

The Stability of *u-fac*-Bis[di(2-aminoethyl)sulfide]cobalt(III) and the Charcoal-catalyzed Racemization of the (–)_D Enantiomer in Acidic Solution

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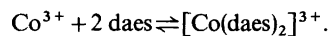
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The charcoal catalyzed racemization of optically active *unsymmetrical facial bis*[di(2-aminoethyl)sulfide]cobalt(III) ion has been investigated. The complex is inert to racemization in the absence of the catalyst but in the presence of charcoal racemization occurs even in 0.01 M acid medium without any detectable decomposition. The formation constant for the complex has been determined from potentiometric measurements together with the available formation constant data for the corresponding cobalt(II) complex. The stability constant is compared to that for bis(diethylenetriamine)cobalt(III), also measured in this work, and it is concluded that the sulfur atom of the thioether function is only a weak ligand for cobalt(III). It is proposed that the catalyzed racemization entails the transient loss of a sulfur from the coordination sphere, resulting in a symmetrical transition state.

Recently, Mureinik and Spiro¹⁻³ carried out an extensive investigation of the racemization of optically active tris(ethylenediamine)cobalt(III), [Co(en)₃]³⁺, in acidic medium. These authors found that charcoal alone did not catalyze racemization under these conditions, whereas charcoal and iodide ions in combination were found to catalyze racemization with only a slight decomposition of the complex. Their results were discussed in terms of the softness of the counter anion, and since iodide was the only efficient halide ion in this respect it was suggested that only a very soft anion in combination with charcoal could catalyze the racemization. This proposal led us to study the charcoal catalyzed racemization of the recently prepared *u-fac* isomer of (–)_D-bis[di(2-aminoethyl)sulfide]-

cobalt(III), (–)_D-[Co(daes)₂]³⁺. In this complex a presumably soft ligand in the form of a thioether is already present in the inner-coordination sphere and on the basis of the above-proposed one might therefore expect that [Co(daes)₂]³⁺ would undergo charcoal-catalyzed racemization under acid conditions.

(–)_D-[Co(daes)₂]³⁺ has been found⁴ to racemize much more rapidly in aqueous solution in the presence of charcoal than [Co(en)₃]³⁺. However, at neutral pH the mechanism of the charcoal-catalyzed racemization may be independent of a soft counter ion or another soft donor. It is possible that charcoal partly reduces some cobalt(III) so that an electron-transfer equilibrium between Co(III) and Co(II) complexes of the type described previously by Dwyer and Sargeson may be established.⁵ In the case of buffered acid solutions such a mechanism should produce Co(H₂O)₆²⁺ in amounts according to the equilibrium constants for the total system, and therefore a study of the stability of [Co(daes)₂]³⁺ ion was undertaken. The Co(II)-daes equilibrium system has been studied by Douglas *et al.*⁶ and their data have been used to calculate the stability constant β₂ for the reaction



A knowledge of the Co(II)/Co(III)/daes equilibrium should enable us to assess the likelihood of a reductive mechanism for the catalysis by charcoal of [Co(daes)₂]³⁺ racemization.

To date, very few stability constants have been measured for Co(III) complexes. To put the meas-

ured β_2 in perspective we therefore also measured the stability of a corresponding cobalt(III) complex with the amine analog of daes, *viz.* diethylenetriamine (dien).

Comparison of the two β_2 values suggests that the thioether function is very loosely bound to cobalt(III). This result will be discussed below in relation to the racemization of $[\text{Co}(\text{daes})_2]^{3+}$.

EXPERIMENTAL

Materials. $(-)_D$ -*u-fac*- $[\text{Co}(\text{daes})_2]\text{Cl}_3 \cdot 2\text{H}_2\text{O}$ and $(+)_D$ -*u-fac*- $[\text{Rh}(\text{daes})_2]\text{Cl}_3 \cdot 2\text{H}_2\text{O}$ were prepared as described previously.^{4,7} $[\text{Co}(\text{daes})_2](\text{NO}_3)_3 \cdot \text{H}_2\text{O}$ used in the equilibrium study was prepared by ion exchange. Anal. $\text{C}_8\text{H}_{26}\text{N}_7\text{O}_{10}\text{S}_2\text{Co}$: C, H, N, S. $[\text{Co}(\text{dien})_2](\text{NO}_3)_3 \cdot \text{H}_2\text{O}$ (a mixture of geometric isomers) was prepared from $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and the ligand (Fluka, techn.) by air oxidation with charcoal as catalyst. Anal. $\text{C}_8\text{H}_{28}\text{N}_9\text{O}_{10}\text{Co}$: C, H, N.

