butyldichlorostibine, methylstibine, ethylstibine, and *n*-butylstibine are described in an earlier publication.[12]

$SbCl_3$ (Alfa) was used as obtained. The organosilicon halides (Alfa) were fractionally distilled before use. Alkylstibines were stored at −196 °C and transferred into reaction tubes on an all-glass vacuum line of standard design as quickly as possible to reduce loss by decomposition. The benzene and carbon tetrachloride employed in all studies were spectrograde and were freshly distilled from molecular sieve. Before each experiment, benzene was degassed thoroughly by repeated freeze–pump–thaw cycles.

IR spectra were recorded on a Perkin-Elmer 221G spectrophotometer using a 10-cm path length gas cell fitted with NaCl windows. NMR spectra were recorded on a Perkin-Elmer R20B spectrometer in sealed 5-mm tubes. All NMR chemical shifts are referred to benzene ($Me_4Si = \delta\ 0.00$) which was the solvent in all NMR studies. Mass spectra were recorded on a Du Pont 21-492 spectrometer at 70 eV at 2×10^{-6} mmHg. Elemental analyses were performed by either Integral Analytical Laboratory, Raleigh, N.C., or Schwarzkopf Microanalytical Laboratory, Woodside, N.Y.

Reactions of Alkylstibines with Iodine Sources. In all cases, a 0.5 M solution of the halogen-containing reactant in benzene was introduced into a medium-wall 5-mm o.d. NMR tube and thoroughly degassed by repetitive freeze–pump–thaw cycles. The alkylstibine was condensed into the NMR tube so that the $RSbH_2$:reactant ratio was 2:1. The NMR tube was then sealed on the vacuum line. Solid products were isolated by opening the tubes on the vacuum line and removing volatile materials by distillation. With I_2, ICl, CI_4, and dimethyliodoarsine, the major antimony-containing reaction products are $RSbI_2$ (identified by ^1H NMR) and $RSbI_{0.4}$, the former being a yellow solid readily soluble in common organic solvents and the latter being an involatile purple-black solid insoluble in the same solvents.

For $RSbI_{0.4}$ the analytically determined R:Sb:I ratio of 1:1:0.4 was nearly constant despite variations in R group and molar ratio of reactants. (Anal. Calcd for $CH_3I_{0.4}Sb$: C, 6.40; H, 1.61; I, 27.07; Sb, 64.92. Found: C, 6.29; H, 1.57; I, 27.37; Sb, 65.09. These data are typical of all results.) The mass spectrum of $EtSbI_{0.4}$ curiously shows no fragments containing both iodine and more than one antimony atom. At 70 eV and 350 °C, the major peaks correspond to $(EtSb)_n^+$, $n = 2$–4.

Reaction of Alkylstibines with Organosilicon Chlorides. Equimolar ratios of alkylstibine and $(CH_3)_2SiCl_2$, $(CH_3)_3SiCl$, or $(C_6H_5)_3SiCl$ were combined as 10% solutions in benzene and monitored by ^1H NMR spectroscopy. In all cases a pale greenish purple, metallic-looking solid, $(RSb)_x$, was found. (Anal. Calcd for CH_3Sb: C, 8.77; H, 2.19. Found: C, 8.51; H, 2.16. Calcd for C_2H_5Sb: C, 15.93; H, 3.34. Found: C, 15.76; H, 3.29. Calcd for C_4H_9Sb: C, 26.85; H, 5.07. Found: C, 26.31; H, 4.94.)

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Registry No. $(CH_3Sb)_x$, 62173-60-8; $(C_2H_5Sb)_x$, 68781-08-8; $(C_4H_9Sb)_x$, 68781-10-2; CH_3SbH_2, 23362-09-6; $C_2H_5SbH_2$, 68781-03-3; n-$C_4H_9SbH_2$, 68781-04-4; $(CH_3)_2SiCl_2$, 75-78-5; $(CH_3)_3SiCl$, 75-77-4; $(C_6H_5)_3SiCl$, 76-86-8; $MeSbI_2$, 30982-87-7; $EtSbI_2$, 68781-05-5; I_2, 7553-56-2; ICl, 7790-99-0; CI_4, 507-25-5; $(CH_3)_2AsI$, 676-75-5; CH_3AsCl_2, 593-89-5; $(CH_3As)_x$, 26403-94-1; CH_3SbCl_2, 42496-23-1; $C_2H_5SbCl_2$, 68781-06-6; $C_4H_9SbCl_2$, 5613-73-0.

