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Reaction of Dinitratobis(pyridine)cobalt(II) with Dihalobis(pyridine)cobalt(II) Complexes. Preparation and Characterization of Dinitratobis(pyridine)cobalt(II) and Chloronitratobis(pyridine)cobalt(II)

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The spectroscopic and magnetic properties of dinitratobis(pyridine)cobalt(II) are very similar to those of analogous cobalt complexes such as dinitratobis(trimethylphosphine oxide)cobalt(II) which has been shown to contain bidentate nitrate ions. In solution dinitratobis(pyridine)cobalt(II) reacts with the dihalobis(pyridine) complexes of cobalt(II) to establish what appears to be an equilibrium of the type $Co(py)_2(NO_3)_2 + Co(py)_2X_2 \rightleftharpoons 2Co(py)_2(NO_3)X$ (where $X^- = Cl^-, Br^-$, or I^-). The equilibrium constants for these reactions exhibit little temperature or solvent dependence. The numerical values of K_{eq} range from approximately 0.3 to 1.5. A mixed-anion complex having the stoichiometry $Co(py)_2(NO_3)Cl$ can be isolated from solutions containing $Co(py)_2(NO_3)_2$ and $Co(py)_2Cl_2$. Although this mixed-anion complex appears to be monomeric in solution, it is a chlorine-bridged dimer in the solid state. The magnetic susceptibility of the material in the 297–77°K range obeys the Curie–Weiss law with a Weiss constant of −10°. These data indicate that the exchange coupling between the two cobalt atoms in the dimer is fairly small.

Introduction

A recent study has suggested that dinitratodiamminecobalt(II) reacts with diiododiamminecobalt(II) in acetonitrile solution to establish the equilibrium[1]

$$Co(NH_3)_2(NO_3)_2 + Co(NH_3)_2I_2 \rightleftharpoons 2Co(NH_3)_2(NO_3)I$$

The mixed-anion complex $Co(NH_3)_2(NO_3)I$ can actually be isolated from solutions containing equimolar quantities of $Co(NH_3)_2(NO_3)_2$ and $Co(NH_3)_2I_2$. The spectroscopic and magnetic properties of $Co(NH_3)_2(NO_3)_2$ indicate that the dinitratodiammine complex is structurally similar to dinitratobis(trimethylphosphine oxide)cobalt(II) which has been shown by X-ray diffraction to adopt a distorted six-coordinate structure where the nitrate ions coordinate in bidentate fashion.[2] The diiododiammine complex has been determined to be tetrahedral by infrared studies,[3] while the mixed-anion species $Co(NH_3)_2(NO_3)I$ has not been completely characterized. A number of other dinitratobis(ligand)cobalt(II) complexes have been prepared and appear to have structures which resemble that of the trimethylphosphine oxide complex. Numerous tetrahedral dihalo species of the type $Co(L)_2X_2$ have been made and characterized. It seems reasonable to assume that dinitrato and dihalo complexes containing a variety of ligands might react in the same manner as the diammine complexes. This paper presents a study of the reaction between dinitratobis(pyridine)cobalt(II) and dichloro-, dibromo-, and diiodobis(pyridine)cobalt(II). The pyridine complexes were chosen because they are soluble in a variety of organic solvents and are relatively easy to prepare and handle. The objectives of this investigation were, first, to establish that the anion-exchange equilibrium takes place with complexes containing ligands other than ammonia and, second, to isolate and elucidate the solution and solid-state structure of a mixed-anion complex of the type $Co(L)_2(NO_3)X$.

Experimental Section

Solvents. The solvents used in this study were all carefully dried. Reagent grade acetonitrile, methylene chloride, and chloroform were distilled from P_2O_5 under nitrogen and stored over molecular sieves. Petroleum ether and ligroin were allowed to stand over anhydrous calcium sulfate for at least 24 hr.

