In eq 7 the factors f_D, f_κ, and f_{g_i} are regarded as weight factors. Squaring eq 7, the contributions to the matrix elements of the normal equation are obtained for a particular resonance condition. Summing up all of the contributions of the various resonance conditions of the EPR spectra a symmetric matrix (I) is obtained. The summation runs over the number n of

$$\begin{array}{c|ccccc} & \Delta D/D & \Delta\kappa/\kappa & \Delta g_x/g_x & \Delta g_y/g_y & \Delta g_z/g_z \\ \dfrac{\Delta D/h\nu}{D/h\nu} & \Sigma f_D{}^2 & \Sigma f_D f_\kappa & \Sigma f_D f_{g_x} & \Sigma f_D f_{g_y} & \Sigma f_D f_{g_z} \\ \Delta\kappa/\kappa & & \Sigma f_\kappa{}^2 & \Sigma f_\kappa f_{g_x} & \Sigma f_\kappa f_{g_y} & \Sigma f_\kappa f_{g_z} \\ \Delta g_x/g_x & & & \Sigma f_{g_x}{}^2 & \Sigma f_{g_x} f_{g_y} & \Sigma f_{g_x} f_{g_z} \\ \Delta g_y/g_y & & & & \Sigma f_{g_y}{}^2 & \Sigma f_{g_y} f_{g_z} \\ \Delta g_z/g_z & & & & & \Sigma f_{g_z}{}^2 \end{array} \qquad \text{(I)}$$

experimental resonance values included in the calculation. If the inverted matrix I is multiplied by $(\sum(\Delta H/H)^2)/(n-5)$ then the covariancy matrix is obtained. The roots of this matrix give the relative errors of the parameters. The nondiagonal elements give the covariancies between the parameters. The denominator $(n-5)$ gives the number of independent normal equations (i.e., the number of observations minus the number of parameters).

Registry No. *cis*-$[Cr(ox)_2(H_2O)_2]^-$, 15489-30-2; *cis*-$[Cr(ox)_2(H_2O)(OH)]^{2-}$, 53992-86-2; *cis*-$[Cr(ox)_2bpy]^-$, 21748-32-3; *cis*-$[Cr(ox)_2acac]^{2-}$, 57620-63-0; *cis*-$[Cr(ox)_2en]^-$, 21827-84-9; *cis*-$[Cr(ox)_2phen]^-$, 21748-33-4; *cis*-$[Cr(bpy)_2(H_2O)_2]^{3+}$, 36513-26-5; *cis*-$[Cr(bpy)_2(H_2O)(OH)]^{2+}$, 57651-38-4; *cis*-$[Cr(bpy)_2Cl_2]^+$, 27803-22-1; *cis*-$[Cr(bpy)_2ox]^+$, 32629-19-9; *cis*-$[Cr(phen)_2(H_2O)_2]^{3+}$, 47667-82-3; *cis*-$[Cr(phen)_2(H_2O)(OH)]^{2+}$, 57651-39-5; *cis*-$[Cr(phen)_2Cl_2]^+$, 27803-06-1; *cis*-$[Cr(phen)_2ox]^+$, 32626-76-9.

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Electrochemical Properties of Cobalt(II) Complexes of the Tridentate Ligands Tri(2-pyridyl)amine, Tri(2-pyridyl)phosphine, Tri(2-pyridyl)phosphine Oxide, and Tri(2-pyridyl)arsine[1]

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The electrochemical properties of the Co(II) complexes of the tridentate ligands tri(2-pyridyl)amine (TPAm), tri(2-pyridyl)phosphine (TPP), tri(2-pyridyl)phosphine oxide (TPPO), and tri(2-pyridyl)arsine (TPAs) have been investigated in acetonitrile. It was found that in the complexes $[Co(TPX)_2](ClO_4)_2$ and $Co(TPX)(NO_3)_2$, TPP, TPPO, and TPAs will yield a stable one-electron reduction product while TPAm will not. A one-electron oxidation was observed for the $[Co(TPX)_2](ClO_4)_2$ complexes in which TPX is TPAm, TPP, or TPAs. No oxidation waves were observed for $[Co(TPPO)_2](ClO_4)_2$ or for any of the $Co(TPX)(NO_3)_2$ complexes. Mixed complexes of the type $[Co(TPX)(TPY)](ClO_4)_2$ (TPX ≠ TPY) were prepared by the reaction of $Co(TPX)(NO_3)_2$ with TPY. Only electrochemical means were able to show conclusively that a mixed complex had formed.

