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Cyclic Amine Complexes of Cobalt(I), -(II), and -(III). Electrochemistry, Preparation, and Properties

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The electrochemistry, preparation, and properties of cobalt complexes containing cyclic ligands are reported. The ligands contain four nitrogens as the donor atoms. Complexes containing Co(I), Co(II), and Co(III) and having essentially identical coordination environments are obtained. The properties and behavior of the cobalt compounds are compared to those of the corresponding nickel and copper complexes.

Introduction

The monovalent and tervalent nickel and copper complexes of the macrocyclic tetramines shown in Figure 1 have been described previously.[1-3] The compounds were prepared by reduction and oxidation of the corresponding divalent species. The copper(III) and the nickel(I) and -(III) oxidation states are rare and were unknown with the type of saturated system represented by the cyclic amine ligands.

The remarkable ability of the macrocyclic amines to stabilize a number of oxidation states would be expected to extend to other first-row transition metals. Therefore, a study of the cobalt complexes was carried out. Cobalt(III) complexes have been studied[4-9] to some extent. The investigations have dealt principally with the preparation of CoL^{3+} and its properties as a function of the anion. This report deals with the complete series of oxidation states of cobalt that are stabilized by the cyclic ligands. The isomerically pure *trans-meso*-diene and *trans-meso*-tetramine complexes of cobalt(I) and -(II), as well as cobalt(III), have been prepared and isolated. A complete discussion of the various possible isomers can be found elsewhere.[3,10,11]

The electrochemistry, preparation, spectra, and other properties of the cobalt complexes are reported. The redox properties and spectra of the cobalt compounds are compared to those of nickel and copper. Such a comparison is of interest because it is very rare that a group of metals has essentially identical ligand environments in a series of three oxidation states.

Experimental Section

Apparatus.—The electrochemical equipment is discussed in previous reports.[1,3] Descriptions are given of the polarograph, the recorder, the potentiostat, the electronic integrator, the polarographic cell and the electrodes, and the constant-potential electrolysis cell.

Infrared spectra wre measured using a Beckman IR8. Ultraviolet and visible spectra were obtained with a Cary 14 automatic recording spectrophotometer.

Reagents.—The acetonitrile used for the electrochemical work was Matheson Coleman and Bell Pesticide quality purified by a published procedure.[12] Acetonitrile used under other circumstances was distilled from CaH_2. Ethyl ether was distilled from Na–K alloy and THF, from $LiAlH_4$. Other solvents were dried with CaH_2 or powdered activated 4A sieves. All the solvents were distilled and kept under a nitrogen atmosphere.

Eastman Kodak tetraethylammonium perchlorate recrystallized five times from water and dried under vacuum at 70° was used as the supporting electrolyte. All other chemicals were reagent grade (as obtained from the suppliers).

Spectral and Electrochemical Measurements.—Infrared spectra were taken in a potassium bromide matrix. The sample compartment was provided with a nitrogen purge.

Ultraviolet and visible spectra were obtained in 0.1–10-mm quartz cells. Cell length was varied in order to avoid dilution. In this way small amounts of solvent impurities would not destroy the very reactive complexes. The measurements were made at room temperature in a nitrogen atmosphere. The concentrations ranged between 10 and 50 m*M*.

The electrochemical procedures have been described.[1,3] For polarographic measurements, 1–5 m*M* solutions of the complexes were prepared. A weighed quantity of the complexes was dissolved in a measured volume of acetonitrile which was 0.10 *M* in tetraethylammonium perchlorate. The electrochemical measurements were carried out at 25.0 ± 0.1°.

Nearly all the work was done in a Vacuum Atmospheres Dri Lab containing an N_2 atmosphere. The oxygen and water concentrations were a few parts per million or less.

All the measurements were made on freshly prepared samples.

Preparative Chemistry. Co(*trans*-diene)(ClO$_4$).—The Co(I) compound can be prepared by reduction of the Co(II) compound either electrochemically or with sodium amalgam. The chemical method is described here. One gram of recrystallized Co(*trans*-diene)$(ClO_4)_2$ was dissolved in 75 ml of acetonitrile and reduced with sodium amalgam (250 mg of Na/200 g of Hg) for 20 min at room temperatures. A color change from yellow to blue-green occurred during the initial few minutes. The solution was filtered and the volume was reduced to about 5 ml by evaporation under vacuum. A dark green precipitate (320 mg) formed which was filtered and dried under vacuum at room temperature. A polarogram showed the product to be pure Co(*trans*-diene)-(ClO_4). The remaining solution contained a mixture of Co(*trans*-diene)(ClO_4) and an impurity believed to be the product from the reaction of Co(*trans*-diene)$^+$ with water present in the starting material. The impurity gives an anodic wave at −0.61 V. *Anal.* Calcd for Co(*trans*-diene)(ClO_4): Co, 13.4; C, 43.7; H, 7.3; N, 12.7; Cl, 14.6; O, 8.0. Found: Co, 12.2; C, 43.3; H, 7.3; N, 13.3; Cl, 15.3; O, 8.1.

During one preparation of Co(*trans*-diene)(ClO_4) by the above method, an unusual light green product crystallized. The infrared spectrum indicated that the compound may be HCo-(*trans*-diene).

Co(*trans*-tetramine)(BF$_4$).—The Co(*trans*-tetramine)$^+$ complex can only be prepared chemically in THF. A sodium amalgam was prepared by dissolving 0.75 g of the alkali metal in 150 g of mercury. Tetrahydrofuran (125 ml) was added followed by the

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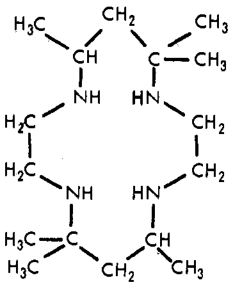
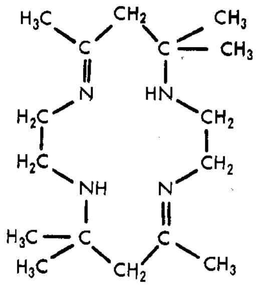


trans-TETRAMINE



trans-DIENE

Figure 1.—The macrocyclic ligands.

Co(*trans*-tetramine)$(BF_4)_2$ complex (0.9 g). The mixture was stirred for 15 min and then was filtered.

Removal of solvent under vacuum at room temperature yielded a green product Co(*trans*-tetramine)(BF_4). Because of the reactivity of the cobalt(I) compound, it was identified by comparing its ir, visible, and uv spectra to those of Ni(I) and Cu(I).[1,3] Similarly the chemistry, for example, reaction with oxygen, indicates a Co(I) species. Several preparations gave identical products.