Dinitratobis(pyridine)cobalt(II). The $Co(py)_2(NO_3)_2$ complex was prepared by a number of procedures. The method described below is considered to be the most convenient. Reagent grade cobalt(II) nitrate hexahydrate was dried at room temperature under vacuum for 36 hr. This partially dehydrated material was determined from a cobalt analysis to be $Co(NO_3)_2{\cdot}3H_2O$. Approximately 10 g of this trihydrate was added to a 250-ml round-bottom flask containing 100 ml of benzene and 20 ml of acetonitrile. A stoichiometric amount of pyridine (~6.6 g) was added and the flask was stoppered. The mixture was stirred overnight at room temperature with a magnetic stirrer. The solvent was then distilled from the mixture under a stream of dry nitrogen. The cobalt salt was dehydrated by the formation of the benzene–water azeotrope which was distilled from the mixture. During the distillation all the solid material dissolved forming a maroon solution. When only 50 ml of solution remained, an additional 50 ml of benzene was added and the distillation was continued. when the total volume was again reduced to 50 ml, the solution was allowed to cool to room temperature. The remaining solvent was removed by evaporation under vacuum at room temperature. The evacuated flask was transferred to a nitrogen-filled glove bag and the residue was dissolved in 70 ml of dry methylene chloride. The solution was filtered and added to a 250-ml erlenmeyer flask with a ground-glass stopper. Approximately 50 ml of dry petroleum ether was added to the methylene chloride solution and the flask was stoppered. The flask was placed in a freezer taking care not to mix the contents any more than necessary. After 1 or 2 days the petroleum ether diffused into the methylene chloride solution and the $Co(py)_2(NO_3)_2$ crystallized out of solution. The flask was then transferred to the glove bag and the solution was decanted. The red-violet crystalline solid was washed first with a mixture of petroleum ether and methylene chloride and finally with pure petroleum ether. The product (~7.5 g) was dried under vacuum. The material is quite stable but rapidly picks up water when exposed to the atmosphere. The melting point of the complex is 109–111° taken in a sealed capillary. Anal. Calcd for $Co(py)_2(NO_3)_2$: Co, 17.27; C, 35.19; H, 2.95; N, 16.42. Found: Co, 17.27; C, 35.06; H, 2.96; N, 15.95.

Dichloro-, Dibromo-, and Diiodobis(pyridine)cobalt(II). The dihalobis(pyridine)cobalt(II) complexes were prepared in the same manner. Anhydrous $CoCl_2$ and $CoBr_2$ were prepared by heating the hydrated salts to 500–600° in a stream of HCl or HBr. Anhydrous CoI_2 was purchased from Alfa Inorganics. The anhydrous halide was dissolved in a minimum amount of dry acetonitrile. A stoichiometric quantity of pyridine was added to the solution. The bis(pyridine) complexes were then precipitated by slowly adding ligroin to the solution. The solid complexes were washed with ligroin and dried under vacuum. Dichlorobis(pyridine)cobalt(II) can exist in two forms, a violet form and a blue form. The procedure described above yielded the violet form.[4]

Chloronitratobis(pyridine)cobalt(II). Equimolar quantities of $Co(py)_2Cl_2$ (3.87 g) and $Co(py)_2(NO_3)_2$ (4.60 g) were dissolved separately in minimum amounts of dry methylene chloride. The two solutions were then poured into a 250-ml erlenmeyer flask with a ground-glass top. The mixture was stirred and allowed to stand for a few minutes. Dry ligroin was slowly added in 2-ml portions to the solution until solid began to precipitate from solution. The flask was stoppered and allowed to stand overnight in a freezer. During that time a purple solid crystallized from solution. This solid was washed with ligroin and dried under vacuum. This material was recrystallized from methylene chloride. All the manipulations were carried out in a glove bag. The melting point of the purple complex is 141–143° taken in a sealed capillary. Anal. Calcd for $Co(py)_2(NO_3)Cl$: Co, 18.66; C, 38.21; H, 3.18; N, 13.36; Cl, 11.29. Found: Co, 18.71; C, 38.19; H, 3.21; N, 12.91; Cl, 11.27.

Infrared Spectra. Infrared spectra in the 4000–600-cm^{-1} range were recorded on a Perkin-Elmer 521 spectrometer using Nujol and Halocarbon mulls supported between NaCl plates. In the 600–200-cm^{-1} range, spectra were obtained on a Beckman IR-11 using Nujol mulls between polyethylene plates. All the mulls were prepared in a dry atmosphere.

Visible and Near-Infrared Spectra. The visible and near-infrared spectra were recorded on a Cary 14 spectrophotometer. The solid-state spectra were obtained from Kel-F mulls supported between glass plates. A mull of $CaCO_3$ was used as a reference. Spectra at liquid nitrogen temperature were taken using a dewar with glass windows. The temperature studies of the solution spectra were carried out using a jacketed cell compartment connected to a Neslab variable-temperature circulating bath.