The charcoal used throughout this work was Norit W supplied by Norit Sales Co. Ltd., Amsterdam, Holland.

Physical measurements. Absorption spectra were recorded on a Cary 118 spectrophotometer and circular dichroism spectra were measured on Rousell-Jouan mark I and III dichrographs. Radiometer PHM 52 and PHM 64 pH-meters in conjunction with Radiometer electrodes were used for pH measurements.

Kinetic of racemization. Reactions were performed in a 200 ml water-jacketed glass vessel maintained at 60.0 ± 0.2 °C by circulating water from a thermostat. The vessel was fitted with a polyethylene lid having holes for a thermometer and for glass and calomel electrodes. There was also an opening allowing the introduction of reagents as well as permitting sample collection. Light was excluded by wrapping the vessel in Al-foil. The apparatus was not completely air-tight, slight evaporation from the reaction mixture being observed over long runs.

Before each experiment a weighed amount of charcoal and a magnetic stirred bar were placed in the dry vessel and 100.0 ml of a pre-prepared solution of sodium nitrate and nitric acid was introduced. The mixture was stirred for at least 15 h. When the potential was constant (± 0.005 pH) over a period of 1 h equilibration of the charcoal and solution was considered to be complete. A weighed amount of the solid complex salt was then introduced at $t=0$. At suitable intervals 3 ml aliquots of the stirred mixture were withdrawn using a simple glass tube, and each aliquot was filtered through fine porosity filter paper. The removal of the charcoal and cooling to room temperature were achieved within 1 min, so that the catalytic reaction was quickly quenched.

The absorbance at 485 nm (the maximum of the first band) and the circular dichroism at 512 nm and 457 nm were measured for each sample filtrate. The absorbance measurements revealed a small continuous loss of complex in solution during each run due to adsorption. This adsorption corresponded to at most 13% of the initial amount of complex when the optical activity had reached half its initial value. Repeated attempts to detect cobalt(II) as $\text{H}_2\text{Co}(\text{NCS})_4$ by extraction into amyl alcohol were all unsuccessful.

The degree of racemization of $(-)_D$ - $[\text{Co}(\text{daes})_2]^{3+}$ was determined as the ratio of the difference between the negative CD peak at 512 nm and the positive peak at 457 nm to the absorbance at the absorption maximum of 485 nm. This ratio is concentration independent since for 1 cm cell length $\Delta(\Delta A)/A = [\Delta A(512) - \Delta A(457)]/A(485) = [\Delta \epsilon(512) - \Delta \epsilon(457)]/\epsilon(485)$. The experimental rate constants for the rate law

$$\ln \left[\frac{\Delta[\Delta A(0)]}{A(0)} \bigg/ \frac{\Delta[\Delta A(t)]}{A(t)} \right] = 2kt$$

were found by a least squares fit.

Equilibrium measurements. Stock solutions of 0.2000 M HNO_3 ("Fixanal", Riedel-de-Haen), 0.5 M daes, 1.0 M dien, 0.4 M $\text{Co}(\text{NO}_3)_2$, 0.4 M $[\text{Co}(\text{daes})_2](\text{NO}_3)_3 \cdot \text{H}_2\text{O}$ and 0.2 M $[\text{Co}(\text{dien})_2](\text{NO}_3)_3$ were prepared and analysed. The concentration of the ligand solutions were determined by titration with the nitric acid. The cobalt-containing solutions were analysed by atomic absorption with a Perkin Elmer 403 instrument.

