

Figure 6. Internal twist mechanism of $\text{fac-M}(\text{CO})_3\text{L}_2\text{X}$ to $\text{mer-trans-M}(\text{CO})_3\text{L}_2\text{X}$.

via a twist mechanism on the basis of measurements of the entropy of activation, due to the nonsolvent dependence of the rate constants, and for other reasons. By analogy we believe the fast isomerization in oxidation state II in $[\text{M}(\text{CO})_3\text{L}_2\text{X}]^+$ also occurs via a twist mechanism of the type shown in Figure 6.

Conclusions

From the above studies it seems apparent that the 17-electron manganese(II) and rhenium(II) complexes are in general extremely kinetically labile, powerful oxidants and are very light sensitive. In all cases, therefore, they can be classified as much more reactive complexes than the corresponding 18-electron metal(I) compounds. This clearly has significant synthetic consequences as has been demonstrated in this work and enables a range of otherwise inaccessible complexes to be made.

Acknowledgment. We are very grateful to Dr. D. P. Kelly, Organic Chemistry Department, University of Melbourne, who kindly obtained the ^{31}P and ^{13}C NMR spectra.

Registry No. $\text{mer-Mn}(\text{CO})_3(\text{PPh}_3)_2\text{Br}$, 15662-31-4; $\text{mer-Mn}(\text{CO})_3(\text{ppt})_2\text{Br}$, 67124-88-3; $\text{mer-Mn}(\text{CO})_3(\text{pmt})_2\text{Br}$, 67113-79-5; $\text{mer-Mn}(\text{CO})_3[\text{P}(\text{O}^i\text{Pr})_3]_2\text{Br}$, 15614-85-4; $\text{mer-Mn}(\text{CO})_3(\text{AsPh}_3)_2\text{Br}$, 63527-66-2; $\text{mer-Mn}(\text{CO})_3(\text{SbPh}_3)_2\text{Br}$, 67145-45-3; fac-Mn

$(\text{CO})_3[\text{P}(\text{O}^i\text{Pr})_3]_2\text{Br}$, 19195-71-2; $\text{fac-Mn}(\text{CO})_3(\text{SbPh}_3)_2\text{Br}$, 63511-08-0; $\text{fac-Re}(\text{CO})_3(\text{PPh}_3)_2\text{Cl}$, 25246-23-5; $\text{fac-Re}(\text{CO})_3(\text{PPh}_3)_2\text{Br}$, 54082-96-1; $\text{fac-Re}(\text{CO})_3(\text{pmt})_2\text{Cl}$, 67145-44-2; $\text{fac-Re}(\text{CO})_3(\text{pmt})_2\text{Br}$, 67145-43-1; $\text{fac-Re}(\text{CO})_3[\text{P}(\text{O}^i\text{Pr})_3]_2\text{Cl}$, 25045-02-7; $\text{fac-Re}(\text{CO})_3[\text{P}(\text{O}^i\text{Pr})_3]_2\text{Br}$, 49742-38-3; $\text{mer-Re}(\text{CO})_3(\text{PPh}_3)_2\text{Cl}$, 19394-85-5; $\text{mer-Re}(\text{CO})_3(\text{PPh}_3)_2\text{Br}$, 51446-58-3; $\text{mer-Re}(\text{CO})_3(\text{pmt})_2\text{Cl}$, 67113-78-4; $\text{mer-Re}(\text{CO})_3(\text{pmt})_2\text{Br}$, 67113-77-3; $\text{mer-Re}(\text{CO})_3[\text{P}(\text{O}^i\text{Pr})_3]_2\text{Cl}$, 67145-42-0; $\text{Mn}(\text{CO})_4(\text{pmt})\text{Br}$, 67113-76-2; $\text{Re}(\text{CO})_4(\text{pmt})\text{Cl}$, 67113-75-1; $\text{Re}(\text{CO})_4(\text{pmt})\text{Br}$, 67113-74-0; pmt , 6224-63-1; ^{13}C , 14762-74-4.

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Polarographic Studies of the Geometric Isomers of the Bis(diethylenetriamine)cobalt(III) and -cobalt(II) Cations in Acetone

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Extensive studies have been made previously on the kinetically inert geometric isomers of $[\text{Co}^{\text{III}}(\text{dien})_2]^{3+}$ (dien = the tridentate ligand diethylenetriamine); however, virtually no information has been available on the corresponding isomers of $[\text{Co}^{\text{II}}(\text{dien})_2]^{2+}$. Electrochemical reduction of the cobalt(III) complexes has been studied by dc polarography, differential pulse polarography, cyclic voltammetry, and controlled-potential electrolysis. Results have enabled equilibrium constants for the redox and isomer distribution to be calculated. Two reduction waves are found for each of the meridional (*mer*), symmetrical facial (*s-fac*), and unsymmetrical facial (*u-fac*) isomers. The step (*mer*, *u-fac*, *s-fac*) $[\text{Co}^{\text{III}}(\text{dien})_2]^{3+} + e^- \rightleftharpoons (\text{mer}, \text{u-fac}, \text{s-fac}) [\text{Co}^{\text{II}}(\text{dien})_2]^{2+}$ occurs with retention of geometry on the electrochemical time scale. With respect to redox behavior, the *s-fac*- $[\text{Co}^{\text{III}}(\text{dien})_2]^{3+}$ species is the hardest to reduce and the *mer*- $[\text{Co}^{\text{II}}(\text{dien})_2]^{2+}$ cation is the hardest to oxidize. In oxidation state II the complexes are kinetically labile and under conditions of controlled-potential electrolysis, the thermodynamically favored *mer*- $[\text{Co}^{\text{II}}(\text{dien})_2]^{2+}$ species is the only species found. Calculations suggest that compared with oxidation state III, the stability of the meridional form is considerably enhanced with respect to the facial isomers. On further reduction no cobalt(I) complexes are found and a two-electron step leading to formation of cobalt metal occurs: (*mer*, *u-fac*, *s-fac*) $[\text{Co}^{\text{II}}(\text{dien})_2]^{2+} + 2e^- \rightarrow \text{Co} + 2\text{dien}$. With the N-methylated complex $[\text{Co}^{\text{III}}(\text{medien})_2]^{3+}$ (medien = $\text{NH}_2\text{CH}_2\text{CH}_2\text{N}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{NH}_2$) stabilization of the *s-fac* isomer is enhanced remarkably and it is the only isomer detected in either oxidation state III or II.