Magnetic Susceptibilities. The magnetic susceptibilities of powdered samples of $Co(py)_2(NO_3)_2$ and $Co(py)_2(NO_3)Cl$ were measured at 297, 195, and 77°K on a Gouy balance using $HgCo(SCN)_4$ as a standard. The apparatus has been previously described.[5] The molar susceptibilities were corrected for atomic diamagnetism using the constants given by Mulay.[6]

Conductance Measurements. Solution conductances were determined at 25° with a Yellow Springs Industries conductance bridge using a cell with unblacked platinum electrodes. The cell was calibrated with aqueous KCl solution.

Crystallographic Studies. Crystals of $Co(py)_2(NO_3)_2$ were sealed in 0.3-mm capillaries. Precession photographs were taken with Mo Kα radiation. The crystal system is monoclinic with unit cell constants of $a = 12.07$ Å, $b = 8.01$ Å, $c = 14.40$ Å, and $\beta = 90°$. The systematic absences are consistent with the space group $P2_1/c$. The density of the material indicates that there are four molecules per unit cell ($\rho_{obsd} = 1.61$, $\rho_{calcd} = 1.63$ g cm^{-3}).

Results and Discussion

Characterization of $Co(py)_2(NO_3)_2$ and $Co(py)_2(NO_3)Cl$. The preparation of dinitratobis(pyridine)cobalt(II) was first reported by Katzin, Ferraro, and Gebert[7] in 1950; however, the existence of this complex as a well-defined species in the solid state has been disputed.[8] Herlocker and Rosenthal observed $Co(py)_2(NO_3)_2$ in solution but did not isolate a solid complex.[9] Our studies indicate that a solid material having the stoichiometry $Co(py)_2(NO_3)_2$ is easily prepared and purified. The solid is crystalline and has a sharp melting point, and the analytical data are consistent with the formulation $Co(py)_2(NO_3)_2$. The observed unit cell constants and density are also consistent with this stoichiometry. There remains little doubt that this material is a pure compound.

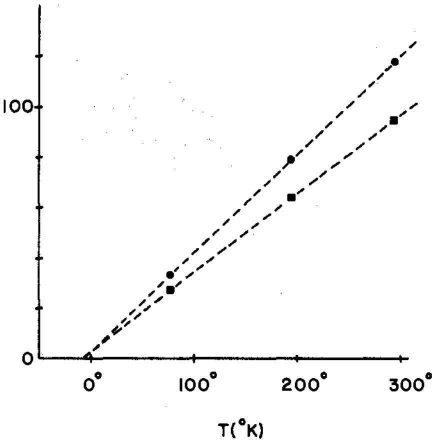


Figure 1. Plots of the reciprocals of the molar susceptibilities of $Co(py)_2(NO_3)_2$ and $Co(py)(NO_3)Cl$ vs. the absolute temperature. The solid circles represent the $Co(py)_2(NO_3)_2$ data while the solid squares represent the data for $Co(py)_2(NO_3)Cl$.

The physical properties of $Co(py)_2(NO_3)_2$ are very similar to those of a number of related dinitratobis(ligand)cobalt(II) complexes. Cotton and coworkers[10] have prepared and characterized several phosphine oxide and arsine oxide complexes, while Lever[11] has studied a group of dinitratobis(amine) complexes. These authors conclude that all of these compounds are similar in structure to the dinitratobis(trimethylphosphine oxide)cobalt(II). The basis for this conclusion is the striking similarity of the spectroscopic and magnetic properties of all of the $CoL_2(NO_3)_2$ complexes. The magnetic moments and infrared and electronic spectra of these compounds are quite distinctive. The magnetic moments fall in the 4.4–4.7-BM range. These moments are significantly lower than would be expected for normal octahedral cobalt(II) complexes and are more typical of tetrahedral species. The effects of coordination on the vibrational frequencies of the nitrate ion are readily observed in the infrared spectra of the $CoL_2(NO_3)_2$ complexes. The degenerate asymmetric stretch (ν_3) is split into two components separated by about 200 cm^{-1} and the normally forbidden symmetric stretch (ν_1) is allowed. The electronic spectra contain one or more weak bands ($\epsilon > 30$) in the near-infrared region and a strong, broad absorption ($\epsilon > 100$) in the visible region. The visible band is considerably more intense than typical spectra of octahedral complexes but much less intense than the bands observed with tetrahedral complexes.