For each experiment weighed amounts of KNO_3 and charcoal were introduced into a measuring flask together with measured amounts of acid and ligand. Nitrogen was passed through the mixture for 15 min before the measured amounts of Co(II) and Co(III) solutions and water were added to make up the final solutions. The mixture was shaken to ensure complete mixing and then introduced into the measuring vessel similar to the one used for the kinetic runs. The solution was thermostated to 30.0 ± 0.2 °C and was protected from atmospheric oxygen by bubbling oxygen-free nitrogen through it with an excess pressure corresponding to 5 mm H_2O .

The potential difference between a saturated calomel electrode and a platinum spiral immersed in the solution was followed until a constant value was obtained (0–60 min). The potential was noted when it had been constant for at least 10 min.

Racemization of $(+)_D$ -*u-fac*- $[\text{Rh}(\text{daes})_2]^{3+}$. Using a method similar to that employed for the kinetic runs mentioned above the charcoal catalyzed racemization of the rhodium complex was followed in a chloride medium. The absorbance maximum

at 312 nm and the circular dichroism peaks at 336 and 308 nm were used to follow the racemization. No change in the absorption spectrum other than that due to a 10% decrease in concentration was observed during the operations.

The complex $(+)_D$ -[Rh(en)₃]Cl₃·2H₂O (supplied by Dr. F. Galsbøl) was found not to racemize under exactly the same conditions.

Molecular sieves as a racemization catalyst. To a solution of 1 g of $(-)_D$ -[Co(daes)₂]Cl₃·2H₂O in 25 ml of water was added 2 g of 10 Å Molecular Sieves (Merck, powder). The mixture was shaken and kept at 60 °C for 24 h. After filtration the filtrate was found to contain the fully optically active complex. The molecular sieves were strongly coloured by adsorbed complex and were treated with 10 ml of 2 M Al₂(SO₄)₃. After degradation of the aluminosilicate 20 ml of water was added and after 1 h most of the silicate could be filtered off. The filtrate contained the completely racemized complex. No cobalt(II) species were detected.

RESULTS AND DISCUSSION

Kinetic results. The experimental conditions and data for the rate of racemization of $(-)_D$ -[Co(daes)₂]³⁺ in acidic (sodium) nitrate solutions with activated charcoal as catalyst are summarized in Table 1. The experimental conditions were chosen such that the complex adsorbed on the charcoal at most amounts to ca. 10% of the cobalt(III) complex. Complete adsorption equilibrium between the catalyst and the reaction medium was ensured by allowing the mixture to attain a constant

pH before introducing the complex. For low [Co(daes)₂³⁺]/[H⁺] ratios the pH remained constant during an experiment, whereas for the highest ratios the pH decreased by up to 0.2 pH units.

As predicted by Mureinik and Spiro the racemization rate, $V = k \times C_{Co}$, obeys the McKay equation (see Table 1). The deviations from the average values may represent the uncertainties which are otherwise hard to estimate. Within uncertainty, however, the results suggest that the rate, V , is proportional to $[H^+]^{-1}$. The rate is also influenced by the concentration of inert salt, an effect which is believed to reflect competition for the active sites on the charcoal. The cobalt complex cation may compete strongly with the sodium ions due to its high charge whereas the hydrogen ion may compete efficiently because of more specific bonding.

From the observed simple rate law it is not possible to deduce any mechanism for the reaction. In fact it is at present not clear that charcoal equilibrates the complex or only causes it to racemize. Judging from the results of the equilibrium study (*vide infra*) the latter would appear to be the case.

Stability constants. Very few determinations of stability constants for cobalt(III) systems have been made since J. Bjerrum's early work in this field.⁸ In a sense it is surprising that it is possible to measure equilibrium constants for robust systems. However, when an electron-transfer equilibrium with the corresponding labile cobalt(II) complex of known stability can be established then simple

Table 1. Rate constants, k , for the charcoal catalysed racemization of $(-)_D$ -*u-fac*-[Co(daes)₂]Cl₃ in acid solution at 60 °C.