Introduction

Isomerism in complexes of the type $[\text{Co}^{\text{III}}(\text{dien})_2]^{3+}$ (dien = the tridentate ligand diethylenetriamine) has been studied extensively since Mann⁴ first isolated the complex cation as

the iodide salt.

The geometric isomers shown in Figure 1 may be designated in terms of the facial or meridional arrangement of the ligands. An additional specification *u-fac* (unsymmetrical) and *s-fac*

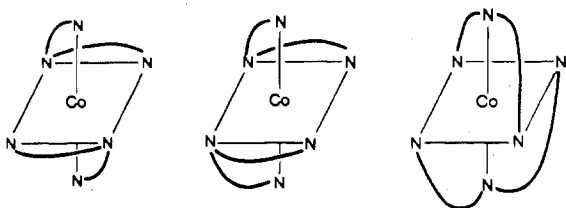


Figure 1. Geometric isomers of $[\text{Co}(\text{dien})_2]^{2+/3+}$: left, *s-fac*; center, *u-fac*; right, *mer*.

(symmetrical) is necessary to distinguish the two facial forms. The *u-fac* and *mer* isomers have only a twofold rotation axis and can therefore also exhibit optical isomerism. Keene and Searle⁵ have separated the three geometric isomers and resolved the *u-fac* and *mer* forms into optical isomers; characterization of the isomers was made from IR, NMR, and optical rotation measurements followed by chromatographic separation of the Co(III) species and spectrophotometric estimation of the relative proportions of the isomers. In a subsequent study⁶ the same authors examined the factors which influence the equilibrium isomer proportions of the cobalt(III) complexes and compared the experimental data with predictions from energy-minimized conformational analysis calculations. In these investigations equilibrium proportions of the three geometric isomers of $[\text{Co}(\text{dien})_2]^{3+}$ were generally determined from aerial oxidation of cobalt(II) salts under various conditions.

Thus, while it is apparent that considerable information is available on the $[\text{Co}^{\text{III}}(\text{dien})_2]^{3+}$ cation, virtually no data are available on the corresponding isostructural Co(II) complexes which presumably are implicated as intermediates in the aerial oxidation studies to produce the kinetically inert $[\text{Co}^{\text{III}}(\text{dien})_2]^{3+}$ complexes in their various isomeric forms. Since $[\text{Co}^{\text{III}}(\text{dien})_2]^{3+}$ itself must exhibit the same isomeric forms as the well-documented Co(III) system and in this oxidation state cobalt is generally kinetically labile, the thermodynamically favored situation should be reached readily. Thus in principle equilibrium data should be easier to obtain than for the inert Co(III) cation where lengthy periods and/or addition of catalysts are required to reach the equilibrium values.

Electrochemical investigations in these laboratories of isomerization in a range of carbonyl complexes⁷⁻⁹ has shown that extensive thermodynamic and kinetic data can be obtained for the isomers in different oxidation states. Since the $[\text{Co}^{\text{III}}(\text{dien})_2]^{3+}$ geometric isomers can all be isolated in a pure form and they are known to be kinetically inert, the possibility of reducing each of them to the kinetically labile cobalt(II) state exists. Monitoring of reaction pathways following reduction should provide unambiguous data as to the thermodynamic stability of oxidation state II $[\text{Co}^{\text{II}}(\text{dien})_2]^{2+}$ cations. Using the usual thermodynamic cycles, data applicable to both the Co(II) and Co(III) systems are therefore also easily generated. The present paper describes an investigation of the geometric isomerization of $[\text{Co}^{\text{III}}(\text{dien})_2]^{3+}$ and $[\text{Co}^{\text{II}}(\text{dien})_2]^{2+}$ complexes using predominantly the techniques of dc and differential pulse polarography, cyclic voltammetry, and controlled-potential electrolysis. A non-aqueous solvent, acetone, was chosen as the medium in which to carry out the investigations since all cobalt(III) and cobalt(II) complexes are soluble with the cobalt(II) complexes being stable under an inert atmosphere of nitrogen. Previous work by Sherwood and Laitinen¹⁰ on this system has been undertaken in aqueous media and in the presence of excess dien, but the isomeric distribution was not considered in the interpretation or results.

Experimental Section

Preparations and Instrumentation. The geometric isomers of $[\text{Co}(\text{dien})_2]^{3+}$ were prepared as their perchlorate salts using the method

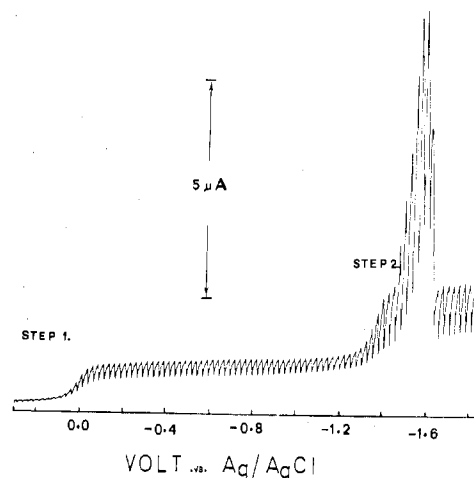


Figure 2. Dc polarogram of a 5×10^{-4} M solution of *mer*- $[\text{Co}^{\text{III}}(\text{dien})_2](\text{ClO}_4)_3$ in acetone (0.1 M Bu_4NPF_6). Drop time = 0.5 s.

of Keene and Searle.^{5,6} The electrolyte used for all experiments was 0.1 M tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) dissolved in acetone. All solutions were degassed with nitrogen at $20 \pm 1^\circ \text{C}$ prior to undertaking any measurements.

For dc and differential pulse measurements a mechanically controlled mercury drop time of 0.5 or 1.0 s was usually employed. The reference electrode was $\text{Ag}[\text{AgCl}$ (saturated LiCl ; acetone) separated from the test solution by a salt bridge containing the supporting electrolyte solution, and the auxiliary electrode was a platinum wire. For cyclic voltammetry, the scan at a rate of 500 mV/s was commenced 1 s after the commencement of the drop life. Polarographic data were obtained with a Princeton Applied Research (PAR) Corp. Model 174 polarographic analyzer.

Controlled-potential electrolysis was achieved using a PAR Model 173 potentiostat/galvanostat at a mercury pool electrode. The reference electrode was the same as used for the polarography, but the auxiliary electrode was made from platinum gauze and separated from the test solution by a salt bridge constructed from porous Vycor sinters and filled with supporting electrolyte solution. Coulometric data were obtained from the controlled-potential electrolysis experiments using a PAR Model 179 digital coulometer.