Introduction

Metal(II) perchlorate and metal(II) nitrate complexes with tri(2-pyridyl)phosphine (TPP), tri(2-pyridyl)phosphine oxide (TPPO), and tri(2-pyridyl)arsine (TPAs) of the composition $[M(TPX)_2](ClO_4)_2$,[2] $[M(TPX)_2](NO_3)_2$, and $M(TPX)(NO_3)_2$[3] (TPX is one of the above ligands and M is Mn, Co, Ni, Cu, or Zn) have previously been reported. Coordination of the ligands occurs in a tridentate manner through the pyridyl nitrogens with no indication of coordination by the ligand central atom. The coordination sphere of the metal contains six pyridyl groups and may be compared to $[M(py)_6]^{n+}$, $[M(bpy)_3]^{n+}$, $[M(phen)_3]^{n+}$, and $[M(terpy)_2]^{n+}$ (py is pyridine, bpy is 2,2'-bipyridine, phen is 1,10-phenanthroline, and terpy is 2,2',2''-terpyridine). Numerous complexes containing py, bpy, phen, and terpy have been reported and for the latter three ligands, reduced species with the metal ion in a formal oxidation state of +1, 0, or −1 have been observed.[4-12] It is generally concluded that these ligands stabilize formal low oxidation states of metal ions by their ability to accept electrons via a $t_{2g} \rightarrow \pi^*$ back-bonding mode.[13] The $[M(py)_6]^{n+}$ complexes also have this type of backbonding available, yet there are no reports that pyridine stabilizes low oxidation states

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Table I. Electrochemical Data for the $[Co(TPX)_2](ClO_4)_2$ Complexes in Acetonitrile[a]

	DME			RPE		SPE[e]		
Complex reactions[b]	$E_{1/2}$	i_d	Slope,[c] mV	$E_{1/2}$	i_l	$E_{1/2}$	E_p	i_p
$[Co(TPAm)_2](ClO_4)_2$								
$Co^{II} \rightarrow Co$	d			−1.35	98			
$Co^{II} \rightarrow Co^{III}$				+0.13	42	$+0.13_5$	+0.20	7.2
$Co^{III} \rightarrow Co^{II}$						+0.11	$+0.05_5$	7.3
$[Co(TPP)_2](ClO_4)_2$								
$Co^{II} \rightarrow Co^{I}$	−1.30	4.7	64	−1.27	52	−1.27	−1.29	7.4
$Co^{I} \rightarrow Co^{II}$						−1.25	−1.22	7.6
$Co^{II} \rightarrow Co^{III}$				$+0.17_5$	53	+0.17	+0.22	6.8
$Co^{III} \rightarrow Co^{II}$						+0.15	+0.12	7.2
$[Co(TPPO)_2](ClO_4)_2$								
$Co^{II} \rightarrow Co^{I}$	-1.08_5	4.2	81	−1.09	42	−1.08	−1.12	7.6
$Co^{I} \rightarrow Co^{II}$						−1.04	−1.00	7.3
$Co^{II} \rightarrow Co^{III}$								
$Co^{III} \rightarrow Co^{II}$								
$[Co(TPAs)_2](ClO_4)_2$								
$Co^{II} \rightarrow Co^{I}$	-1.34_5	4.0	66	−1.37	73	−1.35	−1.39	7.0
$Co^{I} \rightarrow Co^{II}$						-1.34_5	-1.31_5	7.0
$Co^{II} \rightarrow Co^{III}$				+0.25	59	$+0.27_5$	0.30	5.8
$Co^{III} \rightarrow Co^{II}$						+0.25	0.22	5.9

[a] All E values in V vs. Ag–Ag$^+$ (0.10 M) in acetonitrile; all i_d and i_l values are in μA mmol^{-1}. [b] The actual site of reduction or oxidation is not known with certainity in these complexes and $Co^{II} \rightarrow Co^{I}$ and $Co^{II} \rightarrow Co^{III}$ are meant to imply only the formal oxidation state of the metal ion. [c] E vs. log $[(i_d - i)/i]$. [d] Maximum prevented analysis of wave. [e] i_p is the peak current for a sweet rate of 8.3 mV s^{-1}; E_p is the peak potential; $E_{1/2} = E$ at $0.852 i_p$ (see ref 17).

of metals. bpy, phen, and terpy contain the 2,2'-diimine chromophore which imparts a stability to many of the complexes and may account for stabilization of low oxidation states.