Co(*trans*-diene)$(ClO_4)_2$.—The method of Curtis and Hay[13] was used to prepare (*trans*-diene)·$2HClO_4$. The hexahydrate of $Co(C_2H_3O_2)_2$ (0.025 mol) was placed in 150 ml of acetonitrile. A sparingly soluble purple acetonitrile complex was formed in a few hours. The hydroperchlorate of *trans*-diene was added (0.025 mol) and the mixture was stirred for several hours. The yellow Co(*trans*-diene)$(ClO_4)_2$ complex precipitated. More product could be forced out by addition of diethyl ether. The Co(*trans*-diene)$^{2+}$ could then be recrystallized from fresh acetonitrile and was washed with acetone. The final product that is obtained in general tends to be a mixture of Co(*trans*-diene)$(ClO_4)_2$ and Co(*trans*-diene)$(ClO_4)_2 \cdot H_2O$. The two products can be separated by careful fractional crystallization. *Anal.* Calcd for Co(*trans*-diene)$(ClO_4)_2$: Co, 10.9; C, 35.7; H, 5.8; N, 10.4; Cl, 13.2; O, 23.8. Found: Co, 9.8; C, 34.6; H, 6.0; N, 10.6; Cl, 14.2; O, 24.6.

Co(*trans*-tetramine)$(BF_4)_2 \cdot xCH_3CN$.—The Co(*trans*-tetramine)$^{2+}$ complex was prepared by allowing $Co(BF_4)_2 \cdot 6CH_3CN$ to react with anhydrous *trans*-tetramine. The preparation of the metal tetrafluoroborate and of *trans*-tertramine has been described previously.[3]

The $Co(BF_4)_2 \cdot 6CH_3CN$ salt (0.022 mol) was dissolved in 250 ml of acetonitrile. To the solution was added the dry amine (6.28 g). The solution turned from pink to a dark purple. The contents were refluxed for 2 hr. Half of the solvent was evaporated and an equivalent amount of diethyl ether was added. Upon standing, purple crystals of Co(*trans*-tetramine)$(BF_4)_2 \cdot xCH_3CN$ formed. The product was identified by electrochemistry (100% pure) and by its infrared spectrum and was found to be identical with a previously analyzed and pure Ni(*trans*-tetramine)$^{2+}$ complex.

The Co(*trans*-tetramine)$(BF_4)_2$ was used to prepare the Co(I) complex.

Co(*trans*-tetramine)$(ClO_4)_2$.—Five grams of $Co(ClO_4)_2 \cdot 6H_2O$ was dissolved in dry ethanol. Next 4.7 g of (*trans*-tetramine)·$2H_2O$ was added and the mixture was refluxed for 2 hr. Cooling and filtration gave 8 g of product. The complex was dissolved in 75 ml of hot acetonitrile. Upon cooling ~7 g of the pure product was obtained. It was dried under vacuum. *Anal.* Calcd for Co(*trans*-tetramine)$(ClO_4)_2$: Co, 10.8; C, 35.1; H, 6.7; N, 10.3; Cl, 13.1; O, 23.6. Found: Co, 10.7; C, 35.5; H, 6.7; N, 11.1; Cl, 13.1; O, 23.6.

The Co(*trans*-tetramine)$(ClO_4)_2$ salt was used for the electrochemical measurements and in the preparation of the Co(III) complex.

$(CH_3CN)_2$Co(*trans*-diene)$(ClO_4)_3$.—One gram of Co(*trans*-diene)$(ClO_4)_2$ was dissolved in 125 ml of acetonitrile which was 0.10 *M* in tetraethylammonium perchlorate. The complex was oxidized to 95% completion at a platinum foil electrode set at +0.75 V. An orange solid precipitated. Evaporation of the solvent to about 50 ml under vacuum produced additional precipitate. The solution was filtered yielding 350 mg of product. The orange solid was washed with acetonitrile and was dried at room temperature under vacuum. Although elemental analyses clearly indicated that the product was $(CH_3CN)_2$Co(*trans*-diene)$(ClO_4)_3$, reproducible results were difficult to obtain due to explosion of the sample on heating. *Anal.* Calcd for $(CH_3CN)_2$Co(*trans*-diene $(ClO_4)_3$: Co, 8.18; C, 33.4; H, 5.3; N, 11.7; Cl, 14.8. Found: Co, 7.58; C, 32.2; H, 5.2; N, 11.2; Cl, 14.6.

$(CH_3CN)_2$Co(*trans*-tetramine)$(ClO_4)_3$.—One gram of Co(*trans*-tetramine)$(ClO_4)_2$ was dissolved in 150 ml of acetonitrile which was 0.10 *M* in tetraethylammonium perchlorate. The complex was oxidized at a platinum foil electrode at +0.70 V until the current dropped to 5% of its original value. An orange precipitate formed. The volume was reduced to about 50 ml under vacuum producing more precipitate. The solution was filtered and the orange solid was washed with acetonitrile. The product was dried at room temperature under vacuum. One gram was obtained. Elemental analyses showed that the Co(*trans*-tetramine)$^{3+}$ precipitated with two acetonitriles of solvation. *Anal.* Calcd for $(CH_3CN)_2$Co(*trans*-tetramine)$(ClO_4)_3$: Co, 8.1; C, 33.1; H, 5.5; N, 11.6; Cl, 14.7. Found: Co, 8.0; C, 33.3; H, 5.9; N, 11.8; Cl, 14.5.

Results

Electrochemistry. Co(II) Complexes.—A polarogram of *Co*(*trans*-tetramine)$^{2+}$ at the dropping mercury electrode (dme) revealed that the complex undergoes both oxidation and reduction in acetonitrile. An anodic and two cathodic waves were observed as seen in Figure 2. The anodic and first cathodic waves gave linear log plots $[E \text{ } vs. \text{ } (i/i_d - i)]$ with slopes in agreement with reversible single-electron processes: $CoL^{2+} - e^- \rightarrow CoL^{3+}$ and $CoL^{2+} + e^- \rightarrow CoL^+$. The second cathodic wave was irreversible and due to the reaction $CoL^+ + e^- \rightarrow Co + L$.