Determination of the Charcoal-Catalyzed Equilibration of the Isomers of $[\text{Co}(\text{dien})_2]^{3+}$ in Acetone Solution. $\text{Co}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.37 g, 10^{-3} mol) was dissolved in acetone (100 mL, AR), and water molecules of hydration were removed by drying the solution over molecular sieves (4-Å) for several hours. This solution was then added to another solution in acetone (200 mL) of dien (0.18 g, 1.67×10^{-3} mol), $\text{dien} \cdot 3\text{HClO}_4$ (0.14 g, 0.33×10^{-3} mol), activated charcoal (5 g), and Bu_4NPF_6 (15.7 g, 0.04 mol), and the total volume of the solution was made up to 400 mL with acetone. The mixture was aerated for 36 h, the charcoal removed by filtration, and the filtrate evaporated to near dryness (rotary evaporator). The residue was extracted with water (1 L) to remove the $[\text{Co}(\text{dien})_2]^{3+}$ species from the sparingly soluble Bu_4NPF_6 , and the filtered aqueous solution was applied to a column of SP-Sephadex C-25 cation exchanger and eluted with 0.5 M NaClO_4 . After the removal of several brown and orange bands from the column, the slowest moving band (yellow) was collected, diluted with water, and reapplied to the column. Elution with 0.3 M sodium (+)-tartrate solution resulted in the separation of $[\text{Co}(\text{dien})_2]^{3+}$ into its three isomers, which were collected and estimated spectrometrically as described previously.⁶ The percentage figures are each considered accurate to ± 1 .

Results and Discussion

Figure 2 is a dc polarogram of *mer*- $[\text{Co}^{\text{III}}(\text{dien})_2]^{3+}$ in acetone. Two reduction waves are seen. Step 1 corresponds to the one-electron reduction $\text{Co}(\text{III}) + e^- \rightleftharpoons \text{Co}(\text{II})$ and is extremely well defined. The limiting current of this step is diffusion controlled. The second step contains an extremely pronounced maximum, but on reaching the limiting current region a well-defined diffusion-controlled plateau is obtained. The limiting current for the second wave is exactly twice that

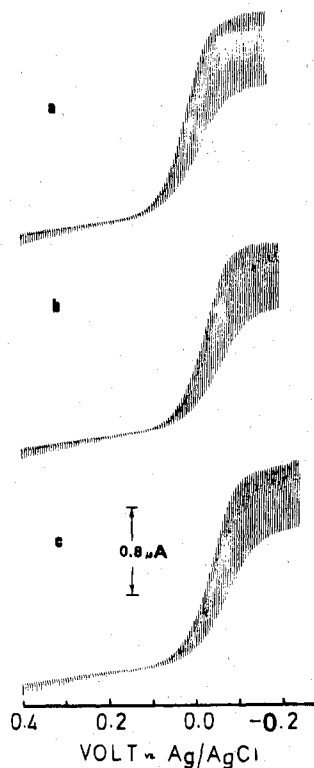


Figure 3. Expanded scale dc polarograms of the first reduction wave of 5×10^{-4} M solutions of (a) *mer*- $[\text{Co}^{\text{III}}(\text{dien})_2](\text{ClO}_4)_3$, (b) *u-fac*- $[\text{Co}^{\text{III}}(\text{dien})_2](\text{ClO}_4)_3$, and (c) *s-fac*- $[\text{Co}^{\text{III}}(\text{dien})_2](\text{ClO}_4)_3$ in acetone (0.1 M Bu_4NPF_6). Drop time = 0.5 s.

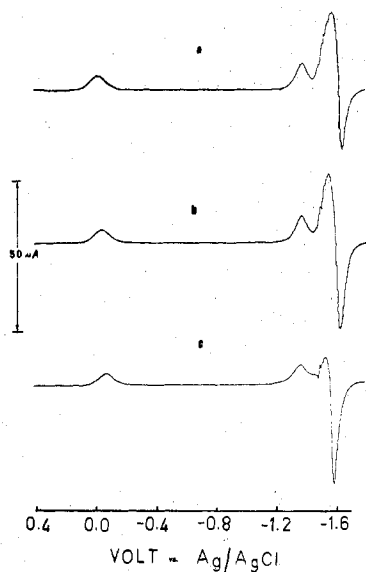


Figure 4. Differential pulse polarograms of 5×10^{-4} M solutions of (a) *mer*- $[\text{Co}^{\text{III}}(\text{dien})_2](\text{ClO}_4)_3$, (b) *s-fac*- $[\text{Co}^{\text{III}}(\text{dien})_2](\text{ClO}_4)_3$, and (c) *u-fac*- $[\text{Co}^{\text{III}}(\text{dien})_2](\text{ClO}_4)_3$ in acetone (0.1 M Bu_4NPF_6). Drop time = 0.5 s, scan rate = 5 mV/s, and pulse amplitude = -25 mV.

for step 1 and is assigned to an overall two-electron step $\text{Co}(\text{II}) + 2e^- \rightarrow \text{Co}(\text{I})$.

Figure 3 displays the first $\text{Co}(\text{III})|\text{Co}(\text{II})$ dc polarographic reduction step for the three geometric isomers. All three complexes are characterized by the same two-electrode processes. However, the first reduction step clearly occurs at different potentials with the *mer* complex being easiest to reduce and the *s-fac* the most difficult. Some differences in shape are also found for the more negative electrode process which includes the maximum. The amplitude and shape of

Table I. Dc Polarographic Data for Reduction of Isomers of $[\text{Co}^{\text{III}}(\text{dien})_2]^{3+}$ in acetone (0.1 M Bu_4NPF_6) at 20 °C

isomer	$E_{1/2}$ (V vs. Ag AgCl) $\text{Co}(\text{III}) + e^- \rightleftharpoons \text{Co}(\text{II})$	$E_{1/2}$ (V vs. Ag AgCl) $\text{Co}(\text{II}) + 2e^- \rightarrow \text{Co}(\text{I})$
<i>mer</i>	+0.030	-1.350
<i>u-fac</i>	-0.015	-1.352
<i>s-fac</i>	-0.035	-1.345