$C_{[Co(daes)_2]Cl_3}$ ^a mM	C_{HNO_3} ^a mM	$C_{NO_3^-}$ ^a M	Charcoal g/l	$10^6 \times k$ s ⁻¹	$10^9 \times V^b$ M s ⁻¹	$10^9 \times V C_{HNO_3}$ M ² s ⁻¹
1.25	10	1	2	36	46	0.46
1.66	10	1	2	29	48	0.48
2.50	10	1	2	15	38	0.38
5.00	10	1	2	8	41	0.41
2.50	10	0.1	2	28	70	
2.50	7.5	1	2	23	58	0.43
5.00	7.5	1	2	12	69	0.52
5.00	7.5	1	1	2.6	1.3	
2.50	5.0	1	2	45	111	0.56
5.00	5.0	1	2	23	117	0.58

^a C denotes a total starting concentration. ^b $V = k C_{[Co(daes)_2]Cl_3}$, the first four results demonstrate the typical variance in the experimental results.

Table 2. Redox potentials of solutions of varying ratios $[\text{Co}(\text{daes})_2^{3+}]/[\text{Co}(\text{daes})_2^{2+}]$ and of varying hydrogen ion concentration at 30.0 °C.

$\text{C}_{\text{Co}(\text{daes})_2(\text{NO}_3)_3}$ (M)	$\text{C}_{\text{Co}(\text{NO}_3)_2}$ (M)	C_{daes} (M)	C_{HNO_3} (M)	[daes] (M)	$-\log[\text{H}^+]$	I (M)	$0.0601 \log \frac{[\text{Co}(\text{daes})_2^{3+}]}{[\text{Co}(\text{daes})_2^{2+}]}$ (V)	E (V)	E_{H} (V)	E° (V)
0.0167	0.0155	0.137	0.0800 ^(a)	0.026	9.15	1.23	0.0020	-0.1589	0.0828	0.0808
0.0167	0.0155	0.171	0.0800 ^(a)	0.060	9.51	1.23	0.0019	-0.1590	0.0827	0.0808
0.0244	0.00724	0.156	0.0800 ^(a)	0.062	9.53	1.25	0.0318	-0.1297	0.1120	0.0802
0.00828	0.0229	0.193	0.0800 ^(a)	0.068	9.57	1.20	-0.0266	-0.1868	0.0549	0.0815
0.00414	0.0267	0.193	0.0800 ^(a)	0.060	9.51	1.19	-0.0487	-0.2097	0.0320	0.0807
0.00814	0.0217	0.185	0.0800 ^(a)	0.062	9.53	1.19	-0.0256	-0.1901	0.0516	0.0772
0.00814	0.0217	0.176	0.0200 ^(a)	0.112	10.39	1.13	-0.0256	-0.1897	0.0520	0.0776
0.00814	0.0217	0.176	0.0200 ^(b)	0.112	10.39	1.19	-0.0256	-0.1917	0.0500	0.0756
0.00814	0.0217	0.185	0.120 ^(c)	0.022	8.90	1.19	-0.0255	-0.1910	0.0507	0.0762
0.00814	0.0219	0.195	0.120 ^(c)	0.031	9.06	1.19	-0.0257	-0.1896	0.0521	0.0778
mean ^(d)										0.0788 ± 0.0022

^a $\text{C}_{\text{KNO}_3} = 1.00 \text{ M}$. ^b $\text{C}_{\text{KNO}_3} = 1.06 \text{ M}$. ^c $\text{C}_{\text{KNO}_3} = 0.96 \text{ M}$. ^d All the reported measurements were obtained with 20 mg charcoal/50 ml solution to ensure fast equilibrium.

Table 3. Redox potentials of solutions of varying ratios $[\text{Co}(\text{dien})_2^{3+}]/[\text{Co}(\text{dien})_2^{2+}]$ and of varying hydrogen ion concentrations at 30.0 °C.