On a platinum electrode Co(*trans*-tetramine)$^{2+}$ gave an anodic and a cathodic peak (Figure 3). The anodic peak appeared electrochemically irreversible by cyclic voltammetry, but a cathodic peak due to the oxidation product was observed on the reverse scan. The irreversibility is believed to be due to a film formed on the electrode by the insoluble electrode product. The height of the cathodic peak of Co(*trans*-tetramine)$^{2+}$ was characteristic of a reversbile one-electron reduction. However, the separation of the peak potentials, ΔE_p, of the peaks obtained on the forward and reverse scans indicated at best quasireversibility.[14] Another test of reversibility is the ratio $(i_p)_r/(i_p)_f$, where i_p is the peak current and r and f refer to the forward and reverse scans. A ratio of 0.57 was obtained whereas a value of 1.0 is expected for a reversible process.[14] The low value can be explained by a rapid following chemical reaction[14] of CoL^+ with some component of the solution, probably acetonitrile. This interpretation is supported by the fact that Co(*trans*-tetramine)$^+$ is not obtained on constant-potential reduction of the

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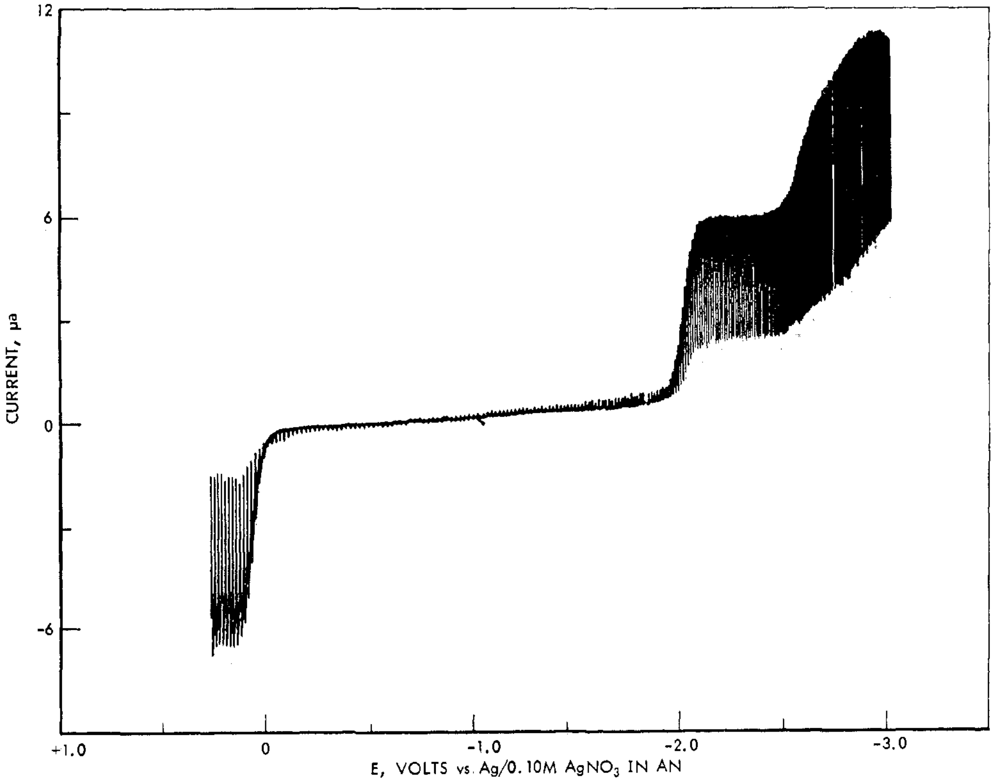

Figure 2.—Polarogram of 10^{-3} *M* Co(*trans*-tetramine)$^{2+}$ in acetonitrile.

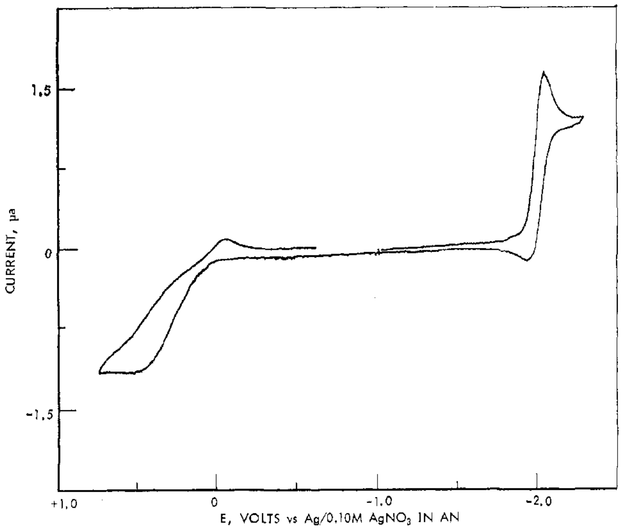

Figure 3.—Cyclic voltammogram of 10^{-3} *M* Co(*trans*-tetramine)$^{2+}$ in acetonitrile.

Co(II) complex, but rather a mixture of products results.

A polarogram of Co(*trans*-diene)$^{2+}$ at the dme gave a reversible single-electron anodic wave (Figure 4). The number of cathodic waves depended on the degree of purity of the starting material. A mixture of anhydrous and hydrated forms is usually obtained. If the amount of the hydrated form is considerable, two closely spaced waves with $E_{1/2}$ values of -1.65 and -1.85 V are obtained. The total height of the two waves corresponded to a one-electron reduction. On recrystallization of the sample, a distorted single-electron wave at -1.76 V was observed. At more negative potentials an irreversible wave with a maximum due to the reduction of Co(*trans*-diene)$^{+}$ was also obtained for all Co(*trans*-diene)$^{2+}$ samples.

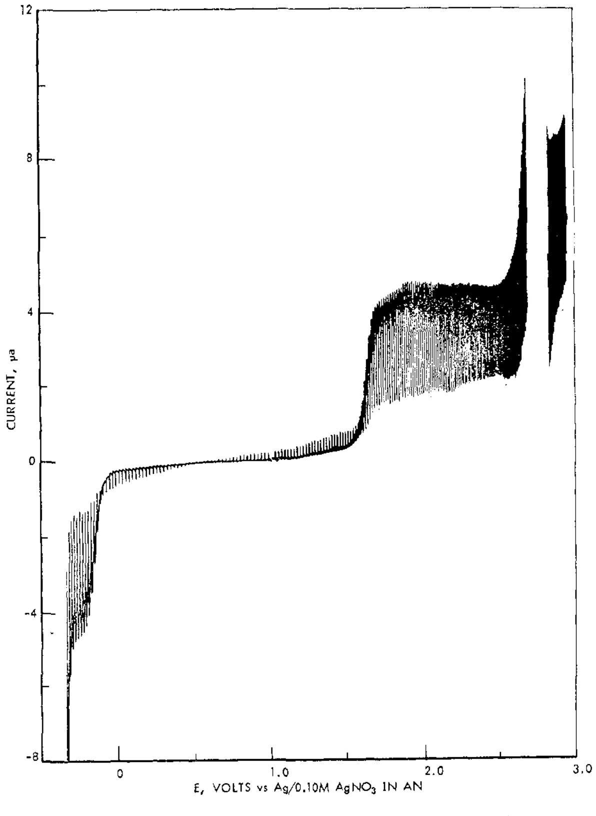

Figure 4.—Polarogram of 10^{-3} *M* Co(*trans*-diene)$^{2+}$ in acetonitrile.