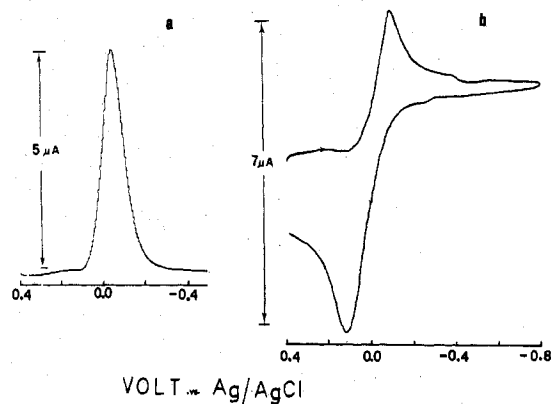


Figure 5. (a) Expanded scale differential pulse polarogram of the first reduction wave for a 5×10^{-4} M solution *u-fac*- $[\text{Co}^{\text{III}}(\text{dien})_2](\text{ClO}_4)_3$ in acetone (0.1 M Bu_4NPF_6). Drop time = 1 s, scan rate = 5 mV/s, and pulse amplitude = -25 mV. (b) Cyclic voltammogram at a dropping mercury electrode of the same solution using a scan rate of 500 mV/s.

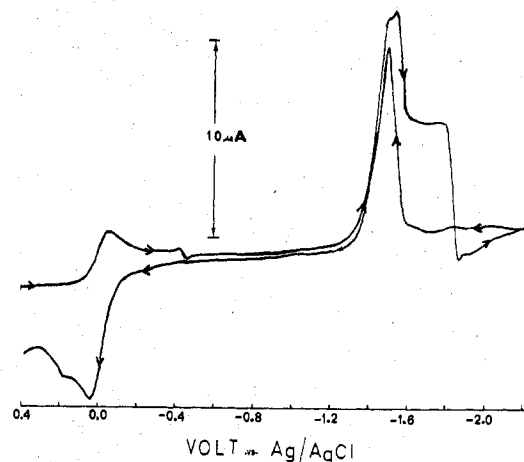


Figure 6. Cyclic voltammogram at a dropping mercury electrode of a 5×10^{-4} M solution of *mer*- $[\text{Co}^{\text{III}}(\text{dien})_2](\text{ClO}_4)_3$ in acetone (0.1 M Bu_4NPF_6). Scan rate = 500 mV/s.

the maxima were in fact found to be extremely oxygen dependent indicating that the $[\text{Co}^{\text{II}}(\text{dien})_2]^{2+}$ species is air sensitive and reacts with oxygen on the polarographic time scale. Relevant dc polarographic data are contained in Table I.

Figure 4 shows a comparison of the differential pulse polarograms for the three complexes. In the region where a sharp maximum is found in the dc polarograms, a region of negative current is found in the differential pulse curves. However, the *s-fac* complex has a markedly different shape in the second wave compared with the other isomers. The shapes of the differential pulse curves for the first wave were similar for each isomer, and the *u-fac* isomer is represented in Figure 5. Also included in Figure 5 is a cyclic voltammogram of the first reduction wave which indicates a considerable degree of chemical reversibility. Figure 6 illustrates an unusual occurrence in cyclic voltammetry where positive currents are

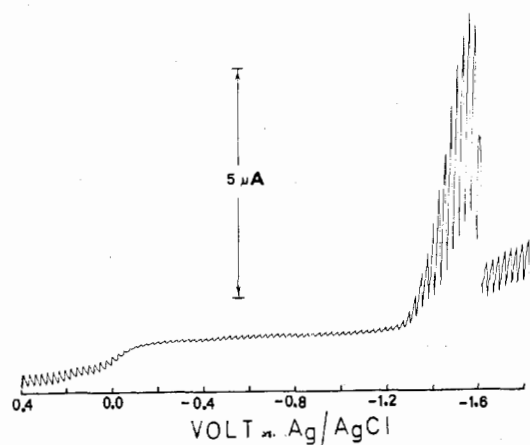


Figure 7. Dc polarogram of electrolysis products after a one-electron reduction of 5×10^{-4} M *s-fac*-[Co^{III}(dien)₂](ClO₄)₃ in acetone (0.1 M Bu₄NPF₆). Drop time = 0.5 s.

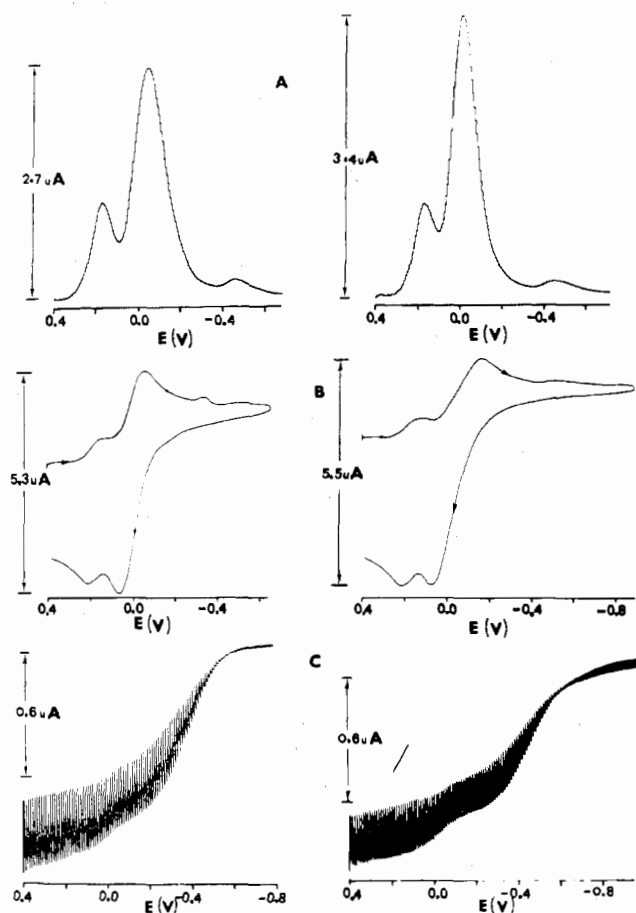


Figure 8. Voltammograms of electrolysis products resulting from one-electron reductions of 5×10^{-4} M solutions of *mer*-[Co^{III}(dien)₂](ClO₄)₃ (left) and *s-fac*-[Co^{III}(dien)₂](ClO₄)₃ (right): (A) differential pulse polarograms recorded using a scan rate of 5 mV/s, a drop time of 0.5 s, and a pulse amplitude of -25 mV; (B) cyclic voltammograms at a dropping mercury electrode using a scan rate of 500 mV/s; (C) dc polarograms recorded using a drop time of 0.5 s. All potentials are vs. the Ag|AgCl reference electrode.

obtained in both the forward and reverse sweep directions for the second step. Similar behavior was observed for all geometric isomers.