Although an X-ray determination has not been carried out, we feel fairly certain that dinitratobis(pyridine)cobalt(II) adopts a six-coordinate structure similar to that of dinitratobis(trimethylphosphine oxide)cobalt(II). The magnetic susceptibility of $Co(py)_2(NO_3)_2$ obeys the Curie–Weiss law in the 297–77°K range (see Table I and Figure 1). The μ_{eff} value of 4.59 BM is essentially the same as those of the other $CoL_2(NO_3)_2$ complexes. Similarly the nitrate ion vibrations in the pyridine complex occur at frequencies very similar to those reported for the other complexes (see Table II). The electronic spectrum of $Co(py)_2(NO_3)_2$ in solution and in the solid state is shown in Figure 2. The solid and solution spectra contain essentially the same features. There is a broad, weak band (ϵ 22) at approximately 8700 cm^{-1} and a more intense band (ϵ 180) at 18,800 cm^{-1} (see Table III). Although our spectral data cover a wider energy range, the results are similar to those reported by Katzin and Gebert for the reflectance spectrum of solid $Co(py)_2(NO_3)_2$.[12] The close resemblance of the spectroscopic and magnetic properties of $Co(py)_2(NO_3)_2$ to those of the other $CoL_2(NO_3)_2$ complexes is strongly in-

Table I. Magnetic Susceptibilities[a]

Compd	Temp, °K	$10^6\chi$, esu/mol	$1/\chi$, mol/esu
$Co(py)_2(NO_3)_2$	295	8,450	118
	195	12,620	79
	77	30,180	33
$Co(py)_2(NO_3)Cl$	295	10,670	94
	195	15,620	64
	77	36,650	27

[a] Curie–Weiss law: $\chi = C/(T - \Theta)$; $\mu_{eff} = 2.84C^{1/2}$. For $Co(py)_2(NO_3)_2$, $\Theta = -10 \pm 5°$ and $\mu_{eff} = 4.59$ BM; for $Co(py)_2(NO_3)Cl$, $\Theta = -10 \pm 5°$ and $\mu_{eff} = 5.07$ BM.

Table II. Selected Infrared Frequencies (cm^{-1})

Assignment[a]	$Co(py)_2(NO_3)_2$	$Co(py)_2(NO_3)Cl$	$Co(Me_3PO)_2(NO_3)_2$[b]
$\nu_1(NO_3)$[c]	1485	1485	1517
			1492
			1469
$\nu_4(NO_3)$	1260	1280	1317 sh[e]
			1304 sh
			1282
$\nu_2(NO_3)$	1010	1020	1024
$\nu_5(NO_3)$	805	805	812
Co–O	285	260	
Co–py	250	230	
	230	215	
Co–Cl		205[d]	

[a] Assignments were made on the basis of careful comparisons of the spectra of related complexes. [b] Reference 9. [c] Nitrate ion vibrations designated as in ref 1. [d] Tentative. [e] sh = shoulder.

Table III. Electronic Spectra

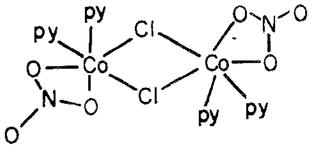
Compd	Medium	λ, nm	$\bar{\nu}$, cm^{-1}	ε, cm^{-1} M^{-1}
$Co(py)_2(NO_3)_2$	Chloroform	1180	8,500	22
		530	18,900	180
	Mull (77°K)	1060	9,400	
		625 sh[a]	16,000	
		515	19,400	
		500 sh	20,000	
		416	24,000	
$Co(py)_2(NO_3)Cl$	Mull (77°K)	1130	8,800	
		658 sh	15,200	
		560 sh	17,800	
		538	18,600	
		513	19,500	

[a] sh = shoulder.

dicative of a structural similarity.

Solution conductances indicate that $Co(py)_2(NO_3)_2$ ionized to a small extent in acetonitrile but not at all in dichloromethane (see Table IV). Apparently ionization is suppressed as the coordinating ability and dielectric strength of the solvent decrease. The conductance of $Co(py)_2(NO_3)_2$ in acetonitrile is similar to those reported by Lever for other dinitratobis(amine)cobalt(II) complexes in acetone.[11]

The structure of chloronitratobis(pyridine)cobalt(II) has been recently determined by X-ray analysis.[13] The complex is a centrosymmetric dimer with bridging chloride ions, i.e.