With the TPX ligands coordinated in a tridentate fashion, the overall geometry of the $[M(TPX)_2]^{2+}$ complexes more closely resembles that of the pyridine rather than the bpy, phen, or terpy complexes. The 2,2'-diimine chromophore is not present but an atom capable of π bonding has been placed between the pyridine rings. A fourth ligand, tri(2-pyridyl)amine (TPAm), coordinates as the other TPX ligands,[14,15] but the ligand central atom does not have π-bonding capabilities. This research was undertaken to determine if the ligands TPAm, TPP, TPPO, and TPAs can stabilize low oxidation states of metals and if the central atom will affect the electrochemical behavior of these complexes. The results of this investigation with $[Co(TPX)_2](ClO_4)_2$ and $Co(TPX)(NO_3)_2$ are reported herein.

Experimental Section

Synthesis. The synthesis of the ligands and the complexes have been reported elsewhere.[2,3]

Reagents. Tetraethylammonium perchlorate (Eastman Chemical Co., Rochester, N.Y.) was recrystallized three times from water and dried at 60° in vacuo. Acetonitrile (Aldrich Chemical Co., Milwaukee, Wis., and Nanograde by Mallinckrodt Chemical Works, St. Louis, Mo.) was purified by a modification of the method of Sherman and Olson.[16] Acetonitrile was refluxed and deaerated for several days over calcium hydride (10 g/l.) and then distilled under a nitrogen atmosphere through a column packed with freshly activated F-20 chromatographic alumina (Alcoa Chem.). The acetonitrile was collected in a standard taper Erlenmeyer flask and stored in a nitrogen-filled glovebag (I^{2}R, Cheltenham, Pa.).

Electrochemical Measurements. Voltammetric investigations were made with a Heathkit Model EUA-19-2 polarographic system. Three-electrode voltammetry with a dropping mercury electrode, a hanging mercury drop electrode, a rotating platinum electrode (600 rpm), and a stationary platinum electrode was carried out in a 0.100 M acetonitrile solution of tetraethylammonium perchlorate with a silver–silver nitrate (0.100 M in acetonitrile) couple as the reference electrode. All potentials quoted in this work are vs. this electrode. An $E°$ value for this system has been reported to be +0.637 V vs. the normal hydrogen electrode.[17] Nitrogen (99.99%) that had been passed through a column of molecular sieves (4A and 5A) and presaturated with acetonitrile was used to deaerate all solutions and to blanket the solutions during the voltammetric scan. All voltammetric measurements were carried out in a 75-ml weighing bottle equipped with a tapered Teflon top which held three electrodes and a nitrogen bubbler. The platinum electrode was cleansed after each scan with nitric acid (8 M) and ferrous sulfate (0.01 M) in a 0.05 M sulfuric acid solution and then preelectrolyzed at +0.50 V prior to each scan.[18]

Current vs. time data at a constant potential were obtained with a Brinkman Instruments, Inc., Wenking electronic potentiostat using a conventional H cell. A mercury pool was used as the working electrode and a platinum gauze electrode served as the counterelectrode. Before adding the species to be reduced to the cell, both sides of the H cell were deaerated and the solvent plus supporting electrolyte preelectrolyzed at the desired potential until the residual current was less than 0.1 mA. The data were analyzed by a least-squares analysis for the slope and the intercept of the plot.

Results

The $[Co(TPX)_2](ClO_4)_2$ complexes in which TPX is TPP, TPPO, and TPAs, behave in a similar manner when reduced at the dropping mercury electrode (DME) or the rotating platinum electrode (RPE). Two reduction waves are observed for each complex; the first has an $E_{1/2}$ value between −1.05 and −1.40 V and is observed at both the DME and the RPE (Table I) while the second wave is found to be an irreversible, multielectron ligand wave and is observed only at the DME (Figure 1). The $E_{1/2}$ values for the second wave are cathodic to −2.2 V, past the limit of the range available with a platinum electrode. They are due to the dissociation of the complexes and the subsequent reduction of the ligand and are not considered further.

The first reduction wave is reversible or quasireversible at the hanging mercury drop electrode (HMDE) and at the stationary platinum electrode (SPE). Plots of E vs. $\log[(i_d - i)/i]$ from the polarographic waves for the $[Co(TPX)_2](ClO_4)_2$ complexes gave slopes near the value of 59 mV predicted by the Nernst equation for a one-electron reduction. The larger slope (81 mV) obtained for $[Co(TPPO)_2](ClO_4)_2$ may indicate a slight electrochemical irreversibility although the ratio of i_{p_c}/i_{p_a} (i_{p_c} is the cathodic peak current and i_{p_a} is the anodic peak current) at the SPE shows the reduction product is not unstable. A plot of i_d vs. $h^{1/2}$ (h is the height of the mercury head) is linear and shows that each wave is diffusion controlled.