Controlled-potential electrolysis coupled with coulometry gave an n value of 1.00 ± 0.02 for the number of electrons transferred in the first reduction step for all isomers. An n value of 2.0 ± 0.1 was found for the second process confirming

Table II. Dc Polarographic Data for Electrolysis Products following a One-Electron Reduction of [Co^{III}(dien)₂]³⁺ in Acetone (0.1 M Bu₄NPF₆) at 20 °C

isomer	$E_{1/2}$ (V vs. Ag AgCl) Co(II) \rightleftharpoons Co(III) + e ⁻	$E_{1/2}$ (V vs. Ag AgCl) Co(II) + 2e ⁻ \rightarrow Co(0)
<i>mer</i>	+0.032	-1.350
<i>u-fac</i>	+0.034	-1.367
<i>s-fac</i>	+0.037	-1.342

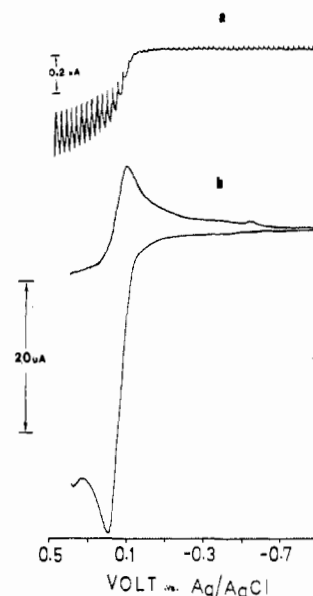


Figure 9. (a) Dc polarogram of 2.5×10^{-4} M dien in acetone (0.1 M Bu₄NPF₆), using a drop time of 0.5 s. (b) Cyclic voltammogram at a dropping mercury electrode of the same solution, using a scan rate of 500 mV/s.

the assignment of the two-electrode processes as Co(III) + e⁻ \rightleftharpoons Co(II) and Co(II) + 2e⁻ \rightarrow Co(0), respectively. Polarographic monitoring of the products of electrolysis after a one-electron reduction of a 5×10^{-4} M *s-fac* solution at a potential between the two waves is shown in Figure 7. As would be expected for a chemically reversible system there is an oxidation wave corresponding to the Co(II)|Co(III) couple; however, the $E_{1/2}$ value for this wave is at a slightly more positive potential than observed for reduction of *s-fac* Co(III). In addition there is another oxidation wave, much smaller in magnitude at a slightly more positive potential than for oxidation of Co(II). This wave is just detectable in Figure 7 but quite distinct in Figure 8C. The *s-fac* electrolysis products also gave a reduction wave which showed the presence of the characteristic maxima associated with the two-electron reduction process Co(II) + 2e⁻ \rightarrow Co(0). A comparison of results with those for a reduced solution of the *mer* Co(III) cation (Figure 8) shows dc and differential pulse polarograms and cyclic voltammograms are essentially identical except the magnitude of the more positive oxidation wave is less pronounced in the *mer* case. Reduction of the *u-fac* Co(III) complex produced polarograms which were also identical with those of the other reduced solutions with respect to the number of waves and their positions. After a three-electron step reduction, the only polarographic wave present was the oxidation step observed at the more positive potential after the one-electron reduction. Table II shows the relevant polarographic data after controlled-potential electrolysis experiments. These data should be compared with those in Table I.

A dc polarogram and cyclic voltammogram of the ligand (dien) is shown in Figure 9 along with curves obtained after the addition of mercuric nitrate (Figure 10). Clearly, from

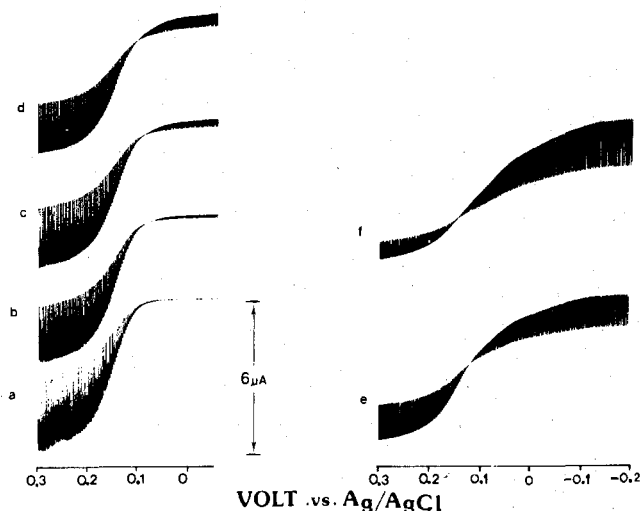
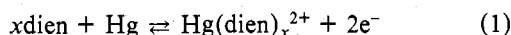


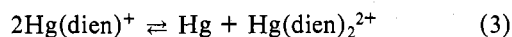
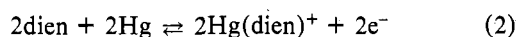
Figure 10. Dc polarograms illustrating the effect of progressively (a-f) adding mercuric nitrate to a 2.5×10^{-4} M solution of dien in acetone ($0.1 \text{ M Bu}_4\text{NPF}_6$). Curve (a) represents the dien ligand in the absence of $\text{Hg}(\text{NO}_3)_2$.

the $E_{1/2}$ value and wave shape the additional oxidation wave obtained after the reduction of the cobalt complexes is the same as for this process, i.e., is that for the ligand. This wave is assigned to the overall electrode process of the kind



Roe et al.,¹¹ in a polarographic study of dien and mercuric complex formation, found that the bis- and tris(diethylenetriamine)mercury(II) complexes are the predominant species formed in aqueous media and that these complexes have extremely high stability constants. Therefore in eq 1, x is most likely to have the value 2 or 3. Controlled-potential electrolysis at a mercury electrode gave an n value of 1.00 ± 0.05 indicating that the bis complex is the major species formed.