The nitrate ions are bidentate. For the most part the spectroscopic, magnetic and physical properties of the complex resemble those of dinitratobis(pyridine)cobalt(II). The magnetic susceptibility of $Co(py)_2(NO_3)Cl$ obeys the Curie–Weiss law, but the μ_{eff} value of 5.07 BM is noticeably larger

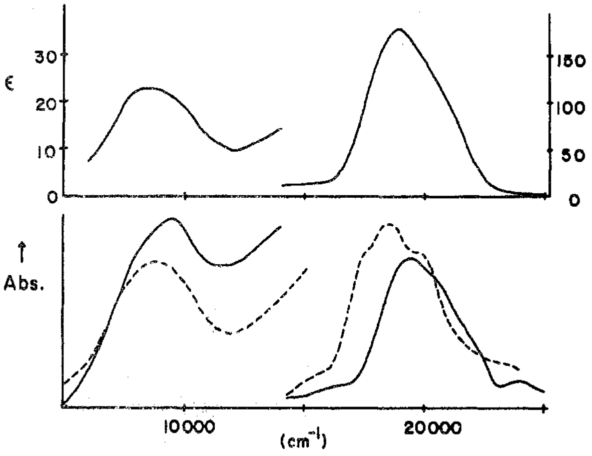


Figure 2. Electronic spectra of $Co(py)_2(NO_3)_2$ and $Co(py)_2(NO_3)Cl$. The upper trace is the spectrum of $Co(py)_2(NO_3)_2$ in $CHCl_3$. The ε values on the right pertain to the portion of the spectrum above 14,000 cm^{-1} while the ε values on the left apply to the spectrum below 14,000 cm^{-1}. The lower trace is the mull spectra of $Co(py)_2(NO_3)_2$ (solid line) and $Co(py)_2(NO_3)Cl$ (dashed line) taken at 77°K.

Table IV. Solution Conductances

	$Co(py)_2(NO_3)_2$		$Co(py)_2(NO_3)Cl$	
Solvent	Concn, *M*	Λ_M[a]	Concn, *M*	Λ_M
Acetonitrile[b]	1.3×10^{-2}	19	6.7×10^{-3}	18
	9.1×10^{-3}	23	3.9×10^{-3}	22
	6.9×10^{-3}	25	1.6×10^{-3}	27
	4.0×10^{-3}	30	7.6×10^{-4}	31
Dichloromethane[c]	6.8×10^{-3}	<0.05	6.4×10^{-3}	<0.05

[a] Molar conductances, Λ_M, are in units of ohm^{-1} cm^{-1} M^{-1}. [b] Observed conductivity of pure acetonitrile is 5×10^{-7} ohm^{-1} cm^{-1}. [c] Observed conductivity of pure dichloromethane is $<4 \times 10^{-7}$ ohm^{-1} cm^{-1}.

than that of $Co(py)_2(NO_3)_2$. The frequencies of the nitrate ion vibrations are about the same as those of the $CoL_2(NO_3)_2$ complexes which is consistent with bidentate bonding. The electronic spectrum in the solid state contains a weak band in the near-ir region and a more intense, somewhat structured band in the visible region (see Figure 2 and Table III). Conductance measurements indicate that $Co(py)_2(NO_3)Cl$, like $Co(py)_2(NO_3)_2$, may ionize slightly in acetonitrile but the complex is a nonelectrolyte in dichloromethane.

It is interesting to note that the nitrate ion frequencies and electronic spectrum of $Co(py)_2(NO_3)Cl$ are quite similar to those reported for $Co(NH_3)_2(NO_3)I$.[1] Thus, the spectroscopic data suggest that $Co(NH_3)_2(NO_3)I$ also forms a bridged dimer.

In light of the dimeric structure, perhaps the most noteworthy property of the $Co(py)_2(NO_3)Cl$ complex is the magnetic susceptibility. One might expect to observe effects due to exchange interactions; however, it is difficult to determine *a priori* what the effects will be. The magnetic properties of dimeric cobalt(II) complexes show considerable variation. For example, the quinoline complex of cobalt benzoate, which adopts a dimeric structure similar to that of copper(II) acetate, has a magnetic susceptibility at 93°K that is less than one-fifth as large as that expected for a normal cobalt(II) salt.[14] This behavior is indicative of substantial antiferromagnetic coupling between the two cobalt(II) ions. In contrast the magnetic susceptibility of bis(*N*-methylsalicylaldimato)cobalt(II) in the 298–77°K range is only slightly affected by what appear to be very weak antiferromagnetic interactions.[15,16] This dimeric complex has a five-coordinate structure with two bridging oxygen atoms.[17] In the case of $Co(py)_2(NO_3)Cl$ the magnetic susceptibility, even at 77°K, gives little indication of exchange interactions. In the 298–77°K range the material behaves as a typical "dilute" cobalt(II) complex.