Current vs. time measurements at −1.40 V for $[Co(TPP)_2](ClO_4)_2$ gave a value of 1.17 electrons transferred per

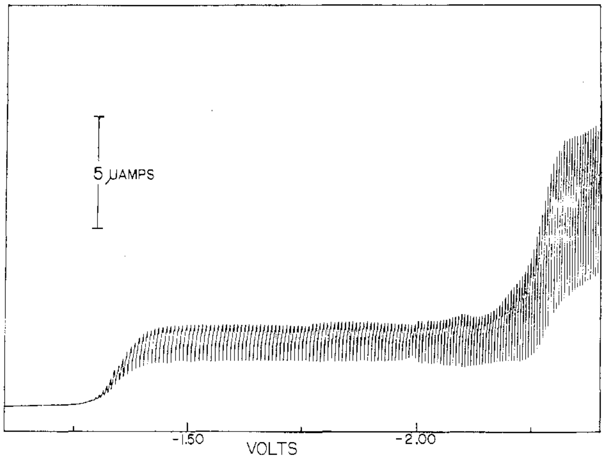

Figure 1. Reduction of $[Co(TPAs)_2](ClO_4)_2$ in acetonitrile at the DME.

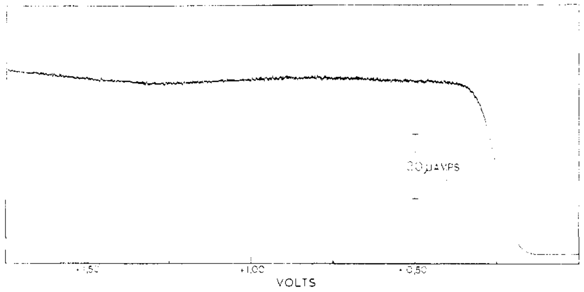

Figure 2. Oxidation of $[Co(TPAs)_2](ClO_4)_2$ in acetonitrile at the RPE.

$[Co(TPP)_2]^{2+}$. The solution became deep blue after it had been electrolyzed for about 30 s. Oxygen was allowed to enter the electrolytic cell after exhaustive electrolysis and the solution quickly reverted to its original light tan color. A polarographic reduction wave with the same height as that of the original solution was then obtained indicating that the reduction is chemically reversible. The determination by constant-potential electrolysis of the number of electrons transferred for $[Co(TPPO)_2](ClO_4)_2$ and $[Co(TPAs)_2](ClO_4)_2$ was not carried out; however the heights of their reduction waves (pilot-ion method) as well as their E vs. $\log[(i_d - i)/i]$ plots indicate a one-electron reduction.

There is only one reduction wave near −1.40 V for $[Co(TPAm)_2](ClO_4)_2$ at the DME. It is obscured by a maximum and plots of E vs. $\log[(i_d - i)/i]$ could not be used to determine the number of electrons transferred. The height of the reduction wave at the RPE is indicative of a two-electron transfer and at −1.55 V a deposit which is probably metallic cobalt was observed on the electrode surface. Cyclic sweep voltammetry with the SPE showed that the reduction was irreversible. Constant-potential current vs. time curves at −1.30, −1.45, and −1.50 V all indicated a two-electron transfer was occurring. No blue color indicative of a reduced complex species was observed at any time in the constant-potential reductions and it is likely that the reduction proceeds directly to Co(0) with the dissociation of the complex. Although an $E_{1/2}$ value at the DME could not be obtained, it does appear from a visual inspection of the polarogram that the $E_{1/2}$(DME) is anodic to the $E_{1/2}$(RPE) and a mercury-soluble product is indicated. Thus, the reduction can probably be expressed by

$$[Co(TPAm)_2]^{2+} \xrightarrow[\text{DME}]{+2e^-} Co^0(Hg) + 2TPAm$$

TPAm alone is not reduced in the potential range available (∼−2.5 V).

One well-defined oxidation wave at an RPE and an SPE was observed for the $[Co(TPX)_2](ClO_4)_2$ complexes in which TPX is TPAm, TPP, and TPAs (Figure 2). For the analogous TPPO complex, no oxidation was observed. The heights of the oxidation waves obtained with the RPE and SPE are comparable to those found for the one-electron reduction waves and thus are also one-electron transfers. Cyclic sweep voltammetry at the SPE indicated that the oxidations are reversible. None of the ligands alone gave any anodic current until approximately +0.50 V. The complete cyclic voltammogram at a SPE for $[Co(TPP)_2](ClO_4)_2$ is shown in Figure 3.