Porzolt et al.¹² also report the existence of highly stabilized complexes from reactions of $\text{Hg}(\text{CN})_2$ with the dien ligand in aqueous media. A polarographic study by Porubsky¹³ using ac techniques in aqueous media indicated stable Hg^{II} -dien complex formation with evidence of adsorption coupled to the charge-transfer step. Concentration dependence studies in acetone showed that maxima and other anomalous current-time behavior are produced at higher concentrations, and the process is complicated by adsorption. Electrocapillary curves confirmed that considerable adsorption of the neutral ligand and/or mercury complex occurs over a wide potential range. In view of the adsorption, the mechanism of the ligand wave is not completely certain but may occur via disproportionation of mercury(I) because the half-wave potential does not show

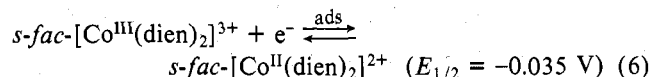
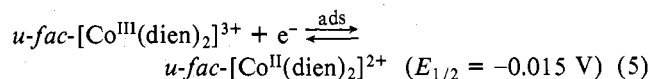
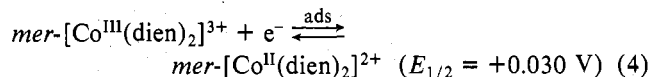


the marked dependence on concentration predicted by eq 1 and the shape (at low concentrations) of the E vs. $\log [(i_d - i)/i]$ plot has a slope close to that for a reversible one-electron step as required by eq 2. Some of the behavior at higher concentrations is consistent with the formation of $\text{Hg}_2(\text{dien})_2^{2+}$ at the electrode surface. Addition of mercury(I) nitrate to a solution of ligand also gave the same process as for mercury(II) nitrate as required by eq 2 and 3.

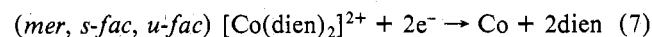
Plots of E vs. $\log [(i_d - i)/i]$ for the one-electron reduction of the three cobalt(III) isomers were not completely linear but gave average gradients of $0.057 \pm 0.005 \text{ V}$. These plots, other dc polarographic data, and results from differential pulse polarography and cyclic voltammetry indicate that the

charge-transfer step is essentially reversible. However, a small amount of adsorption accompanies the charge transfer of the complexed ligand as is the case for the free ligand. Differential pulse polarograms are also consistent with some adsorption being coupled to the charge transfer and the complications reported in aqueous media¹¹ also appear to apply in acetone.

The electrochemical data obtained above demonstrate that on the polarographic time scale, isomerization of cobalt(II) does not occur. Thus the electrode processes may be described as

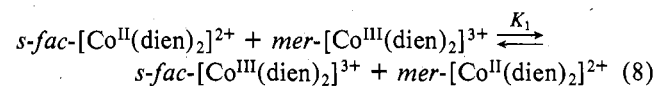


The second step therefore corresponds to the reduction of the cobalt(II) isomer which is isostructural with the cobalt(III) starting material. No evidence of Co(I) is seen as an intermediate in the two-electron reduction and the ligand is released, so the product must be metallic cobalt. The overall process for step 2 is thus



Controlled-potential electrolysis experiments prove that the *mer* Co(II) complex is the complex obtained on the synthetic scale in about 10 min regardless of the starting material. The mechanism for generation of small amounts of dien in addition to the *mer-}[\text{Co}^{\text{II}}(\text{dien})_2]^{2+} cation is not understood. This complex is extremely air sensitive and on aerial oxidation an unidentified cobalt(III) complex (oxo-bridged presumably) is formed. However, the oxygen reaction does not release ligand so air sensitivity is not the cause for ligand release. The adsorption process accompanying the charge transfer, which may be ligand bridging to the mercury electrode, is a plausible source of the ligand.*

From the electrolysis results it can be concluded that in oxidation state II, the *mer* isomer is the thermodynamically favored structural form. The $E_{1/2}$ values given in eq 4, 5, and 6, while slightly removed from E° by adsorption, clearly indicate that in oxidation state III the *s-fac* Co(III) isomer is the hardest to reduce, i.e., the thermodynamically most stable with respect to reduction, whereas the *mer* Co(II) species is the hardest to oxidize. Setting up the usual thermodynamic cycle from E° values ($\sim E_{1/2}$) would result in the conclusion that the equilibrium constant for the reaction



lies substantially to the right.

Assuming $E_{1/2} = E^\circ$, then

$$K_1 = \frac{[\text{s-fac Co(III)}][\text{mer Co(II)}]}{[\text{mer Co(III)}][\text{s-fac Co(II)}]} = \text{antilog} \frac{nF\Delta E^\circ}{2.303RT} = 13 \quad (9)$$

Using the same calculation procedures for the *u-fac*|*mer* distribution gives

$$K_2 = \frac{[\text{u-fac Co(III)}][\text{mer Co(II)}]}{[\text{mer Co(III)}][\text{u-fac Co(II)}]} = 5.7 \quad (10)$$

Similarly for the *u-fac*|*s-fac* distribution:

$$K_3 = \frac{[s\text{-}fac \text{ Co(III)}][u\text{-}fac \text{ Co(II)}]}{[u\text{-}fac \text{ Co(III)}][s\text{-}fac \text{ Co(II)}]} = 2.3 \quad (11)$$

Thus if the equilibrium constants for the isomer distribution in oxidation state III are known, those for the cobalt(II) state can be calculated.

The equilibrium isomeric distribution for $[\text{Co}^{\text{III}}(\text{dien})_2]^{3+}$ in the presence of activated charcoal was determined under the same conditions that were used for the electrochemical measurements (acetone solution, 0.1 M Bu_4NPF_6 ; 20 °C).

In previous studies⁶ of the equilibration of the isomers of $[\text{Co}^{\text{III}}(\text{dien})_2]^{3+}$ on activated charcoal by synthesis using Co(II) salts, yields of the desired complex were observed to be $\geq 94\%$ for both aqueous and nonaqueous solvents (viz., dimethylacetamide, dimethyl sulfoxide). For the present determination in acetone solution, the yield of $[\text{Co}(\text{dien})_2]^{3+}$ was considerably lower (ca. 20%); this may be considered to result from condensation reactions between acetone and dien (either in the free state or while complexed to Co(II) under the conditions of the experiment) thereby modifying the amine and leading to lower yields of the desired product. Certainly, other Co(III) species (predominantly orange) were observed during the chromatographic procedures following the synthesis, but these complexes were not examined further.