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Electrochemistry of Iminodiacetate Complexes of Cobalt at Stationary Electrodes

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The redox behavior of *cis*- and *trans*-bis(iminodiacetato)cobaltate(III) has been studied in aqueous solution at stationary electrodes. The cis complex exhibits quasi-reversible behavior and a reduction potential estimated to be +0.36 V vs. the SHE. The trans isomer, however, exhibits more complex behavior, and upon reoxidation the cis isomer of the Co(III) system forms quantitatively. The results can be interpreted in terms of a model in which the cis isomer of the Co(II) system is the more stable and forms to the virtual exclusion of the corresponding trans species, whereas the trans species is preferred in the case of Co(III). The model also neatly rationalizes the synthetic methods which have been used to prepare the cis and trans isomers of the Co(III) complex. In addition, according to this model, an upper limit of 0.17 V vs. the SHE can be assigned to the reduction potential of the trans system. Finally, complications which occur in studying the complex at a mercury electrode are discussed, and conditions are described under which these effects are minimized.

Introduction

Two isomeric forms of a 2:1 complex of the iminodiacetate ligand with Co(III) have been characterized.[1] Both complexes are pseudooctahedral with the ligands coordinated on opposite triangular faces. The structures are distinguished by the relative disposition of the nitrogen donors. In one structure the nitrogens coordinate in a cis fashion and in the other trans. We became interested in the redox properties of *cis*- and *trans*-bis(iminodiacetato)cobaltate(III), denoted *cis*-$Co(IDA)_2^-$ and *trans*-$Co(IDA)_2^-$, respectively, when we found that these

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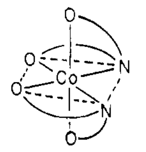
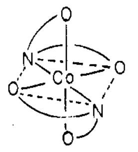


cis



trans

systems are reduced in solution by bis(2,9-dimethyl-1,10-phenanthroline)copper(I) in a photochemical reaction.[2] The half-wave potentials of *cis*- and *trans*-$Co(IDA)_2^-$ had been estimated by polarographic measurements and were reported to be +0.40 and +0.29 V vs. SHE, respectively.[3] However, we have investigated these systems by cyclic voltammetry, observing both the cathodic and anodic reactions at a hanging mercury drop electrode (HMDE), and have found that these systems exhibit rather complex behavior. In particular, we find that on the time scale of this method an equilibrium between the cis and trans isomers of the Co(II) system is established and that the anodic process virtually always leads to *cis*-$Co(IDA)_2^-$. When a mercury electrode is used, a chemical reaction between the mercury and the $Co(IDA)_2^-$ complexes complicates the analysis, but experimental conditions are described under which this effect is minimized.

Experimental Section

Preparation of Complexes. The cis and trans isomers of $K[Co(IDA)_2]$ were prepared by a variation of the method of Tsuchida.[4] An 8.0-g quantity of iminodiacetic acid (Matheson Coleman and Bell) was dissolved in 50 mL of water, and 12.0 g of KOH (Mallinckrodt, reagent grade) was added. To prepare the cis complex the ligand solution was cooled in an ice bath, and 6.0 g of powdered $CoCl_2{\cdot}6H_2O$ (Mallinckrodt, reagent grade) was added. The mixture was stirred, and 8 mL of 30% hydrogen peroxide was added dropwise. The reaction mixture was then refrigerated, and after several hours purple crystals were collected and then recrystallized from warm water. The synthesis of the trans isomer was similar except that the ligand mixture was warmed to 60 °C before the addition of cobalt chloride. Hydrogen peroxide was then added dropwise, and the solution was stirred for 10 min and then refrigerated overnight. The crude product, which contained both the cis and trans isomers, was collected, dissolved in a minimum of warm water, and heated to 85 °C in the presence of activated charcoal for 1 h. The charcoal was removed by filtration, and the solution refrigerated to induce precipitation. Brown needles containing the trans isomer were collected and purified by successive recrystallizations.

Cyclic Voltammetry. All cyclic voltammograms were determined in a conventional three-compartment cell using a Bioanalytical Systems cyclic voltammetry unit and a Hewlett-Packard 7015B X-Y recorder. The supporting electrolyte was 0.10 M KNO_3, and a Ag/AgCl electrode was used as the reference electrode. For the sake of clarity, however, all potentials are quoted relative to the standard hydrogen electrode (SHE). A Brinkman Metrohm hanging mercury drop electrode or a carbon-paste electrode was used as the working electrode. Freshly prepared solutions were used in all experiments described because it was noted that after standing several hours $Co(IDA)_2^-$ solutions exhibited additional anodic and cathodic peaks at higher potentials, which were probably associated with decomposition products. A scan rate of 200 mV/s was usually employed, and all solutions were deaerated with nitrogen. An eightfold excess of ligand was added to all solutions to ensure complexation of the Co(II) species and to mildly buffer the system at pH 7.0.[5]