On a platinum electrode Co(*trans*-diene)$^{2+}$ gave an anodic and a cathodic peak (Figure 5). The anodic

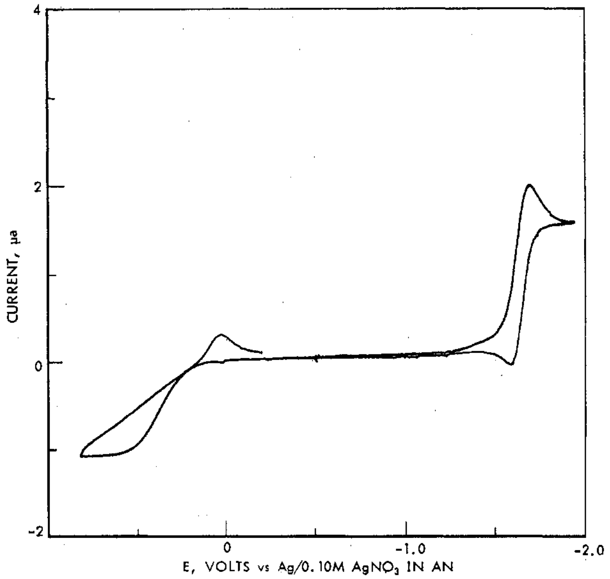

Figure 5.—Cyclic voltammogram of 10^{-3} *M* Co(*trans*-diene)$^{2+}$ in acetonitrile.

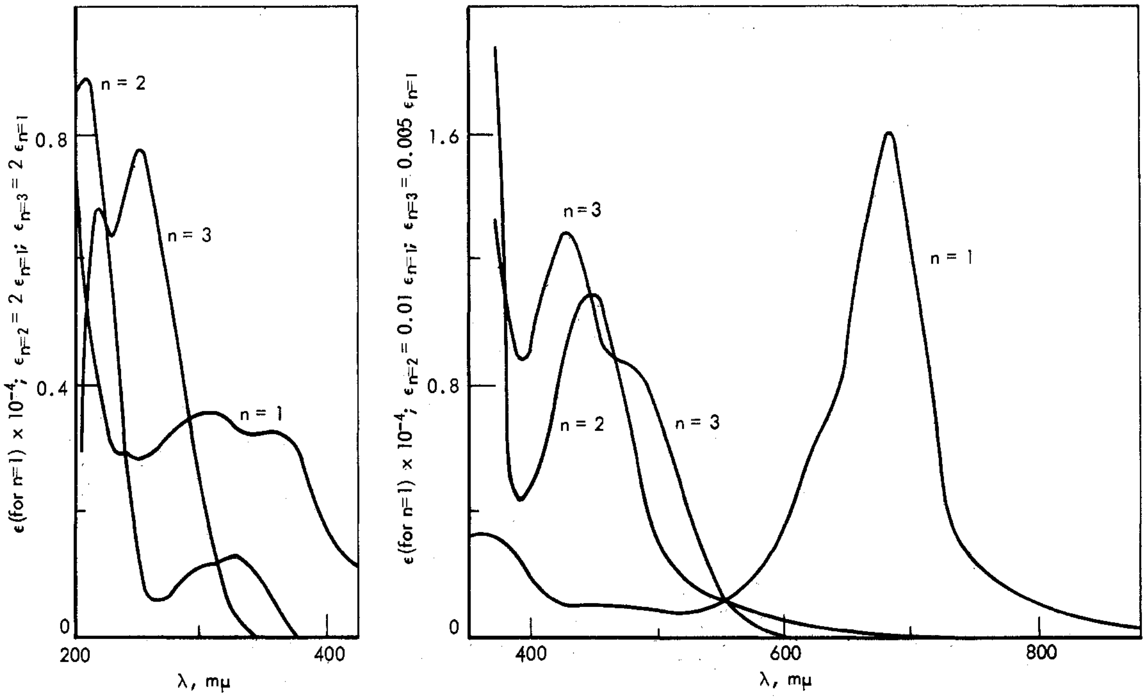

Figure 6.—Ultraviolet and visible spectra of Co(*trans*-diene)(ClO$_4$)$_n$ in acetonitrile.

peak was irreversible but a peak due to the product was observed on the reverse scan. The cathodic process was nearly reversible by the ΔE_p test but the peak current ratio was 0.81 which indicated a following chemical reaction. The reaction probably involves CoL$^+$ with water. This is supported by the observation that on constant-potential reduction of Co(*trans*-diene)$^{2+}$ the compound involved in the reaction with the Co(I) species was exhausted before all of the Co(I) was consumed.

The number of electrons involved in the redox processes was directly measured only for the oxidation of Co(*trans*-tetramine).$^{2+}$ A value of 0.93 was obtained. In all other cases *n* was estimated from heights of the waves and peaks and known diffusion constants for the nickel and copper complexes.[1,3]

Co(I) and Co(III) Complexes.—As indicated by the voltammetry of Co(*trans*-tetramine)$^{2+}$, the reduction product, Co(*trans*-tetramine)$^+$, is unstable in acetonitrile and could not be prepared by constant-potential electrolysis in this solvent. Electrolysis at −2.0 V yielded a brown solution which exhibited several anodic waves, none of which occurred at the potential expected for the process Co(*trans*-tetramine)$^+$ $\rightarrow$ Co(*trans*-tetramine)$^{2+}$. However, Co(*trans*-tetramine)$^+$ could be prepared by sodium amalgam reduction in tetrahydrofuran and was isolated as the tetrafluoroborate salt. Owing to its instability in acetonitrile, polarography of this compound was not carried out.

The voltammetry of Co(*trans*-diene)$^{2+}$ showed that Co(*trans*-diene)$^+$ reacted with some component of the solution (suspected to be water). The reaction consumed only a fraction of the Co(*trans*-diene)$^+$. Therefore, constant-potential reduction of Co(*trans*-diene)$^{2+}$ followed by fractional crystallization yielded Co(*trans*-diene)(ClO$_4$).

The Co(*trans*-diene)$^+$ gave two anodic waves on the dme due to the electrode reactions

$$\mathrm{CoL^+ - e^- \longrightarrow CoL^{2+}}$$

$$\mathrm{CoL^{2+} - e^- \longrightarrow CoL^{3+}}$$

The first step was irreversible but occurred at a potential close to the reduction $E_{1/2}$ of Co(*trans*-diene)$^{2+}$. The second corresponded to the anodic wave of Co(*trans*-diene)$^{2+}$. The heights of both waves were characteristic of one-electron oxidations. Two anodic peaks were also observed on a platinum electrode.