$\text{C}_{\text{Co}(\text{dien})_2(\text{NO}_3)_3}$ (M)	$\text{C}_{\text{Co}(\text{NO}_3)_2}$ (M)	C_{dien} (M)	C_{HNO_3} (M)	[dien] (M)	$-\log[\text{H}^+]$	I (M)	$0.0601 \log \frac{[\text{Co}(\text{dien})_2^{3+}]}{[\text{Co}(\text{dien})_2^{2+}]}$ (V)	E (V)	E_{H} (V)	E° (V)
0.0236	0.0228	0.124	0.0600	0.019	9.44	1.27	0.0009	-0.4620	-0.2203	-0.2212
0.0238	0.0236	0.207	0.0600	0.100	10.16	1.27	0.0001	-0.4625	-0.2208	-0.2209
0.0238	0.0236	0.249	0.0600	0.142	10.31	1.27	0.0001	-0.4621	-0.2209	-0.2209
0.0117	0.0347	0.209	0.0600	0.079	10.06	1.23	-0.0284	-0.4885	-0.2468	-0.2184
0.00778	0.0385	0.209	0.0600	0.072	10.02	1.22	-0.0417	-0.5010	-0.2593	-0.2176
0.00786	0.0395	0.188	0.0600	0.049	9.95	1.26	-0.0421	-0.5013	-0.2596	-0.2175
0.0236	0.00785	0.125	0.0600	0.050	9.90	1.26	0.0287	-0.4300	-0.1883	-0.2170
0.0393	0.00785	0.125	0.0600	0.050	9.90	1.32	0.0421	-0.4200	-0.1783	-0.2204
0.0236	0.0231	0.207	0.0600	0.101	10.17	1.27	0.0006	-0.4630	-0.2213	-0.2219 ^a
0.00685	0.0200	0.128	0.0521	0.036	9.78	1.15	-0.0283	-0.4881	-0.2464	-0.2181
0.0204	0.0199	0.135	0.0517	0.043	9.86	1.23	0.0007	-0.4619	-0.2202	-0.2209
0.00693	0.0203	0.114	0.0530	0.020	9.52	1.15	-0.0279	-0.4883	-0.2466	-0.2187
mean ^b										0.0017

^a All the reported measurements except this one were obtained with 20 mg charcoal/50 ml solution. ^b $\text{C}_{\text{KNO}_3} = 1.00 \text{ M}$ for all solutions.

potentiometric measurements are sufficient to obtain the necessary information about the cobalt(III) system. In the case of di(2-aminoethyl)sulfide and diethylenetriamine equilibrium data for the cobalt(II) systems are available.^{6,9,10} In order to use these published data we have used the same experimental conditions, *viz.* 30 °C and 1 M KNO_3 medium, as in the previous investigations.

Typical sets of experimental data are given in Tables 2 and 3. The reported data were obtained using 20 mg of charcoal per 50 ml of solution, but other experiments indicate that charcoal is not essential for obtaining equilibrium under the rather basic conditions used in the equilibrium work. The measured potentials of the Pt-electrode relative to SCE were then calculated relative to the standard hydrogen electrode.

The standard potential for the electron-transfer reaction between CoL_2^{2+} and CoL_2^{3+} was calculated from

$$E^\circ = E_H - 0.0601 \log\left(\frac{[\text{CoL}_2^{3+}]}{[\text{Co}_2^{2+}]}\right),$$

in which $[\text{CoL}_2^{3+}]$ is obtainable directly from the analytical composition of the solution and $[\text{CoL}_2^{2+}]$ is calculated from the composition and the stability constants of the cobalt(II) system. The conditions were chosen to be such that $[\text{CoL}_2^{2+}]$ constituted at least 99 % of the total concentration of cobalt(II). Inspection of Tables 2 and 3 shows that the above Nernst equation is obeyed. The spread in the data may arise from the presence of uncertain amounts of oxygen adsorbed to the charcoal and from the minor variation in the ionic strength, I , in the series of runs.

The standard potentials obtained were used in combination with Bjerrum's⁸ value of $E^\circ = 1.837$ for $\text{Co}^{3+} + e \rightleftharpoons \text{Co}^{2+}$ in 1 M HNO_3 at 30 °C to calculate the cumulative stability constant, β_2^{III} , for the cobalt(III)–L system:

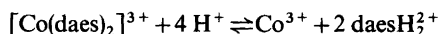
$$\log \beta_2^{\text{III}} = \log \beta_2^{\text{II}} + (E_{\text{Co}^{3+}/\text{Co}^{2+}}^\circ - E_{\text{CoL}_2^{3+}/\text{CoL}_2^{2+}}^\circ) / 0.0601,$$

where β_2^{II} is the cumulative stability constant for CoL_2^{2+} .