The $Co(TPX)(NO_3)_2$ complexes in which TPX is TPP, TPPO, and TPAs gave one reduction wave between −1.15 and −1.35 V at the DME or the RPE (Table II). A second wave of undetermined origin ($E_{1/2}$ = −1.86 V and i_d = 3.7 μA mmol^{-1}) for $Co(TPPO)(NO_3)_2$ was observed at the DME but

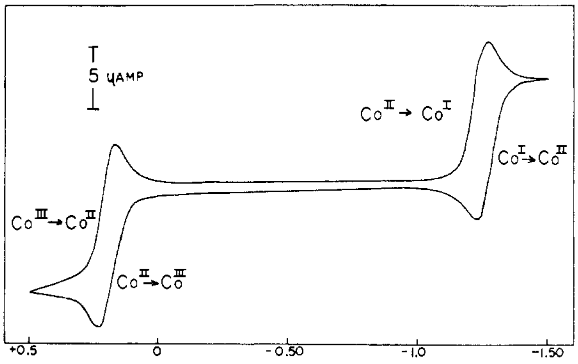

Figure 3. Cyclic-sweep voltammetry of $[Co(TPP)_2](ClO_4)_2$ in acetonitrile at the SPE.

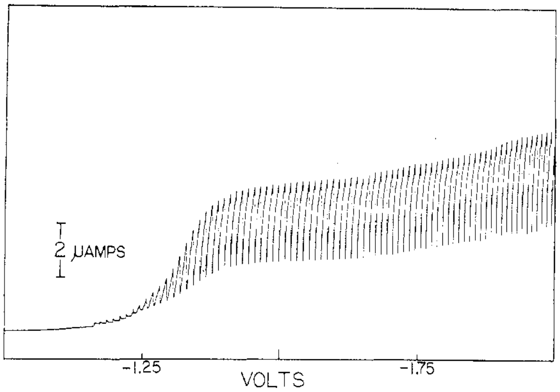

Figure 4. Reduction of $Co(TPAs)(NO_3)_2$ in acetonitrile at the DME.

Table II. Electrochemical Data for the $Co(TPX)(NO_3)_2$ Complexes in Acetonitrile[a]

Complex reactions[b]	DME		RPE		SPE[c]		
	$E_{1/2}$	i_d	$E_{1/2}$	i_l	$E_{1/2}$	E_p	i_p
$Co(TPAm)(NO_3)_2$	*d*						
$Co(TPP)(NO_3)_2$, $Co^{II} \rightarrow Co^{I}$	-1.27_5	5.7	−1.27	65	−1.27	−1.29	8.6
$Co(TPPO)(NO_3)_2$, $Co^{II} \rightarrow Co^{I}$	-1.15_5 −1.86	4.7 4	−1.25	79	−1.26	−1.30	9.2
$Co(TPAs)(NO_3)_2$, $Co^{II} \rightarrow Co^{I}$	−1.32	5.2	−1.35	79	−1.37	−1.41	7.0

[a] All E values in V are vs. Ag–Ag$^+$ (0.10 M) in acetonitrile; all i_d and i_l values are in μA mmol^{-1}. [b] The actual site of reduction is not known with certainity in these complexes and $Co^{II} \rightarrow Co^{I}$ is meant to imply only the formal oxidation state of the metal ion. [c] i_p is the peak current for a sweep rate of 8.3 mV s^{-1}; E_p is the peak potential; $E_{1/2} = E$ at $0.852i_p$ (see ref 17). [d] Maximum prevented analysis of wave.

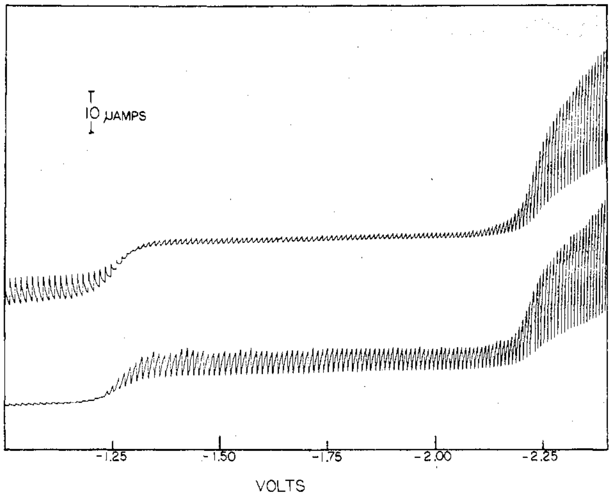

Figure 5. Polarogram of $Co(TPP)(NO_3)_2$ after the solution had been reduced at −1.40 V for 20 min (top) and after oxygen had diffused into the reaction cell (bottom).