Both Co(III) complexes were prepared by constant-potential electrolysis and precipitated as (CH$_3$CN)$_2$-

$CoL(ClO_4)_3$. They gave three cathodic waves on the dme corresponding to the electrode reactions

$$CoL^{3+} + e^- \longrightarrow CoL^{2+}$$
$$CoL^{2+} + e^- \longrightarrow CoL^+$$
$$CoL^+ + e^- \longrightarrow Co + L$$

The first wave was reversible and the remaining two corresponded to the cathodic waves exhibited by the Co(II) complexes. On a platinum electrode two cathodic peaks were observed due to the first two of the above reactions. See Tables I and II for a summary of polarographic and voltammetric data.

TABLE I

POLAROGRAPHIC DATA OBTAINED ON THE DME AT 25.0°

Ligand	Electrode reaction	$E_{1/2}$, V	Slope, mV	I_d
trans-Tetramine	$CoL^{2+} + e^- \rightarrow CoL^+$	−2.028	63	2.57
trans-Tetramine	$CoL^+ + e^- \rightarrow Co + L$	−2.52	*a*	
trans-Tetramine	$CoL^{2+} - e^- \rightarrow CoL^{3+}$	+0.078	56	2.73
trans-Tetramine	$CoL^{3+} + e^- \rightarrow CoL^{2+}$	+0.087	62	2.71
trans-Diene	$CoL^{2+} + e^- \rightarrow CoL^+$	−1.76	*a*	2.65
trans-Diene	$CoL^+ + e^- \rightarrow Co + L$	−2.7	*a*	
trans-Diene	$CoL^+ - e^- \rightarrow CoL^{2+}$	−1.62	92	2.49
trans-Diene	$CoL^{2+} - e^- \rightarrow CoL^{3+}$	+0.126	63	2.72
trans-Diene	$CoL^{3+} + e^- \rightarrow CoL^{2+}$	+0.129	59	2.97

[a] Distorted wave. [b] $I_d = i_d/Cm^{2/3}t^{1/6}$, where i_d is in microamperes, C is in moles per milliliter, m is in milligrams per second, and t is in seconds.

TABLE II

VOLTAMMETRIC DATA OBTAINED ON A PLATINUM-SPHERE ELECTRODE AT 25.0°

Ligand	Electrode reaction	$E_{1/2}$ or E_p, V
trans-Tetramine	$CoL^{2+} + e^- \rightarrow CoL^+$	-2.037^a
trans-Tetramine	$CoL^{2+} - e^- \rightarrow CoL^{3+}$	$+0.42^b$
trans-Tetramine	$CoL^{3+} + e^- \rightarrow CoL^{2+}$	$+0.021^b$
trans-Diene	$CoL^{2+} + e^- \rightarrow CoL^+$	-1.693^a
trans-Diene	$CoL^+ - e^- \rightarrow CoL^{2+}$	-1.658^a
trans-Diene	$CoL^{2+} - e^- \rightarrow CoL^{3+}$	$+0.240^b$
trans-Diene	$CoL^{3+} + e^- \rightarrow CoL^{2+}$	$+0.010^b$

[a] $E_{1/2} = E$ at $i = 0.852i_p$. [b] E_p.

Spectra. The ultraviolet and visible spectra of Co(*trans*-tetramine)$^+$ were taken in THF. The spectra of the remaining complexes were measured in acetonitrile. All of the results are shown in Figures 6 and 7. Table III lists the wavelengths (mμ) and the intensities of all the main transitions of the cobalt macrocyclic ligand complexes, as well as the nickel and copper complexes for comparison. Infrared spectra were also obtained and the frequencies are given in Table IV.

Discussion

The electrochemical study of the nickel,[1] copper,[3] and cobalt macrocyclic tetramine complexes indicates that there exists a similar pattern of redox behavior in this group. M(I), -(II), and -(III) states are observed in acetonitrile and would probably exist in other nonaqueous solvents. The compounds can be prepared and isolated as the perchlorate or tetrafluoroborate salts. Similarities are also apparent in the spectra. In view of the above, it may be possible to correlate the redox potentials or spectra to a known or easily measurable quantity. Part of the discussion deals with what appears to be such a correlation.

The main differences between the three metal systems is the fact that a M(I) → M(0) reduction step is observed for copper and cobalt but not for nickel. As a consequence the cathodic wave obtained for the nickel complex corresponding to the reduction of the C═N groups does not appear for cobalt or copper. Apparently the imine group has to be coordinated to a metal in order to be electroactive in the available potential range, *i.e.*, to −3.2 V. It is most probable that decomposition of the transient M(0) complex takes place before reduction of C═N can occur with Cu and Co.

The electrochemical data made available by the investigation of the nickel, copper, and cobalt complexes provide an unprecedented opportunity to study the re-

TABLE III

THE VISIBLE AND ULTRAVIOLET ABSORPTION SPECTRA OF M(I), -(II), AND -(III) COMPLEXES WHERE M = Co, Ni, AND Cu

Complex	M = Co		M = Ni		M = Cu	
	λ^a	ϵ^b	λ	ϵ	λ	ϵ
M(*trans*-tetramine)$^+$	393	2,690	375	5,350	560	7
	325	3,170	263	4,350	241	7,570
	245	4,150			219	9,670
	207	8,120				
M(*trans*-diene)$^+$	679	15,950	600	1,820	415	5,700
	357	3,300	472	5,860	283	5,600
	307	3,600	345	3,750		
	245	2,950	308	4,940		
	<200	>8,300	283	4,620		
M(*trans*-tetramine)$^{2+}$	479	74.6	471	66	517	138
	325	30.8	233	13,830	273	9,400
	216	11,060	200	9,270		
M(*trans*-diene)$^{2+}$	445	110.6	441	89	502	120
	315	2,595	283	5,400	262	7,400
	210	17,870	230	15,200	192	15,800
			216	17,280		
M(*trans*-tetramine)$^{3+}$	469	112	655	116	425	15.010
	275	24,200	407	11,600	375	12,000
			330	11,800	275	6,700
			275	7,800		
M(*trans*-diene)$^{3+}$	475	43.7	565	76	395	14,530
	425	64.4	380	8,660	335	12,690
	252	15,550	318	12,500		
	220	13,640	203	13,500		

[a] In millimicrons. [b] In liters per mole per centimeter.