Coulometry. Controlled-potential electrolysis of *trans*-$Co(IDA)_2^-$ was carried out at a Hg pool electrode using a Bioanalytical Systems potentiostat and a Ag/AgCl reference electrode. The auxiliary electrode consisted of a Pt wire in supporting electrolyte solution joined to the system via a KNO_3 salt bridge. The electrolysis was performed under a continuous stream of nitrogen, and current vs. time data were recorded using an electronic integrator. Supporting electrolyte background current was found to be negligible. Changes in the composition of the solution following bulk oxidation or reduction were monitored using a McPherson EU-700-D UV–vis spectrophotometer.

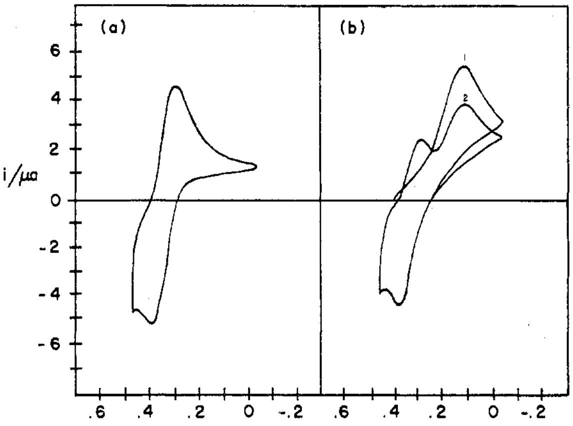


Figure 1. Cyclic voltammograms at a HMDE and at a scan rate 0.2 V s^{-1} of (a) 2.0 mM *cis*-$KCo(IDA)_2$/16 mM IDA^{2-} and (b) 2.0 mM *trans*-$KCo(IDA)_2$/16 mM IDA^{2-} in 0.1 M KNO_3. Scans were begun at +0.45 V vs. SHE and swept cathodically.

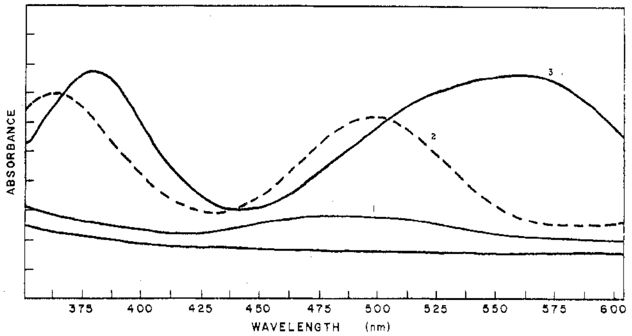


Figure 2. UV–vis absorption spectra of 3 mM *trans*-$KCo(IDA)_2$ in 0.1 M KNO_3 after reduction at +0.02 V vs. SHE (1), before electrolysis (2), and after reoxidation at +0.42 V (3). The lowest curve is the baseline.

Potentiometry. Potentiometric determination of the $Co(IDA)_2^{2-}/Co(IDA)_2^-$ reduction potential was made by measuring the potentials of solutions containing different concentration ratios of $Co(IDA)_2^{2-}/Co(IDA)_2^-$ using a carbon-rod electrode referenced to a Ag/AgCl electrode. To ensure that stable potential values were obtained, the potential was monitored using a Hewlett-Packard 7015B X-Y recorder in the time base mode. Both the initial Co(II) solution and the initial Co(III) solution used contained a 50% excess of ligand. The pH of each was adjusted to 7.0, and the ionic strength was set to 0.12 by the addition of KNO_3.

Results and Discussion

The cyclic voltammogram of 2 mM *cis*-$Co(IDA)_2^-$ and 16 mM IDA^{2-} in aqueous solution is presented in Figure 1a and shows the system to be quasi-reversible having a peak separation of 100 mV. Two successive scans of the cyclic voltammogram of the trans isomer are depicted in Figure 1b. During the first scan, a cathodic feature appears at +0.13 V vs. SHE, and an anodic feature is observed at +0.41 V. On the second scan the previous cathodic feature appears with diminished intensity, and a new cathodic feature appears at +0.31 V. The anodic feature and the cathodic feature which grows in occur at the same potentials as those seen in Figure 1a, suggesting that the reduced form of *trans*-$Co(IDA)_2^-$ rapidly isomerizes to the corresponding cis isomer and that *cis*-$Co(IDA)_2^-$ is formed at the electrode upon reoxidation. Sweep rates of up to 30 V/s were used, but no additional anodic features were observed.