not at the RPE. The drawn out appearance of the initial wave for all the complexes (Figure 4) indicates the reduction is not completely reversible. Cyclic sweep voltammetry at a sweep rate of 8.3 mV s^{-1} for $Co(TPP)(NO_3)_2$ did reveal some anodic current but the ratio of i_{p_a}/i_{p_c} was considerably less than unity indicating electrochemical irreversibility or a following chemical reaction. Two current vs. time curves at a constant potential of −1.40 V for $Co(TPP)(NO_3)_2$ gave a deep violet solution within 1 min and values of 1.17 and 1.15 electrons transferred per $Co(TPP)(NO_3)_2$ were obtained. A plot of i_d vs. $h^{1/2}$ and the measurement of i_d at an elevated temperature (45 °C) showed that this wave was diffusion controlled.

The nitrate ion was initially suspected to be involved in a following reaction and experiments in the presence of a large excess of nitrate ions were carried out. Increments of tetraethylammonium nitrate were successively added to a solution of $Co(TPP)(NO_3)_2$ and a polarogram was run after each addition. The $E_{1/2}$ value was increasingly shifted in a cathodic direction indicating that the nitrate ion is coordinated to the species undergoing reduction but the i_d was only slightly increased. Two current vs. time curves at a constant potential of −1.40 V obtained from a $Co(TPP)(NO_3)_2$ solution which was 0.10 M in both tetraethylammonium perchlorate and tetraethylammonium nitrate gave a linear relationship up to approximately 10 min after which the slope began to decrease. Integration of the equation $Q = \int_0^t i\,dt$ between $t = 0$ and the time the slope changed gave 0.87 and 1.02 electrons transferred per $Co(TPP)(NO_3)_2$. Integration of the equation between $t = 0$ and $t = \infty$ gave 1.03 and 1.13 electrons transferred per $Co(TPP)(NO_3)_2$. A deep violet color similar to that previously obtained for the reduction of $Co(TPP)(NO_3)_2$ in tetraethylammonium perchlorate was observed. After one of the above solutions had been electrolyzed for 20 minutes, a polarogram yielded anodic current (~1.0 μA) and a small amount of cathodic current (~0.2 μA) (Figure 5). Oxygen was allowed to diffuse into the electrolytic cell and the polarogram then showed no anodic current but the amount of cathodic current had increased to 1.1 μA. If the nitrate ion was involved in a following chemical reaction, it is unlikely that the amount of cathodic current would increase in the presence of such a large excess of nitrate ion.

The polarogram of $Co(TPAm)(NO_3)_2$ like that of $[Co(TPAm)_2](ClO_4)_2$ is obscured by a large maximum and an $E_{1/2}$ value could not be determined. Although current vs. time curves at −1.50 V gave results intermediate between a one- and two-electron transfer, no deep blue or deep violet color was observed.

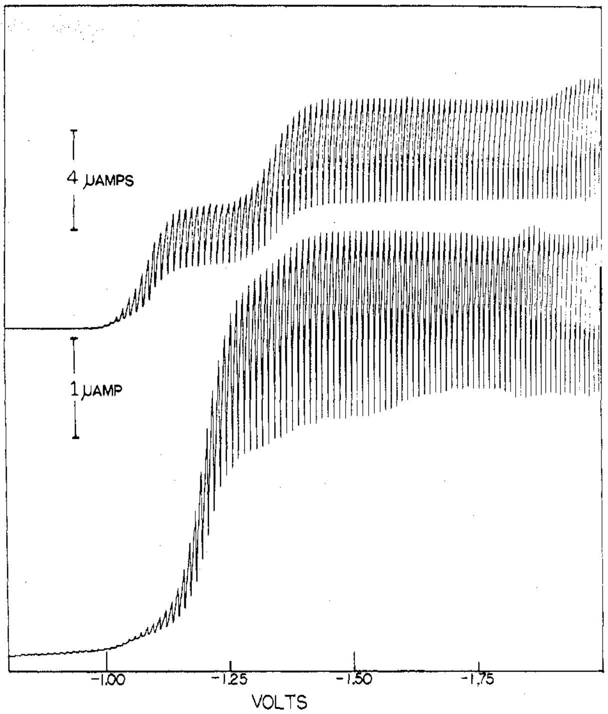

Figure 6. Reduction of a mixture of $[Co(TPPO)_2](ClO_4)_2$ and $[Co(TPAs)_2](ClO_4)_2$ (top) and reduction of the product from $Co(TPPO)(NO_3)_2$ plus TPAs (bottom) in acetonitrile at the DME.