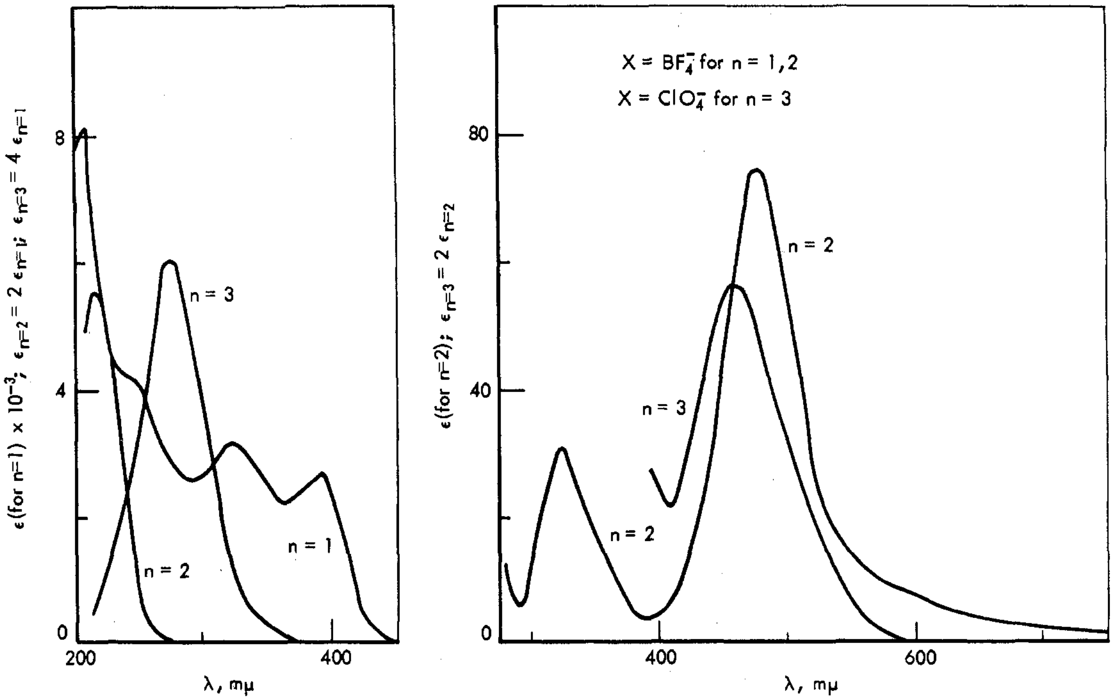

Figure 7.—Ultraviolet and visible spectra of Co(*trans*-tetramine)$(X)_n$: $n = 1$, in tetrahydrofuran; $n = 2$ or 3, in acetonitrile.

TABLE IV

INFRARED SPECTRA (FROM 4000 TO 1100 CM^{-1})

a	*b*	*c*	*d*	*e*
3215 s	3240 s	3225 s	3200 s	3200 s
2980 s	2975 s	2990 s	3005 s	3010 m
2950 s	2950 s	2950 m	2950 s	2990 s
2890 m	2915 m	2900 m	2900 w	2950 s
2850 m	2890 m			2880 w
			2305 s	2315 m
				2250 m
1655 w		1665 s		1650 s
1645 w		1650 m		1630 m
1590 w				
1575 w				
1550 s				
1525 w				
1545 s				
1465 w	1480 w	1485 w	1465 s	1475 w
1450 m	1465 s	1475 m	1425 s	1465 m
1440 w	1430 s	1435 m	1380 m	1445 s
1425 w	1400 m	1415 m	1370 m	1425 s
1390 m	1375 s	1400 w	1360 m	1405 s
1370 s	1360 m	1380 s	1340 m	1375 s
1355 s	1340 w	1360 w	1305 w	1355 m
1340 m	1315 w	1305 w		1340 w
				1300 m
1290 w	1290 s	1280 w	1290 w	1265 w
1270 w	1235 w	1255 w	1235 w	1250 s
1250 m	1190 w	1240 w	1200 w	1235 w
1240 w		1210 w		1205 w
1230 w		1180 w		1180 w

[a] Co(*trans*-diene)(ClO_4). [b] Co(*trans*-tetramine)$(BF_4)_2$. [c] Co(*trans*-diene)$(ClO_4)_2$. [d] Co(*trans*-tetramine)$(ClO_4)_3 \cdot 2CH_3CN$. [e] Co(*trans*-diene)$(ClO_4)_3 \cdot 2CH_3CN$.

lationship between the redox potentials of metal complexes and the electronic structure of the central metal ion. It should be emphasized that the macrocyclic tetramines represent a family of complexes in which the ligand environment is essentially constant, and any trends in redox behavior resulting from changes in the central metal ion may, therefore, be attributed exclusively to changes in the electronic structure of the metal.

The half-wave potentials of the saturated complexes, which tend to give the most reversible waves, are assembled below to aid the reader in the following discussion. It may be recalled that for reversible electrode reactions, $E_{1/2}$ is essentially equal to the standard redox potential, $E°$, so that these terms may be used interchangeably.

Electrode reaction	$E_{1/2}$, V
d^{10} Cu(I) $\longrightarrow$ d^9 Cu(II) + e^-	~ -1.0
d^9 Ni(I) $\longrightarrow$ d^8 Ni(II) + e^-	-1.57
d^9 Cu(II) $\longrightarrow$ d^8 Cu(III) + e^-	$+1.22$
d^8 Ni(II) $\longrightarrow$ d^7 Ni(III) + e^-	$+0.88$
d^8 Co(I) $\longrightarrow$ d^7 Co(II) + e^-	-2.03
d^7 Co(II) $\longrightarrow$ d^6 Co(III) + e^-	$+0.08$

It is apparent from the above data that $E_{1/2}$ has a strong dependence on the nature of the central metal ion. The variety of electronic structures represented makes it possible to separate the effect of the number of d electrons from the effect of the oxidation state of the metal on the redox potential. Thus, increasing the number of d electrons, while keeping the oxidation state constant, causes a positive shift in $E_{1/2}$. The complexes become more difficult to oxidize in the order Co(II), Ni(II), and Cu(II). If the number of d electrons is held constant and the oxidation state is increased, a positive shift in $E_{1/2}$ is again observed. For example, Cu(II) is more difficult to oxidize than Ni(I), and Ni(II) is more difficult to oxidize than Co(I). The $E_{1/2}$ values are much more sensitive to a change of 1 in the oxidation state than a change of 1 in the number of d electrons (~2.8 V *vs.* ~0.5 V).