To establish that isomerization does in fact occur during the electrochemical redox process, bulk electrolysis of aqueous *trans*-$Co(IDA)_2^-$ was carried out at a Hg pool electrode and the reaction was followed spectrophotometrically. Figure 2 shows the UV–vis spectrum of an initial 3 mM solution of the trans isomer, along with the spectra of the solution following reduction at +0.02 V and reoxidation at +0.42 V. As ex-

Table I. Estimated Formal Potentials (V vs. SHE) for the $Co(IDA)_2^-/Co(IDA)_2^{2-}$ Couples

isomeric form	E^a	E^b
cis	0.36	0.40
trans	⩽0.17	0.29

[a] Determined by cyclic voltammetry; this work. [b] Determined by polarography.[3]

pected, the absorption spectrum of *trans*-$Co(IDA)_2^-$ is lost upon reduction. After reoxidation, new absorption maxima appear at 380 and 560 nm, which are characteristic of the *cis*-$Co(IDA)_2^-$ species.[1] For the reduction process the change in concentration of *trans*-$Co(IDA)_2^-$ was calculated from the absorbance change, and the number of electrons transferred was determined by integrating the current over time. From these data the value of n, the number of faradays transferred per mole of *trans*-$Co(IDA)_2^-$ reduced, was found to be 0.98.

Having established that the trans to cis isomerization occurs upon reducing *trans*-$Co(IDA)_2^-$, we propose the following scheme of reactions to explain the cathodic ($E_{p,c}$) and anodic ($E_{p,a}$) peaks observed in the cyclic voltammogram of Figure 1b:

$$trans\text{-}Co(IDA)_2^- \xrightarrow{e^-} trans\text{-}Co(IDA)_2^{2-} \quad E_{p,c} = +0.13\ V$$

$$trans\text{-}Co(IDA)_2^{2-} \xrightarrow{fast} cis\text{-}Co(IDA)_2^{2-}$$

$$cis\text{-}Co(IDA)_2^{2-} \xrightarrow{-e^-} cis\text{-}Co(IDA)_2^- \quad E_{p,a} = +0.41\ V$$

$$cis\text{-}Co(IDA)_2^- \xrightarrow{e^-} cis\text{-}Co(IDA)_2^{2-} \quad E_{p,c} = +0.31\ V$$

Consistent with the fact that no anodic wave attributable to the oxidation of *trans*-$Co(IDA)_2^{2-}$ is observed, spectral analysis of the electrolysis experiment reveals that negligible, if any, quantities of *trans*-$Co(IDA)_2^-$ are formed upon oxidizing a solution of $Co(IDA)_2^{2-}$. Therefore, practically speaking, the transformation of *trans*-$Co(IDA)_2^{2-}$ to the cis isomer would appear to be quantitative. The potential of the *cis*-$Co(IDA)_2^-$/*cis*-$Co(IDA)_2^{2-}$ couple can therefore be estimated from the value of $(E_{p,a} + E_{p,c})/2$, but no analogous calculation is possible for the trans couple. It is, however, possible to assign an upper limit to the potential of the trans couple from the $E_{p,c}$ values associated with the *cis*-$Co(IDA)_2^-$ and *trans*-$Co(IDA)_2^-$ species and from the estimated potential of the cis couple. Subtraction of the voltage difference between the two $E_{p,c}$ values from the estimated potential of the cis couple predicts a value of 0.17 V vs. SHE for the potential of the trans couple. However, the Nernst equation reveals that the depletion of the reduction product of the trans system should facilitate the reduction process; thus the $E_{p,c}$ value for the trans couple should be *anodic* of the value that would be observed if no isomerization of *trans*-$Co(IDA)_2^{2-}$ occurred. We therefore regard 0.17 as an upper limit to the intrinsic potential of the trans system.[7] The potentials are summarized in Table I.

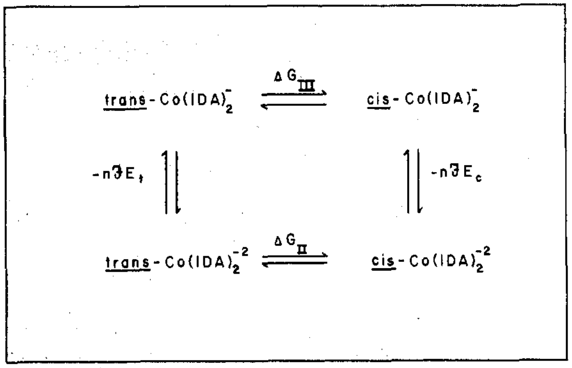


Figure 3. Scheme relating cis and trans isomers of $Co(IDA)_2^-$ and $Co(IDA)_2^{2-}$. E_t and E_c denote the potentials for the trans and cis couples, respectively.