Despite the low yields of $[\text{Co}^{\text{III}}(\text{dien})_2]^{3+}$ in acetone solution, it is likely that the observed relative proportions represent the thermodynamic distribution of the isomers. The observed proportions (*s-fac*:*u-fac*:*mer* = 9:17:74) in the presence of the nonassociating anion (PF_6^-) closely resemble the proportions obtained for equilibrations in other nonaqueous solvents (DMA, Me_2SO) in the absence of added electrolytes (*s-fac*:*u-fac*:*mer* = 7:14:79) and show that the meridional isomer is the most thermodynamically favored with respect to isomer distribution in acetone for the oxidation state III system. The result is also similar to the proportions obtained in water (7:28:65).

The equilibrium constants between the three isomer pairs for $[\text{Co}^{\text{III}}(\text{dien})_2]^{3+}$ under the present conditions are given as

$$K_4 = \frac{[\text{mer Co(III)}]}{[s\text{-}fac \text{ Co(III)}]} = 8.2 \quad (12)$$

$$K_5 = \frac{[\text{mer Co(III)}]}{[u\text{-}fac \text{ Co(III)}]} = 4.3 \quad (13)$$

$$K_6 = \frac{[u\text{-}fac \text{ Co(III)}]}{[s\text{-}fac \text{ Co(III)}]} = 1.9 \quad (14)$$

Substituting eq 12 into eq 9 gives

$$K_7 = \frac{[\text{mer Co(II)}]}{[s\text{-}fac \text{ Co(II)}]} = 107 \quad (15)$$

and the conclusion is reached that in oxidation state II the *mer* Co(II) complex is relatively more stabilized with respect to isomeric form compared with results obtained in oxidation state III.

Substituting eq 13 into eq 10 gives

$$K_8 = \frac{[\text{mer Co(II)}]}{[u\text{-}fac \text{ Co(II)}]} = 25 \quad (16)$$

Again it can be seen that thermodynamic stabilization of the *mer* form with respect to the facial isomer is gained in oxidation state II.

Proceeding through the same calculation procedures and using the K_6 value of 1.75 give

$$K_9 = \frac{[u\text{-}fac \text{ Co(II)}]}{[s\text{-}fac \text{ Co(II)}]} = 4.4 \quad (17)$$

Table III. Summary of Thermodynamic Data for the $[\text{Co}^{\text{III}}(\text{dien})_2]^{3+}/[\text{Co}^{\text{II}}(\text{dien})_2]^{2+}$ System in Acetone (0.1 M Bu_4NPF_6) at 20 °C

Set 1, <i>s-fac/mer</i>	
$s\text{-}fac \text{ Co(II)} + \text{mer Co(III)} \xrightleftharpoons{K_1} s\text{-}fac \text{ Co(III)} + \text{mer Co(II)}$	$K_1 = 13$
$s\text{-}fac \text{ Co(III)} \xrightleftharpoons{K_4} \text{mer Co(III)}$	$K_4 = 8.2$
$s\text{-}fac \text{ Co(II)} \xrightleftharpoons{K_7} \text{mer Co(II)}$	$K_7 = 107$
Set 2, <i>u-fac/mer</i>	
$u\text{-}fac \text{ Co(II)} + \text{mer Co(III)} \xrightleftharpoons{K_2} u\text{-}fac \text{ Co(III)} + \text{mer Co(II)}$	$K_2 = 5.7$
$u\text{-}fac \text{ Co(III)} \xrightleftharpoons{K_5} \text{mer Co(III)}$	$K_5 = 4.3$
$u\text{-}fac \text{ Co(II)} \xrightleftharpoons{K_8} \text{mer Co(II)}$	$K_8 = 25$
Set 3, <i>u-fac/s-fac</i>	
$s\text{-}fac \text{ Co(II)} + u\text{-}fac \text{ Co(III)} \xrightleftharpoons{K_3} s\text{-}fac \text{ Co(III)} + u\text{-}fac \text{ Co(II)}$	$K_3 = 2.3$
$s\text{-}fac \text{ Co(III)} \xrightleftharpoons{K_6} u\text{-}fac \text{ Co(III)}$	$K_6 = 1.9$
$s\text{-}fac \text{ Co(II)} \xrightleftharpoons{K_9} u\text{-}fac \text{ Co(II)}$	$K_9 = 4.4$

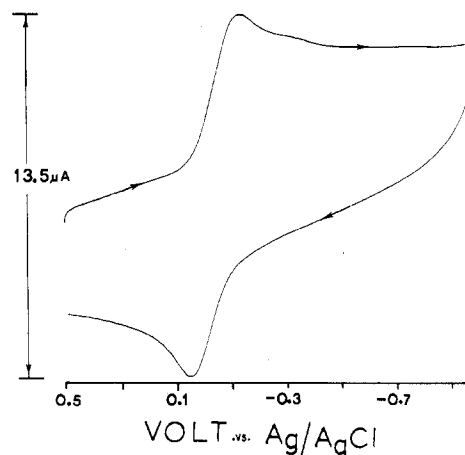


Figure 11. Cyclic voltammogram at platinum electrode of a 5×10^{-4} M solution of *mer*- $[\text{Co}^{\text{III}}(\text{dien})_2](\text{ClO}_4)_3$ in acetone (0.1 M Bu_4NPF_6) solution. Scan rate = 500 mV/s.

This indicates that in oxidation state II the *u-fac* isomer is stabilized further relative to the *s-fac* form compared with the case of oxidation state III. Results from all the thermodynamic calculations are summarized in Table III.

The conclusion to be drawn from these results is that in oxidation state II the isomeric distribution is more discriminating than is the case for cobalt(III). That is, the *mer* isomer is heavily favored and by far the predominant species. However, the order of stability with respect to geometric distribution is the same in both oxidation states.

Voltammetry at platinum electrodes was also attempted and two reduction waves corresponding to those at mercury were found. Figure 11 shows a cyclic voltammogram of the first step at platinum. Waves were drawn out and very dependent on the surface treatment so that no quantitative data of precision comparable to that of mercury electrodes could be obtained. It appears that adsorption noted at mercury is also present at platinum and severely influences the reduction steps at platinum.