We then obtain for $[\text{Co(daes)}_2]^{3+}$ $\log \beta_2 = 38.3$ and for $[\text{Co(dien)}_2]^{3+}$ $\log \beta_2 = 48.8$. Using an estimated value for $\log \beta_2$ per nitrogen donor of 8.1 one arrives at $\log K \sim 3$ for the complexity constant of the thioether function to cobalt(III). This indicates a very low affinity of $>S$ for Co(III). In this

connection it is interesting to note that thioether sulfur of a methionine residue in both oxidized and reduced forms of cytochrome *c* coordinates to the iron ions.^{11,12} The reduced enzyme contains iron(II) which is isoelectronic with cobalt(III) but with the metal having a lower charge one might expect Fe(II) to have even less affinity to thioether sulfur than has Co(III). The Fe(II) surrounded by a porphyrine ligand may have affinities unusual for this metal ion. However, it seems substantiated^{13,14} that thioether sulfur is only a very weak ligand in iron(II) porphyrins in accordance with the above prediction.

Racemization on charcoal occurs without any detectable formation of cobalt(II). From the complexity constant, β_2 , and the acidity constants $\text{p}K_{a1}$ (8.8) and $\text{p}K_{a2}$ (9.6) the equilibrium constant for the process



can be estimated to be ~ 0.1 . The most acidic solutions employed in the kinetic runs should accordingly contain $\sim 10^{-4}$ M Co^{3+} . The aqua cobalt(III) ion is reduced by water and the solution is thereby further acidified. Thus, under the experimental conditions of the racemization studies, the system is thermodynamically unstable relative to its conversion to $\text{Co}(\text{H}_2\text{O})_6^{2+}$. Although we observed decreases in pH, our failure to detect cobalt(II) shows that the catalyst for the racemization cannot be catalyzing the above equilibration process. The decrease in pH which was observed in runs at highest $[\text{Co(daes)}_2^{3+}]/[\text{H}^+]$ ratios is attributed to the ion-exchange effect by the charcoal rather than to a reduction process.

Dwyer and Sargeson explained charcoal catalyzed racemization of tris(ethylenediamine)cobalt(III) in terms of an electron-transfer equilibrium between the cobalt(III) complex and the corresponding labile cobalt(II) complex.⁵ Their experimental conditions were such that both complexes were stable, *i.e.* rather basic conditions. This approach has since been employed quite often in the establishment of equilibrium between isomers of cobalt(III) complexes. Harnung *et al.*¹⁵ showed that equilibrium between the isomers of tris(propylenediamine)-cobalt(III) could be achieved with charcoal. These authors noticed that the rearrangement leading to equilibrium between the Δ and Λ forms takes place at a much faster rate than does the rearrangement between geometric isomers. Keene and Searle¹⁶

determined the equilibrium distribution of the three geometric isomers of $[\text{Co}(\text{dien})_2]^{3+}$. There is thus a general concensus that charcoal is a catalyst for the electron-transfer reaction between cobalt(III) and cobalt(II) complexes of otherwise identical constitution. Under preparative conditions charcoal may also act as a catalyst in the $[\text{Co}(\text{daes})_2]^{3+}/[\text{Co}(\text{daes})_2]^{2+}$ system. However, this catalysis is apparently not operative under acidic conditions such as those used in the racemization experiments in the present work.

Charcoal in acidic medium was used by Bjerrum and Rasmussen as a catalyst for the *trans-cis* isomerization of $[\text{Co}(\text{en})_2(\text{H}_2\text{O})_2]^{3+}$ in 0.05 M HNO_3 .¹⁷ In this case the mechanism of the catalysis cannot involve the same kind of electron-transfer reaction as that discussed above because the corresponding cobalt(II) complexes are highly unstable in 0.05 M HNO_3 . This is therefore one of a number of examples of partial catalysis by charcoal for which no mechanistic postulates have so far appeared. The reaction also proceeds without catalysis, unlike the racemization of $[\text{Co}(\text{daes})_2]^{3+}$.