As we will show, the potentials we report in the table are consistent with the fact that no anodic peak is observed for the oxidation of *trans*-$Co(IDA)_2^{2-}$. In principle both the oxidized and reduced forms of the cobalt complexes will consist of an equilibrium mixture of the cis and trans isomers, eq 1 and 2. Studies by Cooke[1] indicate that at equilibrium the

$$trans\text{-}Co(IDA)_2^{2-} \underset{}{\overset{K_{II}}{\rightleftharpoons}} cis\text{-}Co(IDA)_2^{2-} \qquad (1)$$

$$trans\text{-}Co(IDA)_2^- \underset{}{\overset{K_{III}}{\rightleftharpoons}} cis\text{-}Co(IDA)_2^- \qquad (2)$$

Co(III) system consists of 79% trans isomer and 21% cis so that we may calculate that $K_{III} = 0.27$ and that ΔG_{III}, the free energy change associated with the trans to cis isomerization of the Co(III) system, is +3.2 kJ mol^{-1}. We can estimate the upper limit of ΔG_{II}, the corresponding free energy change associated with the Co(II) system, from the thermodynamic cycle depicted in Figure 3, and we calculate that ΔG_{II} is less than or equal to −15.1 kJ mol^{-1}. (That it is possible only to set an upper limit on the value of ΔG_{II} is a direct result of the fact that we are only able to set an upper boundary on the value of the reduction potential.) This predicts that K_{II} is greater than or equal to 470, suggesting that the formation of the cis isomer is essentially quantitative in the case of the labile Co(II) system. Consistent with this result, the cyclic voltammogram of a pH 7 solution containing 2 mM Co(II) and 20 mM IDA^{2-} ligand gave a current vs. potential profile identical to that presented in Figure 1a. That the cis configuration is strongly favored for the Co(II) system will also rationalize the synthetic methods developed for the isomers.[4] When the preparation, which involves the oxidation of the Co(II) system, is performed at 0 °C, the product is almost exclusively the cis isomer of Co(III). If the preparation is carried out at 60 °C, however, the trans complex can be isolated. The observed products are understandable if *cis*-$Co(IDA)_2^-$ is the predominant species formed by chemical oxidation of the Co(II) system and the formation of significant quantities of *trans*-$Co(IDA)_2^-$ occurs via a thermal isomerization of the Co(III) system.[8]

The above analysis tacitly assumes that the overpotentials for the electron-transfer reactions of the cis and trans isomers have comparable magnitudes. It must be admitted, however, that the preferential formation of *cis*-$Co(IDA)_2^-$ in the anodic process could also be explained if the charge-transfer process of the trans species is significantly *more irreversible* than that of the cis species. If so, then the anodic wave associated with *trans*-$Co(IDA)_2^{2-}$ could in fact be anodic of that associated with *cis*-$Co(IDA)_2^{2-}$ and located beyond the accessible potential range. Evidently no estimate of the potential for the trans couple could be made in this case. Although conclusive evidence that distinguishes between the two explanations is lacking, the model based on the proposal that *cis*-$Co(IDA)_2^{2-}$ forms quantitatively seems the more likely. The Co(II) and Co(III) ions differ markedly in size, and therefore it is quite reasonable to suppose that an appreciably different isomer distribution may occur in the complexes. Moreover, in our photostudies of the reduction of the *cis*- and *trans*-$Co(IDA)_2^-$ systems, no evidence for unusual kinetic effects of *trans*-$Co(IDA)_2^-$ was observed.[2b]

Another interesting phenomenon was observed in the course of our electrochemical studies. For solutions containing no excess ligand, if the scan was begun soon after introducing a fresh drop of mercury, a very intense cathodic current was observed at potentials negative of those in Figure 1 for solutions of either isomer of $Co(IDA)_2^-$. In general, the intense signal disappeared after one or two scans until only the peaks characteristic of the cis and/or trans systems described previously were present. If at this point, however, fresh Hg was exposed to the solution by increasing the size of the Hg drop, the large cathodic response reappeared. When the Hg drop was aged several minutes in the solution before turning on the electrode, the intense peak was not observed. Moreover, the intense feature was never observed in experiments involving solutions of the Co(II) system, nor did it appear in solutions of the Co(III) system which contained added IDA^{2-} ligand. (The intense cathodic wave was unaffected, however, by the addition of $Co(NO_3)_2{\cdot}6H_2O$ to solutions of $Co(IDA)_2^-$.)