Following the study of the dien complexes, a brief investigation of the complex *s-fac*- $[\text{Co}^{\text{III}}(\text{medien})_2](\text{ClO}_4)_3$ was undertaken, where *medien* is the ligand $\text{NH}_2\text{CH}_2\text{CH}_2\text{N}(\text{C}_2\text{H}_5)_2$. When this compound was synthesized, only

the *s-fac* isomer was isolated in oxidation state III.¹⁴ Dc polarography indicated the presence of the same two reduction steps (including the maximum for the Co(II)/Co(0) step) as obtained in the previous cases. However, the $E_{1/2}$ for the Co(III) + $e^- \rightleftharpoons$ Co(II) reduction step was +0.230 V vs. Ag|AgCl, 265 mV more positive than observed in the *s-fac*-[Co^{III}(dien)₂]³⁺ isomer. The half-wave potentials for the two-electron reduction step were the same for both *s-fac* complexes. Dc polarograms of the electrolysis products following a one-electron reduction were recorded. The $E_{1/2}$ values of these polarograms were the same as found for the *s-fac*-[Co(medien)₂]³⁺ starting material, indicative that in oxidation state II the *s-fac* isomer is the most stable species. Free ligand was also found as with the cobalt dien system. The electrolysis products were then oxidized. Dc polarograms gave no change in half-wave potential, again indicating that in oxidation state III the *s-fac* isomer as synthesized originally is produced.

Searle, Petkovic, and Keene¹⁵ found that the stability of the cis isomer (facial) was increased at the expense of the trans (meridional) upon N-methylation of cobalt complexes containing the triethylenetetramine ligand. Clearly the N-methylation of the dien ligand in this instance is responsible for the large enhancement of the stability of the *s-fac* isomer.

So extensive is this enhancement that, in both oxidation states II and III, neither the *mer* nor the *u-fac* isomer could be detected.

Registry No. *mer*-[Co^{III}(dien)₂]³⁺, 38318-06-8; *u-fac*-[Co^{III}(dien)₂]³⁺, 38318-05-7; *s-fac*-[Co^{III}(dien)₂]³⁺, 38318-04-6; *mer*-[Co^{II}(dien)₂]²⁺, 67145-46-4; *u-fac*-[Co^{II}(dien)₂]²⁺, 67145-47-5; *s-fac*-[Co^{II}(dien)₂]²⁺, 67145-48-6; *s-fac*-[Co^{III}(medien)₂]³⁺, 63544-39-8; *s-fac*-[Co^{II}(medien)₂]²⁺, 67113-81-9.

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Synthesis and Further Characterization of Potassium (Ethylenediamine)dicarbonatocobaltate(III) and the Tetraaquo(ethylenediamine)cobalt(III) Ion

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Potassium (ethylenediamine)dicarbonatocobaltate(III) has been prepared from the reaction of potassium tricarbonatocobaltate(III) with limiting amounts of en·2HClO₄. Solutions of this compound have absorption maxima at 394 (ε 164) and 567 nm (ε 159). Addition of excess HClO₄ generates the tetraaquo(ethylenediamine)cobalt(III) ion, which has absorption maxima at 373 (ε 49) and 510 nm (ε 59). At pH > 2, Co(en)(H₂O)₄³⁺ undergoes dimerization. The complex has a pK_a value of ca. 3.7 and undergoes substitution reactions with chloride ion to form mono- and dichloro products, which have been characterized by their ¹H NMR spectra and behavior on cation-exchange resin. Substitution of the first Cl⁻ into Co(en)(H₂O)₄³⁺ is the rate-determining step for the formation of the mono- and dichloro complexes. This rate has an apparent first-order dependence on [Cl⁻] and an inverse first-order dependence on [H⁺]. At 25.8 ± 0.2 °C in 1.00 M Cl⁻ and 0.40 M H⁺, the observed rate constant for the formation of the monochloro complex is 7.88 × 10⁻⁵ s⁻¹. Under these same conditions, E_a = 29.2 kcal/mol, ΔH[‡] = 28.8 kcal/mol, and ΔS[‡] = 18.5 cal/(mol deg). The equilibrium constants for Co(en)(H₂O)₄³⁺ + Cl⁻ ⇌ Co(en)(H₂O)₃Cl²⁺ (K₁) and Co(en)(H₂O)₃Cl²⁺ + Cl⁻ ⇌ Co(en)(H₂O)₂Cl₂⁺ (K₂) equilibria have been measured by spectrophotometry and by ¹H NMR. At 25 °C, K₁ = 16 ± 3, measured at μ = 0.3–0.5 M and pH 1, and K₂ = 1.2 ± 0.3, measured at μ = 1.4, pH 0.5.

Introduction

There has been considerable interest recently in the chemistry of the lower amine substituted members of the series Co(NH₃)_n(H₂O)_{6-n}³⁺.²⁻⁵ In the similar series of ethylenediamine (en) complexes, the simplest member containing only one en ligand has not been thoroughly characterized previously. Both KCo(en)(CO₃)₂·H₂O⁶⁻⁸ and Co(en)(H₂O)₄³⁺⁸ have been synthesized previously, but there was some doubt as to the form of the Co(en)(CO₃)₂⁻ ion. This paper presents a modified synthesis of KCo(en)(CO₃)₂·H₂O and evidence that the fully chelated monomer has been produced. It describes the conditions for the production of the Co(en)(H₂O)₄³⁺ ion in solution and it examines the behavior of Co(en)(H₂O)₄³⁺ in acid solution and the anation of Co(en)(H₂O)₄³⁺ and Co(en)(H₂O)₃Cl²⁺ by Cl⁻.

Ethylenediamine complexes of Co(III) and their analogous ammonia complexes in general undergo substitution reactions at similar rates with similar activation parameters.^{9,10} This is particularly true for complexes of the type CoA₄X₂ where A = 1/2 en or NH₃. In this paper, a comparison is made of the substitution rates for Co(en)(H₂O)₄³⁺ and Co(NH₃)₂(H₂O)₄³⁺.³ It is also expected that the substitution rates for Co(en)(H₂O)₄³⁺ and Co(en)(H₂O)₃OH²⁺ will be faster than the corresponding rates for Co(en)₂(H₂O)₂³⁺ and Co(en)₂(H₂O)(OH)²⁺¹¹ but slower than those for Co(H₂O)₆³⁺ and Co(H₂O)₅OH²⁺.¹²

Experimental

Synthesis of KCo(en)(CO₃)₂·H₂O. A 23.8-g portion of CoCl₂·6H₂O (0.1 mol) was dissolved in a solution containing 10 mL of water and 12 mL of 30% H₂O₂. The bubbling solution was added dropwise to