It was pointed out in the paper on the copper[3] complexes that $E_{1/2}$ correlates well with I_p, the ionization potential of the central metal ion in the gaseous form. A plot of $E_{1/2}$ *vs.* I_p for the above metals is shown in Figure 8. It is evident from the figure that for a given valence change, *i.e.*, M(I) → M(II) + e^- or M(II) → M(III) + e^-, $E_{1/2}$ varies linearly with I_p. The fact that such a relationship exists for the macrocyclic family indicates that those factors, other than I_p, which

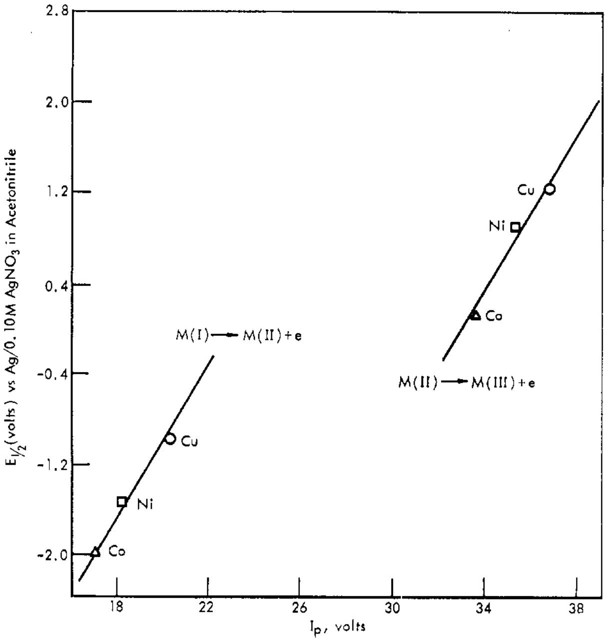

Figure 8.—Relationship between the $E_{1/2}$ values of the redox reactions of the *trans*-tetramine–metal complexes and the ionization potentials, I_p, of the corresponding gaseous metal ions.

contribute to the redox potentials of these complexes either vary little with the number of d electrons or are proportional to I_p. In addition to I_p, two quantities which are expected to contribute to the redox potential are $\Delta\Delta H_{solv}$ and $\Delta\Delta H_c$. $\Delta\Delta H_{solv}$ is the difference in the heats of solvation of the oxidized and reduced forms of the couple and $\Delta\Delta H_c$ is the corresponding difference in the heats of formation of the complexes. For a couple involving a given valence change, $\Delta\Delta H_{solv}$ may well be constant since the macrocyclic complexes have similar geometry and size. On the other hand, $\Delta\Delta H_c$, and in particular the ligand field contribution to $\Delta\Delta H_c$, is usually dependent on the number of d electrons. However, the visible spectra of the complexes also indicate that the ligand field splitting for the macrocyclic compounds varies little with the type of metal ion. For example, nearly all of the M(II) complexes are yellow or orange. The energy of the d–d transition giving rise to the visible spectrum, which depends on the ligand field splitting, varies from 21,200 cm^{-1} for Ni(*trans*-tetramine)$^{2+}$ to 19,400 cm^{-1} for Cu(*trans*-tetramine)$^{2+}$. The difference is equivalent to only 0.2 V.

As one proceeds left in the first transition series, I_p decreases. As a result it should become increasingly more difficult to make the lower oxidation states. At the same time, the higher oxidation states should become stabilized. The M(III) → M(IV) couples might be expected to appear. It is unlikely that oxidation states higher than 4+ can be isolated with the *trans*-tetramine and *trans*-diene ligand complexes of the first transition series. Whether the extrapolation of $E_{1/2}$ *vs.* I_p to include other metals can be expected to be strictly linear for the entire transition series is extremely doubtful. However, the general trends mentioned above should hold.

The $\Delta E_{1/2}$ of the cobalt(II), nickel(II), and copper(II) complexes is very nearly equal to the energy of the first d–d transition band. $\Delta E_{1/2}$ is the difference in the $E_{1/2}$ values for the oxidation and reduction of the M(II) complexes. The data are collected below.

Complex	$\Delta E_{1/2}$, eV	$\Delta h\nu$, eV
Cu(*trans*-tetramine)$^{2+}$	2.22	2.37
Ni(*trans*-tetramine)$^{2+}$	2.43	2.65
Co(*trans*-tetramine)$^{2+}$	2.10	2.58

The above relationship, together with the strong dependence of $E_{1/2}$ on the nature of the central metal ion, indicates that it is the metal and not the ligand that is oxidized and reduced in the redox reactions of the macrocyclic tetraminemetal complexes. In the case of the saturated M(*trans*-tetramine)$^{n+}$ complexes the reduction of the metal would certainly be expected. However, the complexes containing C=N π systems behave in the same manner.

The wavelengths and intensities of the ultraviolet and visible spectra of the cobalt, nickel, and copper complexes appear in Table III. Low-intensity (ϵ <150) d–d transition bands are observed in the visible region for a large number of the complexes. In those cases where such bands are not detected, their absence may be due to one of two factors. High-intensity charge-transfer bands can obscure the metal to metal transition or the intensity of such a transition can be too low to be detected at the available concentrations. The copper–*trans*-diene (ϵ_{415} 5700) and copper–*trans*-tetramine (ϵ 7) complexes are illustrative examples.

The following bands have been assigned to a transition involving the azomethine group (C=N): Ni(*trans*-diene)$^{2+}$, 283 mμ;[15] Cu(*trans*-diene)$^{2+}$, 262 mμ;[2] Ni(*trans*-diene)$^{+}$, 415 mμ;[2] Cu(*trans*-diene)$^{+}$, 472 mμ.[3] This band can also be identified as 315 mμ for Co(*trans*-diene)$^{2+}$. These bands are believed to be due to a metal→ligand transition because of the direction of their shift on changing the central metal ion [Co(II) → Ni(II) → Cu(II) and Ni(I) → Cu(I)]. In the case of Cu(III) the transition is absent in the region accessible with the Cary 14 spectrophotometer. This indicates that it occurs at <200 mμ which is consistent with the shifts expected for the metal→ligand transition. The *trans*-diene complexes not mentioned above also have azomethine transition bands. However, the presence of a large number of charge-transfer bands makes the azomethine assignments impossible.

Other charge-transfer bands occur in all of the complexes. By comparing the spectra of the different d^n series of complexes where n is constant some of the charge-transfer bands can be identified as being metal→ligand or ligand→metal.

Metal→ligand	Ligand→metal
Co(*trans*-tetramine)$^{+}$ 393 mμ	Cu(*trans*-tetramine)$^{3+}$ 425 mμ
Co(*trans*-diene)$^{+}$ 679 mμ	Cu(*trans*-diene)$^{3+}$ 395 mμ
Ni(*trans*-tetramine)$^{+}$ 375 mμ	Ni(*trans*-tetramine)$^{3+}$ 407 mμ
Ni(*trans*-diene)$^{+}$ 600mμ	

The infrared spectra are included for identification purposes and in most cases have no surprising features. The Co(*trans*-tetramine)(BF_4) decomposed before a good spectrum could be obtained. For the rest of the complexes the frequencies (cm^{-1}) are identifiable as follows: NH stretching, ~3200; C=N stretching, ~1650; C≡N stretching, ~2300; CH stretching, ~2850–3000; CH deformation, ~1300–1480; skeletal vibrations, ~1180–1300. The only unusual frequencies

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[15] N. F. Curtis, *J. Chem. Soc.*, 2644 (1964).

that have been observed are those in Co(*trans*-diene)(ClO_4) between 1545 and 1590 cm^{-1}. These are also assigned to C=N but the reason for the shift is not clear. The frequencies are reproducible and the material was shown to be undecomposed Co(*trans*-diene)(ClO_4) by its electrochemistry.