Any discussion of this intense cathodic wave must account for the following observations: (1) no correspondingly intense anodic feature is found in the observable potential range, (2) the cathodic current observed is much too large to involve a diffusion-limited electrode process, and (3) the wave is absent when the iminodiacetate ligand is readily accessible in solution.

For the present we will describe the intense cathodic wave as a process in which a species Ox is reduced to give a product Red. It is apparent from point (1) that, following the reduction, Red undergoes a chemical reaction and is thereby changed into a product which is not accessed by the electrode in the potential range studied. The following scheme summarizes these steps:

$$\mathrm{Ox} \xrightarrow{+ne^-} \mathrm{Red} \xrightarrow{\text{fast}} \text{products}$$

From point (2) it is apparent that the species Ox adsorbs or adheres in some way to the electrode surface so that its local concentration is quite high at the double layer. The first possibility for Ox that we considered was adsorbed $Co(IDA)_2^-$. Our thinking was prompted by Anson's study of $Co(EDTA)^-$ in which, using potentiostatic current integration techniques, he suggested that $Co(EDTA)^-$ extensively adsorbs at Hg.[9] The structural similarity between $Co(EDTA)^-$ and the $Co(IDA)_2^-$ systems stimulated this reasoning. We considered that the absence of the intense cathodic wave in the presence of excess ligand could be explained if the ligand adsorbed preferentially. The species Red would then be $Co(IDA)_2^{2-}$, and the chemical reaction that followed the reduction of adsorbed $Co(IDA)_2^-$ would be dissociation of ligand from the labile Co(II) center to give a cobalt species, e.g., $Co(OH_2)_6^{2+}$, that was electrochemically inactive in the accessible potential range. The driving force for the dissociation would be the adsorption of ligand at the electrode. The fact that the intense cathodic wave was absent on aging the drop in solutions of $Co(IDA)_2^-$ could be explained if a direct *chemical* reaction took place between $Co(IDA)_2^-$ and Hg, producing the labile Co(II) center. Indeed, we showed that such a reaction does occur by stirring a deaerated solution of *cis*-$Co(IDA)_2^-$ over a pool of Hg for several hours and analyzing for Co(II) spectrophotometrically.[10] The above explanation hinges on the postulate that the ligand adsorbs preferentially. However, measurements of the electrocapillary curve of IDA^{2-} at pH 7.0 revealed no obvious specific interaction between the ligand and Hg, indicating Ox could not be adsorbed $Co(IDA)_2^-$.[11]

If Ox is not $Co(IDA)_2^-$, it has to be an oxidized form of Hg, since no other reducible species could be present. (Oxidized Hg is formed, of course, in the relatively slow, direct chemical reaction between Hg and $Co(IDA)_2^-$ discussed above.) That this is the case is shown by studies of aqueous solutions of $Hg(NO_3)_2$ in 0.1 M KNO_3. As seen in Figure 4, an intense cathodic wave (similar to that described for *cis*- and *trans*-$Co(IDA)_2^-$) is present in these solutions. It presumably corresponds to adherent Hg(I) salts which are formed in a chemical reaction between Hg(II) and Hg. Such salts are known to be relatively insoluble and might be expected to deposit at the electrode. Interestingly, the addition of the iminodiacetate ligand tends to suppress this wave in the Hg(II) solutions as well, leaving only the cyclic voltammogram of the reversible Hg(II)/Hg(I) couple which, incidentally, exhibits peak potentials ($E_{p,a}$ = +0.33 V and $E_{p,c}$ = +0.27 V) quite distinct from those of the cobalt systems. Apparently, the ligand effects the dissolution of the adherent Hg(I) species or supresses its formation. In any case, when ligand is available to suppress the Hg(I) species, there should be minimal interference with the electrode reactions of $Co(IDA)_2^-$, which explains why under certain conditions the appearance of the intense cathodic wave does not complicate the results. For example, when the Hg drop is aged in $Co(IDA)_2^-$ solutions, the iminodiacetate ligand becomes accessible because labile $Co(IDA)_2^{2-}$ is generated in the chemical reaction between Hg and $Co(IDA)_2^-$. A likely explanation for the fact that no correspondingly intense anodic wave is observed following the reduction of the adherent Hg(I) salts is that the Hg formed can be expected to dissolve in the electrode.