None of the $Co(TPX)(NO_3)_2$ complexes gave any well-defined oxidation waves. Instead ill-defined waves at potentials anodic to +0.50 V with varying i_l appeared.

On the addition of TPX to an acetonitrile solution containing $Co(TPX)(NO_3)_2$, the resulting complexes exhibit electrochemical properties identical with those of $[Co(TPX)_2](ClO_4)_2$, indicating the reaction

$$Co(TPX)(NO_3)_2 + TPX \rightarrow [Co(TPX)_2](NO_3)_2$$

occurs. In the same manner, mixed complexes such as $[Co(TPX)(TPY)](NO_3)_2$ (TPX ≠ TPY) were prepared by the addition of either TPX to $Co(TPY)(NO_3)_2$ or TPY to $Co(TPX)(NO_3)_2$. A polarogram of a solution containing both $[Co(TPPO)_2](ClO_4)_2$ and $[Co(TPAs)_2](ClO_4)_2$, chosen because their $E_{1/2}$ values are the furthest apart, gave two reduction waves with the $E_{1/2}$ values corresponding to those expected for the separate complexes while a solution containing $[Co(TPPO)(TPAs)]^{2+}$ prepared as above gave only one reduction wave with an $E_{1/2}$ between those found for $[Co(TPPO)_2](ClO_4)_2$ and $[Co(TPAs)_2](ClO_4)_2$ (Figure 6). A plot of E vs. log $[(i_d - i)/i]$ for the reduction wave of the mixed complex gave a slope of 71 mV, indicative of a one-electron transfer.

The mixed complex from $Co(TPAs)(NO_3)_2$ and TPAm was also prepared and only one wave at the DME and at the RPE was seen. A plot of E vs. log $[(i_d - i)/i]$ gave a slope of 58 mV. Current vs. time curves at a constant potential of −1.45 V gave an average value of 1.17 electrons transferred per $[Co(TPAm)(TPAs)]^{2+}$. A deep blue color was obtained after the solution had been electrolyzed for approximately 30 s.

Discussion

The ligands tri(2-pyridyl)amine (TPAm), tri(2-pyridyl)phosphine (TPP), tri(2-pyridyl)phosphine oxide (TPPO), and tri(2-pyridyl)arsine (TPAs) form complexes with the composition $[M(TPX)_2](ClO_4)_2$ and $M(TPX)(NO_3)_2$ where M is Mn, Co, Ni, Cu, or Zn. Although the different ligand central atom has no effect on the mode of coordination of the ligand,[2,3] it does exhibit a strong influence on the electrochemical properties of the Co(II) complexes. For the $[Co(TPX)_2]^{2+}$ complexes with TPP, TPPO, and TPAs, a reversible one-electron reduction yields a species containing a formal Co(I) ion while, for the TPAm complex, an irreversible two-electron reduction yields metallic cobalt and free ligand.

The exact species present in an acetonitrile solution of $Co(TPX)(NO_3)_2$ is not known due to its relatively poor solubility. The complexes dissociate as a 1:1 electrolyte in this solvent[3] and the $E_{1/2}$ dependence on nitrate concentration suggests an equilibrium is established between the acetonitrile and the nitrate of the complex. The reducible species, however, behave in a similar manner to the $[Co(TPX)_2]^{2+}$ ion in that the TPP, TPPO, and TPAs complexes undergo slightly reversible one-electron reductions while the TPAm complex undergoes an irreversible two-electron reduction.

The one-electron reduction products are all highly colored (deep blue or violet) and the visible absorption spectrum of $[Co(TPP)_2]^{2+}$ has two intense bands at 1100 and 680 nm. The latter absorption corresponds closely to a $t_{2g} \rightarrow \pi^*$ metal-to-ligand charge-transfer band found in $Co^I(bpy)_3(ClO_4)$.[9]