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Reduction of Pentaamminecobalt(III) Complexes of Pyridinecarboxylic Acids by Remote Attack of Vanadium(II)

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The specific rates of reduction of N-coordinated (nicotinic acid)- and (isonicotinic acid)pentaamminecobalt(III) complexes by vanadium(II) have been studied as a function of hydrogen ion concentration at 25°. For both complexes the rates of reduction conform to the equation $-d(Co(III))/dt = [a + b/(c + (H^+))](Co(III))(V^{2+})$, where $a = 1.0\ M^{-1}\ sec^{-1}$, $b = 0.25\ sec^{-1}$, and $c = 0.035\ M$ for the nicotinic acid complex and $a = 1.4\ M^{-1}\ sec^{-1}$, $b = 0.97\ sec^{-1}$, and $c = 0.18\ M$ for the isonicotinic acid complex. It is proposed that the second term in the rate equation for these Co(III) complexes arises from attack of V^{2+} at the remote carboxylic acid function, with the formation of a binuclear intermediate which is in steady-state equilibrium with reactants and which, in a deprotonated form, undergoes electron transfer to form products.

Introduction

Recent studies of cobalt(III), chromium(III), and ruthenium(III) complexes of substituted pyridines have shown that their reductions by chromium(II) may proceed *via* remote attack.[1,2] These studies have yielded interesting conclusions concerning the effect of the symmetry of the acceptor orbital upon the mechanism of the electron transfer. In this article we report the reductions of similar complexes by vanadium(II) in which remote attack is an important pathway for reduction. Studies of reactions of this kind in which V^{2+} is the reductant provide a way to investigate the influence of the donor orbital on the electron-transfer mechanism.

Experimental Section

Pyridine-, nicotinamide-, and isonicotinamidepentaamminecobalt(III) perchlorate were prepared as described previously.[1]

Pentaamminecobalt(III) complexes of nicotinic acid and isonicotinic acid (structures I and II) were prepared from the corresponding amide complexes. About 5 mmol of the appropriate pentaamminecobalt(III) perchlorate was dissolved in a minimum of trimethyl phosphate and treated with small portions of nitrosyl perchlorate until gas evolution ceased. The acid complex was isolated from the reaction mixture as the iodide salt by diluting the trimethyl phosphate solution with a few volumes of water and adding sodium iodide. The light-sensitive iodide was converted to the perchlorate by treatment with silver perchlorate in aqueous solution. This salt was isolated by concentrating the solution by rotary evaporation and adding perchloric acid. The salt was purified by recrystallization from perchloric acid solutions. The complexes were also isolated in their deprotonated forms by crystallization from a solution adjusted to pH 6.

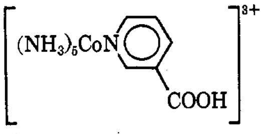
Anal. Calcd for $[(NH_3)_5CoNC_5H_4COOH](ClO_4)_3$: C, 12.74; H, 3.56; N, 14.86; Cl, 18.80; Co, 10.42. Found for (isonicotinic acid)pentaamminecobalt(III) perchlorate: C, 12.85; H, 3.74; N, 14.55; Cl, 18.8; Co, 10.3. Calcd for $[(NH_3)_5CoNC_5H_4COOH](ClO_4)_3\cdot H_2O\cdot HClO_4$: C, 10.53; H, 3.39; N, 12.29; Cl, 20.73; Co, 8.62. Found for the (nicotinic acid)pentaamminecobalt(III) perchlorate: C, 10.65; H, 3.53; N, 12.38; Cl, 19.5; Co, 8.9.

Acid dissociation constants of complexes I and II were determined spectrophotometrically at 25°. Ultraviolet spectra of the acidic and basic forms of each complex were obtained in 1 *M* $HClO_4$ and in a solution of 0.01 *M* $NaHCO_3$ and 1 *M* $LiClO_4$ (pH 8). Seven different equilibrium mixtures of the acidic and basic forms were prepared in $HClO_4$ solutions and chloroacetic acid buffer solutions. Absorbance and pH measurements were made simultaneously on portions of the same equilibrium mixture. All solutions were made up from a single stock solution of cobalt(III) and were adjusted to 1 *M* ionic strength using $LiClO_4$. The hydrogen ion concentrations of the buffer solutions were obtained from pH readings using a glass electrode after the manner of Deutsch.[3] Readings obtained from solutions of known concentrations of $HClO_4$ were used to calibrate this method. K_a was evaluated from absorbance measurements, $A_{\lambda,i}$, of each equilibrium mixture according to the equation

$$K_a = (H^+)_i\left[\frac{A_{\lambda,\text{acid}} - A_{\lambda,i}}{A_{\lambda,i} - A_{\lambda,\text{base}}}\right]$$

$A_{\lambda,\text{acid}}$ and $A_{\lambda,\text{base}}$ refer to the absorbance of the complex at pH 0 and 8, respectively. For the complex of nicotinic acid, measurements at 272 and 256 nm gave $K_a = (2.7 \pm 0.4) \times 10^{-3}$ and $(2.7 \pm 0.3) \times 10^{-3}$, respectively. For the isonicotinic acid complex, measurements at 250 and 285 nm gave $K_a = (4.9 \pm 0.2) \times 10^{-3}$ and $(4.4 \pm 0.6) \times 10^{-3}$, respectively.

Vanadium(II) solutions were prepared by reducing vanadyl perchlorate, $VO(ClO_4)_2$, solutions with amalgamated zinc. Solutions containing V^{2+} were maintained in an atmosphere of nitrogen in vessels stoppered with serum caps. Reaction mixtures were prepared in spectrophotometric cells. Reactions were begun by adding V^{2+} to the reaction mixture with a hypodermic syringe. The reactions were followed by means of absorbance measurements made on a Cary 14 recording spectrophotometer.



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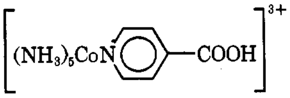

II

Results and Discussion

Cobalt(III) complexes I and II were found to react with V^{2+} to produce equimolar amounts of Co^{2+} and

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