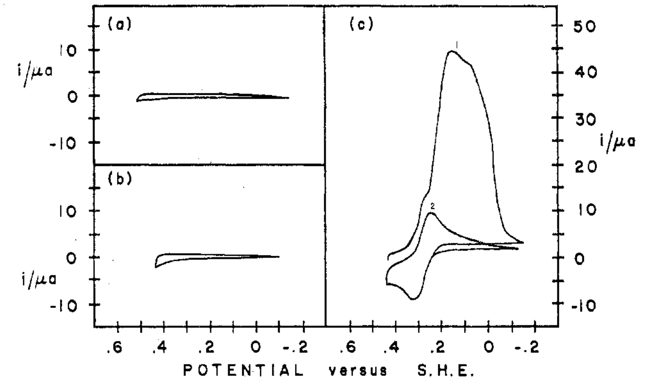


Figure 4. Cyclic voltammograms at a HMDE and at a scan rate of 0.2 V s^{-1} of (a) 0.1 M KNO_3 supporting electrolyte, (b) 0.020 M H_2IDA in 0.1 M KNO_3, and (c) 2 mM $Hg(NO_3)_2$/20 mM IDA^{2-} in 0.1 M KNO_3 (first scan, 1; second scan, 2). Scans were begun at +0.45 V vs. SHE shortly after introducing a fresh Hg drop. Scans of the mercury solution begun after a 2-min aging of the Hg drop are identical with scan 2 of (c).

Because of the complicating chemical reaction observed between $Co(IDA)_2^-$ and the Hg electrode, it has been of interest to determine the potential of the cobalt system at a chemically inert electrode. Attempts to measure the cyclic voltammograms of $Co(IDA)_2^-$ using platinum and gold electrodes have proved unsuccessful because of the highly irreversible nature of the charge-transfer reactions. Oxidation waves at these electrodes have not been observed, presumably because they occur beyond the limits imposed by the supporting electrolyte. Use of a carbon-paste electrode gives more satisfactory results, $(E_{p,a} + E_{p,c})/2$ = +0.35 V for the cis system, although pronounced irreversibility is indicated by the large peak separation of 1.75 V. By employment of potentiometric methods, the potential of the cis cobalt system could also be measured at a carbon-rod electrode. The results of this determination are shown in Figure 5 which is a plot of measured potential E vs. log ([Co(II)]/[Co(III)]). From the Nernst equation, $E = E^\circ - 0.059 \log ([\mathrm{Co(II)}]/[\mathrm{Co(III)}])$, the curve should be linear with a slope of −0.059 and y intercept of E°, the formal reduction potential. Linear regression analysis of the data gives a slope of −0.060 and a y intercept of +0.33 V (r = 0.97). Allowing for problems of overpotential and considering that different adsorption effects may be occurring at the different electrodes, there is reasonable agreement between the carbon-paste results of +0.35 V, the carbon-rod results of +0.33 V, and the mercury results of +0.36 V. The accord among the results obtained using different electrodes is gratifying and supports the validity of

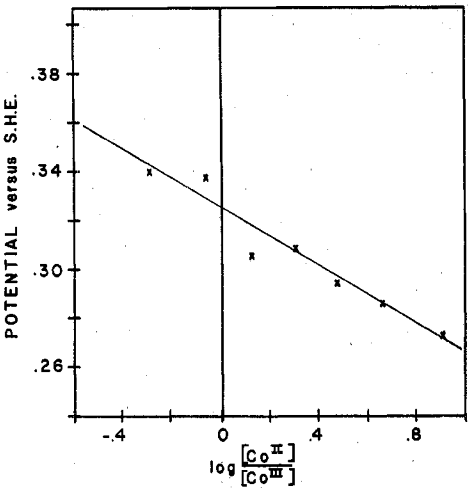


Figure 5. Plot of potential (*E*) measured at a carbon-rod electrode vs. log ([Co(II)]/[Co(III)]).

our conclusions based on the studies at the mercury electrode.

Before concluding, we should comment about the differences between the potentials determined by Gouzerh and those reported herein. (See the table.) Gouzerh noted that the values he reported were only approximate[3] because of anomalies in the polarograms which may in part be related to the $Co(IDA)_2^-/Hg$ reaction described above. Another consideration is that the polarographic work was carried out at pH 5,[3] and we have found that the $Co(IDA)_2^{2-}$ complex is substantially hydrolyzed at this pH. In fact, an *anodic* shift in the half-wave potential is expected if the reduction product is consumed in a follow-up chemical reaction as discussed previously in connection with the reduction of *trans*-$Co(IDA)_2^-$. Since the above complications have been obviated in our experiments, we suggest that the potentials reported herein are the more reliable.

