE–PYRIDINE COMPLEXES

Compd	Phase	λ_{max}, mμ[a]
$[Co(py)_3(NO_3)_2]$	Solid	480 (sh), 530, 625, 710, 890
	$CHCl_3$	≈470 (sh), 527 (135)
	$CHCl_3$ + py	≈470 (sh), 523 (78)
	CH_2Cl_2	≈470 (sh), 527 (157)
	CH_2Cl_2 + py	≈470 (sh), 523 (81)
$[Co(py)_3(NO_3)_2]\cdot 3py$	Solid	480 (sh), 530, 625, 710, . . .[b]
	$CHCl_3$	≈470 (sh), 522 (75)
	$CHCl_3$ + py	≈470 (sh), 519 (63)
	CH_2Cl_2	≈470 (sh), 522 (82)
	CH_2Cl_2 + py	≈470 (sh), 519 (67)
$[Ni(py)_3(NO_3)_2]$	Solid	375, 610, ≈710 (sh), 760 810–1350[c]
	$CHCl_3$	380 (36), 615 (19)
	$CHCl_3$ + py	377 (37), 607 (16)
	CH_2Cl_2	381 (38), 615 (22)
	CH_2Cl_2 + py	377 (38), 608 (17)
$[Ni(py)_3(NO_3)_2]\cdot 3py$	Solid	375, 610, ≈710 (sh), 760, 1020–1350[c]
	$CHCl_3$	377 (45), 607 (20)
	$CHCl_3$ + py	377 (50), 607 (20)
	CH_2Cl_2	377 (45), 608 (19)
	CH_2Cl_2 + py	377 (44), 608 (21)

[a] Numbers in parentheses denote molar extinction coefficients at λ_{max}. [b] Absorption bands above 710 mμ are too weak to resolve. [c] Absorption bands are very broad.

ing to a $^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ transition, but failure to observe this is assumed to be due to a very low intensity.

The spectra of the cobalt(II) complexes in chloroform and dichloromethane indicate that the complexes form octahedral species in these solvents. The maxima at 527 and 522 mμ are close in position to the maxima in the spectra of the corresponding solid complexes. The extinction coefficients are greater than those usually observed for octahedral cobalt(II) complexes but considerably smaller than those consistently observed for tetrahedral complexes (>300).[19–22] It seems reasonable to assign this difference to a large deviation from cubic symmetry, as has been suggested for the large extinction coefficients of octahedral complexes of phosphine and arsine oxides.[16]

The visible portion of the electronic spectra of the solid nickel(II) complexes show absorption maxima at 375 and 610 mμ, typical of octahedral nickel(II) complexes. Additional weak bands at 710 and 760 mμ are not usually observed with octahedral nickel(II) complexes, and it is suggested that these are due to large tetragonal distortions in the complexes.[4,23]

The visible spectra of the nickel(II) complexes in chloroform and dichloromethane are consistent with octahedral configurations for the species in solution. The addition of pyridine to solutions of $[Ni(py)_3(NO_3)_2]$ shifts the maxima to lower wavelengths, and the spectra become identical with those of the hexakis(pyridine) complex, which itself is unaffected by addition of pyridine.

Discussion

Complexes in the Solid State.—The tris(pyridine) complexes have essentially octahedral configurations in which all of the pyridine molecules and nitrate groups are coordinated. The complexes are thus designated as $[Co(py)_3(NO_3)_2]$ and $[Ni(py)_3(NO_3)_2]$, having both monodentate and bidentate nitrate groups. Polymeric structures in which a nitrate group functions as a bridging ligand are possible, but the extensive solubility in chloroform and dichloromethane, solvents of low polarity and low coordinating ability, favors the monomeric structure. Our results are in agreement with those of Rosenthal and Drago[4] on the nature of $[Ni(py)_3(NO_3)_2]$. Because of the unusual nature of this nickel(II) compound, an X-ray crystallographic study of this compound is in progress.

Two reasonable formulations for the octahedral hexakis(pyridine) complexes in which the nitrate groups are coordinated are $[M(py)_3(NO)_2]\cdot 3py$ and $[M(py)_4(NO_3)_2]\cdot 2py$. Thermal analysis, infrared spectra, and electronic spectra all support the first formulation, and the hexakis(pyridine) complexes are thus represented as $[M(py)_3(NO_3)_2]\cdot 3py$. Coordination of only 3 moles of pyridine is somewhat surprising since pyridine is a better ligand than nitrate and since numerous complexes of the type $[M(py)_4X_2]$ are known. The species $[M(py)_6](NO_3)_2$ represents a sterically unfavorable situation.