It has been well established that the magnitude and sign of the magnetic-exchange interaction between metal ions in bridged complexes are strongly dependent on the geometry of the bridging system. On this basis one might expect a similarity between the magnetic properties of chloronitratobis(pyridine)cobalt(II) and those of cobalt(II) chloride dihydrate and the violet form of dichlorobis(pyridine)cobalt(II). Although the latter two complexes consist of linear chains of octahedra sharing edges rather than discrete dimers, the geometries of the bridging systems are very similar to that in $Co(py)_2(NO_3)Cl$. In $Co(py)_2(NO_3)Cl$, the Co–Co separation is 3.56 Å with Co–Cl distances of 2.36 and 2.52 Å, while the Co–Cl–Co angle is 93.5°. Cobalt(II) chloride dihydrate has a Co–Co separation of 3.55 Å, Co–Cl distances of 2.46 and 2.49 Å, and a Co–Cl–Co angle of 92.4°.[18] The dichlorobis(pyridine) complex has a Co–Co separation of 3.66 Å, a Co–Cl distance of 2.49 Å, and a Co–Cl–Co angle of 94.5°.[4] Detailed magnetic susceptibility studies of $CoCl_2{\cdot}2H_2O$[19] and $Co(py)_2Cl_2$[20] have established that cobalt ions within a single chain couple ferromagnetically. In addition to the ferromagnetic intrachain interactions there are weaker antiferromagnetic interactions between chains. Neither the intrachain nor interchain interactions are strong enough to have a noticeable effect on the susceptibilities of the two complexes until the temperature is well below 77°K. In both cases, at high temperatures (above 50°K), the susceptibilities obey the Curie–Weiss law. In light of these observations, the magnetic susceptibility of $Co(py)(NO_3)Cl$ in the 298–77°K region does not seem unusual. Clearly, measurements at temperatures below 77°K will be necessary to understand completely the magnetic properties of this complex.

Attempts to isolate similar mixed-anion complexes containing bromide or iodide [$Co(py)_2(NO_3)Br$ or $Co(py)_2(NO_3)I$] were unsuccessful. Mixtures of the starting materials were the only solid products that were isolated from solutions containing dinitratobis(pyridine)cobalt(II) and the dibromo or diiodo complexes. With a dynamic equilibrium, the relative lattice energies of the different complexes should determine which species will crystallize out of solution. It is worth noting that the structural chemistry of the dihalobis(pyridine)cobalt(II) complexes themselves indicates that chloride has a greater tendency to form bridged structures than the other two halides.[21]

Reaction of $Co(py)_2(NO_3)_2$ with $Co(py)_2Cl_2$, $Co(py)_2Br_2$, and $Co(py)_2I_2$. The reactions of $Co(py)_2(NO_3)_2$ with the three dihalo complexes were studied in chloroform solution. The reaction with the dichloro complex was investigated in more detail since the mixed-anion species $Co(py)_2(NO_3)Cl$ was isolated and characterized. This equilibrium was studied at 25 and 45° in chloroform and at room temperature (23°) in dichloromethane and acetonitrile. The visible spectra of solutions of the dihalobis(pyridine)cobalt(II) complexes exhibit intense bands in the 14,000–17,500-cm^{-1} region which are typical of tetrahedral complexes. The intensities of these absorptions decrease as $Co(py)_2(NO_3)_2$ is added to the solution suggesting that a dynamic equilibrium is established (Figure 3). The fact that the solution spectrum of $Co(py)_2(NO_3)Cl$ is identical with that of a solution containing equimolar amounts of $Co(py)_2(NO_3)_2$ and $Co(py)_2Cl_2$ provides additional evidence for the presence of the equilibrium. The spectra of the solutions do not change with time which indicates that the equilibrium is established fairly rapidly. In general, cobalt(II) complexes are very labile and one would expect their reactions to be fast.