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Registry No. *trans*-$Co(IDA)_2^-$, 33848-79-2; *trans*-$Co(IDA)_2^{2-}$, 68831-75-4; *cis*-$Co(IDA)_2^{2-}$, 68831-76-5; *cis*-$Co(IDA)_2^-$, 21718-59-2.

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(5) By use of β_1 and β_2 for the formation of $Co(IDA)_2^{2-}$ from Martell,[6] calculations show that at pH 7, 10 molar equiv of ligand leads to a greater than 95% complexation of Co(II) as the bis(ligand) complex.
(6) Martell, A. E.; Smith, R. M. "Critical Stability Constants"; Plenum: New York, 1974; Vol. 1, p 118.
(7) We are indebted to a referee for bringing this point to our attention.
(8) We should comment on possible temperature effects. Cooke determined K_{III} at room temperature, taking advantage of the fact that the isomerization at Co(III) is base catalyzed.[1] Therefore, *trans*-$Co(IDA)_2^-$ is indeed the favored isomer of Co(III) under ambient conditions. Also, since the absorption spectrum of a $Co(IDA)_2^{2-}$ solution is essentially independent of temperature in the range +15 to 50 °C, it is unlikely that the high-temperature synthesis yields *trans*-$Co(IDA)_2^-$ because of a change in the equilibrium distribution of the Co(II) isomers.
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Catalysis in Substitution on Ruthenium(III) by Iodide

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The kinetics of replacement of water by iodide on *trans*-$[Ru(NH_3)_4(isn)H_2O]^{3+}$ (isn = isonicotinamide) have been studied in 0.1 M acid at 25 °C (reaction 1). In contrast to anation by chloride and bromide, which proceeds with simple first-order dependence on halide, the rate of iodide anation is given by $-d \ln [Ru^{III}H_2O]/dt = k_a[I^-]^{5/2}[I_3^-]^{-1/2} + k_b[I^-]^2$. The first term arises from catalysis of substitution by $[Ru(NH_3)_4(isn)H_2O]^{2+}$ which is maintained at equilibrium with aquoruthenium(III), I^-, and I_3^-. The second term is believed to indicate a presubstitution electron transfer ($I^- \rightarrow$ Ru(III)) not involving production of free iodine. The data give a value of 0.20 ± 0.04 $M^{-1}\ s^{-1}$ for the specific rate of iodide substitution on $[Ru(NH_3)_4(isn)H_2O]^{2+}$. Stopped-flow experiments give the rate of aquation of I^- in $[Ru(NH_3)_4(isn)I]^+$ as 0.91 ± 0.17 s^{-1}. The equilibrium quotient for reaction 1 was determined (86 ± 4 M^{-1}).

In the course of preparing some Co(III)–Ru(III) complexes with 4,4′-bipyridine bridging the two metal centers, it was observed[1] that SO_4^{2-} on Ru(III) is replaced by I^- at a rate much in excess of that expected for ordinary nucleophilic substitution. It was suspected, and the present work has confirmed this, that the enhanced rate is a special manifestation of the catalysis by Ru(II) of the rate of substitution on Ru(III). Whereas in the cases previously studied[2,3] Ru(II) is produced by an extrinsic process, here we describe a system in which its formation is intrinsic, and this leads to some special kinetic effects. We selected the isonicotinamide complex of Ru(III) for detailed study, and the net change in our system therefore is

$$trans\text{-}[Ru(NH_3)_4(isn)H_2O]^{3+} + I^- = trans\text{-}[Ru(NH_3)_4(isn)I]^{2+} + H_2O \quad (1)$$

Experimental Section

Ruthenium Complexes. The species *trans*-$[Ru(NH_3)_4(isn)H_2O]^{3+}$ was produced in situ as follows: Recrystallized *trans*-$[Ru(NH_3)_4(isn)SO_4]Cl$ was prepared by the method of Isied and Taube.[4] About 80 mg of this complex was dissolved in 1 mL of 0.1 N trifluoromethanesulfonic acid, CF_3SO_3H (obtained neat from 3M Chemical Division and vacuum distilled), and then reduced over zinc amalgam with argon bubbling for 20 min. Coordinated sulfate is rapidly aquated from the inner coordination sphere of Ru(II) ($t_{1/2}$ < 1 s).[4] The solution was rapidly filtered and the complex was precipitated as deep red crystals of $[Ru(NH_3)_4(isn)H_2O](PF_6)_2$ by saturating with ammonium