Complexes in Solution.—Any consideration of the structures of the complexes in solution must be con-

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sidered as tentative. In chloroform and dichloromethane the tris(pyridine) complexes yield octahedral species in which the nitrate groups remain coordinated. The visible spectrum of $[\mathrm{Co(py)_3(NO_3)_2}]$ is essentially the same in both solvents, as is true for the nickel(II) complex. Rosenthal and Drago[4] have shown that $[\mathrm{Ni(py)_3(NO_3)_2}]$ loses 1 mole of pyridine in dichloromethane to form octahedral $[\mathrm{Ni(py)_2(NO_3)_2}]$, which has bidentate nitrate groups. It is probable that the nickel(II) complex undergoes a similar reaction in chloroform, and it is possible that $[\mathrm{Co(py)_3(NO_3)_2}]$ takes part in an analogous reaction, in both solvents.

The absorption maximum of $[\mathrm{Co(py)_3(NO_3)_2}]$ in these two solvents is shifted to a lower wavelength upon addition of pyridine, with a corresponding large decrease in the extinction coefficient. The spectra of these solutions closely resemble the spectra of the hexakis(pyridine) solutions, both as to position of the maxima and magnitude of the extinction coefficients. The shift to lower wavelength would be expected for the substitution of pyridine for nitrate in the coordination sphere. The infrared spectrum of the hexakis(pyridine) complex in chloroform shows, however, that the nitrate group remains coordinated. It is suggested, therefore, that in these two solvents the hexakis(pyridine)cobalt(II) complex forms $[\mathrm{Co(py)_4(NO_3)_2}]$, in which a bidentate nitrate has become monodentate by substitution with pyridine. The decrease in molar extinction coefficients upon addition of pyridine to the solutions of the tris(pyridine) complex also agrees with the formulation of an octahedral species having four coordinated pyridine molecules since $[\mathrm{Co(py)_4(NO_3)_2}]$ would be expected to approach cubic symmetry more closely than the tris(pyridine) complex.

It has been reported that the electronic spectrum of $[\mathrm{Ni(py)_3(NO_3)_2}]$ in dichloromethane is unaffected by the addition of pyridine to the solution,[4] but our results are not in agreement with this observation. The same spectral changes were noted with the nickel(II) complex as with the cobalt(II) complex, and we have concluded that $[\mathrm{Ni(py)_4(NO_3)_2}]$ is formed in the presence of excess pyridine in these solvents.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, HARVEY MUDD COLLEGE, CLAREMONT, CALIFORNIA,
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Complexes of Succinonitrile with Silver(I). A Nitrato–Silver Compound

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The compounds $2\mathrm{AgNO_3\cdot(CN)_2C_2H_4}$ and $\mathrm{AgNO_3\cdot(CN)_2C_2H_4}$ have been isolated from solutions of silver nitrate in succinonitrile. In these silver nitrate complexes and in the compounds bis(succinonitrile)silver(I) perchlorate and bis(succinonitrile)silver(I) tetrafluoroborate, the ligand succinonitrile bridges two silver atoms and assumes the *trans* rotomeric conformation. Nitrato–silver bonding is indicated in the compound $2\mathrm{AgNO_3\cdot(CN)_2C_2H_4}$.

Introduction

The interaction of copper(I) and silver(I) with nitriles is similar in many respects.[2] While the structure of the compound $\mathrm{CuNO_3\cdot 2(CN)_2C_2H_4}$ is now well established,[3,4] the analogous silver(I) compound $\mathrm{AgNO_3\cdot 2(CN)_2C_2H_4}$ has not yet been reported. It was of interest to synthesize this compound and the compounds $\mathrm{Ag((CN)_2C_2H_4)_2BF_4}$ and $\mathrm{Ag((CN)_2C_2H_4)_2ClO_4}$ in order to study the effects of the metal ions and anions on the rotational conformation[4,5] assumed by succinonitrile in these complexes. Attempts to isolate the compound $\mathrm{AgNO_3\cdot 2(CN)_2C_2H_4}$, however, led to the syntheses of the compounds $2\mathrm{AgNO_3\cdot(CN)_2C_2H_4}$ and $\mathrm{AgNO_3\cdot(CN)_2C_2H_4}$. Infrared evidence shows that the nitrate ligand is coordinated to silver in the compound $2\mathrm{AgNO_3\cdot(CN)_2C_2H_4}$.

While nitrato–metal bonding is well known for other transition metals,[6] only few examples exist for nitrato–silver bonding. Silver–oxygen bond lengths of 2.36 and 2.43 A suggest nitrato–silver bonding in the silver nitrate–cyclooctatetraene complex.[7] Recent crystallographic studies indicate that each nitrate is bonded to two silver atoms in the silver tris(acetylacetonato)-nickelate(II)–silver nitrate adduct, $\mathrm{AgNi(C_5H_7O_2)_3\cdot}$

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