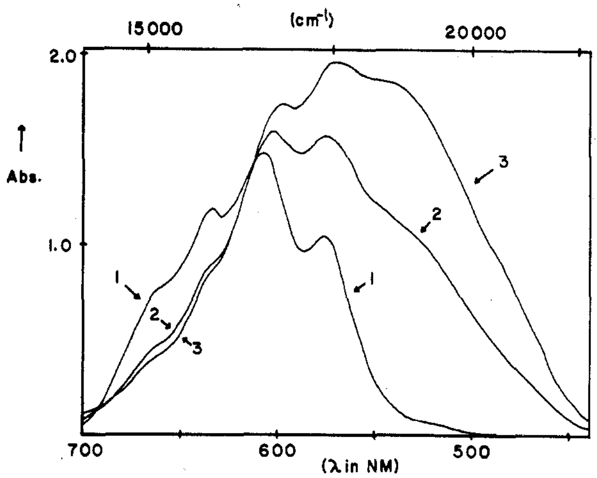


Figure 3. Absorption spectra of chloroform solutions containing (1) 2.47 × 10^{-3} *M* $Co(py)_2Cl_2$, (2) 2.47 × 10^{-3} *M* $Co(py)_2Cl_2$ + 4.28 × 10^{-3} *M* $Co(py)_2(NO_3)_2$, and (3) 2.47 × 10^{-3} *M* $Co(py)_2Cl_2$ + 7.73 × 10^{-3} *M* $Co(py)_2(NO_3)_2$. The spectra were recorded at 25°.

The equilibria were studied quantitatively by following the changes in concentration of the $Co(py)_2X_2$ complex spectrophotometrically. This procedure is complicated by the fact that the absorptions of the $Co(py)_2(NO_3)_2$, the $Co(py)_2X_2$, and the product of the reaction overlap considerably. A fairly reliable estimate of the concentration of the $Co(py)_2X_2$ species could be obtained by measuring the absorbance of the lowest energy band of the $Co(py)_2X_2$ spectrum and correcting for the absorption due to the $Co(py)_2(NO_3)_2$. In all cases the change in concentration of $Co(py)_2X_2$ with added $Co(py)_2(NO_3)_2$ can be rationalized by assuming the following equilibrium is established.

$$Co(py)_2(NO_3)_2 + Co(py)_2X_2 \rightleftharpoons 2Co(py)_2(NO_3)X$$

$$K_{eq} = \frac{[Co(py)_2(NO_3)X]^2}{[Co(py)_2(NO_3)_2][Co(py)_2X_2]}$$

The equilibrium constants for the reactions of dinitratobis(pyridine)cobalt(II) with the dichloro, dibromo, and diiodo complexes are approximately 1.5, 1.0, and 0.3, respectively. (The constant for the reaction of $Co(py)_2(NO_3)_2$ with $Co(py)_2Br_2$ is imprecise because of the extensive overlap of the absorptions of the different species.) There seems to be a small but noticeable variation in the equilibrium constant depending on the halide. There is no significant change in the equilibrium constant for the reaction of $Co(py)_2(NO_3)_2$ and $Co(py)_2Cl_2$ when the temperature is raised from 25 to 45°. The K_{eq} values for the reaction in acetonitrile and dichloromethane are about 0.8 and 1.0, respectively. It would appear that these equilibrium reactions are not strongly dependent on solvent or temperature.

Even though the $Co(py)_2(NO_3)Cl$ complex is a dimer in the solid state, it appears that the mixed-anion species are monomeric in solution. Although our studies were carried out over a relatively narrow range of concentrations (10^{-2}–10^{-3} *M*), the data are definitely not consistent with an equilibrium expression in which the mixed-anion species is dimeric. It is possible that our treatment of these reactions is oversimplified but the fact that at least three species are present in solution when $Co(py)_2(NO_3)_2$ is added to any of the $Co(py)_2X_2$ complexes has clearly been established. The apparent independence of the equilibrium constant of the $Co(py)_2(NO_3)_2$ + $Co(py)_2Cl_2$ reaction from solvent effects suggests that there is little difference between the solvations of the products and reactants. This seems consistent with our proposed anion-exchange reaction since none of the species are ionic or have solvent molecules in the primary coordination sphere. The numerical values for K_{eq} indicate that the free energy changes for the reactions are quite small (less than 1 kcal/mol). It has been observed that anion-exchange reactions of this type are a general characteristic of transition metal complexes in nonaqueous solvents.[22]

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Registry No. $Co(py)_2(NO_3)_2$, 55319-69-2; $Co(py)_2(NO_3)Cl$, 55319-70-5; $Co(py)_2Cl_2$, 14024-92-1; $Co(py)_2Br_2$, 14024-83-0; $Co(py)_2I_2$, 14025-00-4.