Although the site of reduction, i.e., the metal ion or the ligand, is not known with certainty, clearly there is a difference in the ability of the ligands to yield a stable reduced species. The complexes of the ligand containing a central atom with no π-bonding capabilities (TPAm) do not yield a stable reduced species while the complexes of the ligands containing a central atom with π-bonding capabilities (TPP, TPPO, and TPAs) do. Using group theory arguments, it can be shown that the coordinated ligand with C_{3v} symmetry has orbitals available for $d\pi$–$p\pi$ bonding between the α carbon of the pyridyl rings and either the $d_{x^2-y^2}$, d_{xy} or the d_{xz}, d_{yz} orbitals on the ligand central atom. Cobalt(II) complexes of 2,2'-bipyridine (bpy), 1,10-phenanthroline (phen), and 2,2',2''-terpyridine (terpy) behave in a manner similar to TPP, TPPO, and TPAs in that these ligands stabilize formal low oxidation states of cobalt in addition to low oxidation states of other metals. It is generally concluded that the ability of bpy, phen, and terpy to stabilize low oxidation states of metals arises from their ability to accept electron density via a $t_{2g} \rightarrow \pi^*$ back-bonding mode.[13] However, pyridine also has this mode of back bonding available but there are no reports of pyridine stabilizing low oxidation states of metals. bpy, phen, and terpy contain the 2,2'-diimine chromophore which allows further electron delocalization not available in pyridine. Likewise TPP, TPPO, and TPAs contain a central atom capable of $d\pi$–$p\pi$ bonding which may allow delocalization not available in TPAm.

The $[Co(TPX)_2]^{2+}$ species in which TPX is TPAm, TPP, or TPAs undergo a reversible oxidation at a RPE or SPE between +0.10 and +0.25 V. The heights of the oxidation waves at the RPE are approximately the same as those for the one-electron reductions. None of the ligands alone gave any anodic current until approximately +0.50 V. TPAm is oxidized near +1.0 V while the other ligands yield only ill-defined waves of varying current. Thus, the oxidations are probably due to Co(II) → Co(III) although, in the absence of supporting data, the site of oxidation cannot be definitely stated. The $[Co(TPPO)_2]^{2+}$ complex did not give an oxidation wave in a similar potential region.

None of the $Co(TPX)(NO_3)_2$ complexes gave any well-defined oxidation waves. Instead ill-defined waves at potentials anodic to +0.50 V with varying limiting currents were obtained and their origin is uncertain.

The addition of free ligand to an acetonitrile solution of $Co(TPX)(NO_3)_2$ gave a product with the same oxidation–reduction properties as the $[Co(TPX)_2]^{2+}$ species. Likewise, the addition of excess TPY to $Co(TPX)(NO_3)_2$ (TPY is different from TPX) produced mixed complexes. The $E_{1/2}$ values for the oxidation–reduction reactions of the mixed complexes in most cases are between the $E_{1/2}$ values of the two individual complexes. For example, a solution containing $[Co(TPPO)_2]^{2+}$ and $[Co(TPAs)_2]^{2+}$ gave two reduction waves[19] while the mixed complex prepared by the addition of either TPPO to $Co(TPAs)(NO_3)_2$ or TPAs to $Co(TPPO)(NO_3)_2$ gave only one reduction wave.

The complex obtained from $Co(TPAs)(NO_3)_2$ and TPAm yielded a one-electron reduction product as shown by constant-potential electrolysis and a plot of E vs. $\log [(i_d - i)/i]$. In the constant-potential electrolysis experiment, a deep blue color characteristic of the reduced species was observed. If the solution contained $[Co(TPAm)_2]^{2+}$ and $[Co(TPAs)_2]^{2+}$ as might be inferred from the work of McWhinnie et al.[15] rather than $[Co(TPAm)(TPAs)]^{2+}$, 1.5 electrons per Co(II) in the constant-potential electrolysis and a maximum due to $[Co(TPAm)_2]^{2+}$ at the DME should have been observed. In fact neither was observed lending support to the suggestion of the mixed complexes. The results also point out that only one of the two coordinated ligands need contain a central atom with π-bonding capabilities in order to stabilize a reduced species.

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Registry No. $[Co(TPAm)_2](ClO_4)_2$, 15746-81-3; $[Co(TPP)_2](ClO_4)_2$, 38979-66-7; $[Co(TPPO)_2](ClO_4)_2$, 57842-84-9; $[Co(TPAs)_2](ClO_4)_2$, 57842-86-1; $Co(TPAm)(NO_3)_2$, 57842-87-2; $Co(TPP)(NO_3)_2$, 57842-88-3; $Co(TPPO)(NO_3)_2$, 57842-89-4; $Co(TPAs)(NO_3)_2$, 57842-90-7; $[Co(TPPO)(TPAs)]^{2+}$, 57842-80-5; $[Co(TPAm)(TPAs)]^{2+}$, 57842-81-6.

References and Notes

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(19) The Co(II) ion (d^7) must be labile, yet in acetonitrile, ligand exchange did not occur within several hours as evidenced by the two polarographic waves. Since the ligand is tridentate, it would be unlikely that all three donor atoms would be removed from the Co(II) simultaneously, a condition necessary for exchange.