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A Novel Kind of Configurational Dissymmetry. Preparation, Resolution, and Circular Dichroism of *cis*-Bis(1(a)-methyl-2(a),4(a),6(a)-triaminocyclohexane)cobalt(III) Ion

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The ligand 1-methyl-2,4,6-triaminocyclohexane (Metach) has been prepared by a two-step catalytic reduction of 2,4,6-trinitrotoluene. The isomer isolated has all equatorial substituents on the cyclohexane ring. The bis cobalt(III) complex has been prepared and resolved with *d*-bromocamphorsulfonate. The visible–ultraviolet circular dichroism spectrum of the resolved ion has a single gaussian extremum of low magnitude. The enantiomer isolated is tentatively assigned the Λ absolute configuration on the basis of sector rule arguments.

Introduction

1-Methyl-2,4,6-triaminocyclohexane (Metach) has a total of eight stereoisomers (Figure 1). Two of these have cis,cis amino groups. The other six have cis,trans amines. The compound was prepared for the first time by Middleton[1] in 1938, starting from 2,4,6-triaminotoluene.[2] The method of reduction, which involved high-pressure hydrogenation with Raney nickel catalyst, apparently gave entirely a mixture of the cis,trans isomers. Middleton was in any case unable to prepare any bis metal ion complexes.

The two isomers (cis,cis and cis,trans) of the related, more symmetrical compound 1,3,5-triaminocyclohexane have since both been prepared,[3-6] and stable bis complexes of the cis,cis isomer have been made with several metal ions.[4,6,7] In these complexes the cis,cis amines move into a triaxial conformation and occupy the trigonal face of a coordination octahedron. A similar phenomenon would be expected in the formation of complexes of the cis,cis isomers of 1-methyl-2,4,6-triaminocyclohexane. The bis octahedral complex ion resulting from the coordination of two molecules of a single ligand isomer would itself have three isomers: optically inactive *trans*-M(*cis,cis*-Metach)$_2^{n+}$ and a pair of enantiomers, Δ- and Λ-*cis*-M(*cis,cis*-Metach)$_2^{n+}$ (these enantiomers are shown in Figures 2 and 3).

In this work, 1(e)-methyl-2(e),4(e),6(e)-triaminocyclohexane was prepared, separated, and characterized. Its bis cobalt(III) complex, in which the ligand is "flipped" to the all-axial conformation, was synthesized and the cis isomer of the complex was resolved.

The source of dissymmetry in this ion is remote from the cobalt(III) d → d chromophore. The ion is a novel example of pure configurational dissymmetry. Its circular dichroism (CD) spectrum is thus of some theoretical interest.

Experimental Section

Materials. Commercial 2,4,6-trinitrotoluene was purified by recrystallization from ethyl acetate. Rhodium chloride trihydrate was purchased from Alfa Inorganics and used as received. Ammonium *d*-bromocamphorsulfonate was obtained from Aldrich Chemical Co. and converted to the silver salt by metathetical reaction. Palladium on charcoal catalyst was purchased from Matheson Coleman and Bell. All other chemicals were commercial reagent grade or better.

2,4,6-Triacetaminotoluene. (The preparation of the ligand was based on the method used by Stetter, Theisen, and Steffens[5] to make the related *cis,cis*-1,3,5-triaminocyclohexane.) A 22.7-g amount (0.10 mole) of 2,4,6-trinitrotoluene was dissolved in 200 ml of ethyl acetate. A 60-ml amount of acetic anhydride was added. A 1.4-g sample of 10% palladium on charcoal catalyst was added and hydrogenation was carried out at room temperature and 4 psig pressure for 24 hr in a Paar low-pressure hydrogenation apparatus. The reaction was not complete in this time but longer reaction improved the yield little. The product precipitated during the reaction. It was filtered off and separated from the catalyst by dissolving it in hot 30% ethanol. Crude product precipitated upon cooling this solution. It was recrystallized from 50% methanol. The yield was 14.0 g or 53.2%; mp 296–298° (lit.[8] mp 283°).

***cis*-1(e)-Methyl-2(e),4(e),6(e)-triacetaminocyclohexane.** A 12.7-g quantity (1.05 mol) of the crude 2,4,6-triacetaminotoluene prepared above was suspended in 300 ml of glacial acetic acid. A 1.25-g sample of 7:3 rhodium–platinum catalyst, prepared according to the method of Nishimura,[9] was added, and the mixture was hydrogenated at 40 psig gauge pressure and room temperature for 48 hr. At the end of this time all of the suspended reactant had dissolved and the theoretical