In view of the low affinity of cobalt(III) for the thioether sulfur atom of the daes ligand it is tempting to propose that the racemization of $[\text{Co}(\text{daes})_2]^{3+}$ entails Co-S bond rupture. The labilizing effect of the charcoal might arise from a hydrophobic interaction which simply distorts a ligand sufficiently to remove a sulfur atom from the coordination sphere.

This model for the catalytic action of charcoal on the racemization of $[\text{Co}(\text{daes})_2]^{3+}$ is not easily verifiable. However, if it is essentially correct then one would predict that the racemization of the corresponding rhodium(III) complex would likewise be catalyzed by charcoal. We have found this to be true. The process was followed during a period of one week and it was indicated that the racemization of $[\text{Rh}(\text{daes})_2]^{3+}$ is approximately 500 times slower than it is for the cobalt complex. For economic reasons the process has not been studied extensively.

The above mechanistic model would also lead one to predict that the racemization of tris(ethylenediamine)rhodium(III) should not be catalyzed by charcoal, and in agreement with this we were unable to detect any such racemization in agreement with an earlier result.¹⁸

Another obvious prediction to make on the basis of the model is that any material having accessible pores of the right size should produce some catalytic

effect. Such an effect has indeed been observed with 10 Å molecular sieves. These sieves are rather basic and all sorts of trace impurities could play a role in the catalysis. However, we failed to observe any racemization of $[\text{Co}(\text{en})_3]^{3+}$ under the same experimental conditions. This does not entirely exclude the possibility of the type of base hydrolysis often encountered in reactions of cobalt(III) complexes taking place on the surface of the catalysts. Further work is in progress to decide this possibility. However, the predictions based on the mechanistic model involving Co-S bond rupture are fulfilled by the experiments and this gives it some credibility although the suggested mechanism has not before been considered for reactions of coordination compounds. However, a mechanism of the type proposed is generally accepted to be involved in the hydrolysis of substrates by proteolytic enzymes, and since it is so widespread it may also be worth-while to consider the relevance of this mechanism in coordination chemistry.

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REFERENCES

1. Mureinik, R. J. and Spiro, M. *J. Chem. Soc. Dalton Trans.* (1974) 2480.
2. Mureinik, R. J. and Spiro, M. *J. Chem. Soc. Dalton Trans.* (1974) 2486.
3. Mureinik, R. J. and Spiro, M. *J. Chem. Soc. Dalton Trans.* (1974) 2493.
4. Searle, G. H. and Larsen, E. *Acta Chem. Scand. A 30* (1976) 193.
5. Dwyer, F. P. and Sargeson, A. M. *Nature* 187 (1960) 1022.
6. Douglas, B. E., Fernelius, W. C. and Gonick, E. *J. Am. Chem. Soc.* 76 (1954) 4671.
7. Galsbøl, F., Hammershøi, A. and Larsen, E. *Acta Chem. Scand. A 32* (1978). *In press.*
8. Bjerrum, J. *Metal Ammine Formation in Aqueous Solution*, Haase, Copenhagen 1941.
9. Jonassen, H. B., Hurst, G. G., Leblanc, R. B. and Meibohm, A. H. *J. Phys. Chem.* 56 (1952) 16.
10. Jonassen, H. B., LeBlanc, R. B., Meibohm, A. W. and Rogan, R. M. *J. Am. Chem. Soc.* 72 (1950) 2430.

11. Swanson, R., Trus, B. L., Mandel, N., Mandel, G., Kallai, O. and Dickerson, R. E. *J. Biol. Chem.* 252 (1977) 759.
12. Takano, T., Trus, B. L., Mandel, N., Mandel, G., Kallai, O., Swanson, R. and Dickerson, R. E. *J. Biol. Chem.* 252 (1977) 776.
13. Harburg, H. A., Cronin, J. R., Fanger, M. W., Hettinger, T. P., Murphy, A. J., Myer, Y. P. and Vinogradov, S. N. *Proc. Natl. Acad. Sci. U.S.A.* 54 (1965) 1658.
14. Castro, C. E. *Bioinorg. Chem.* 4 (1974) 45.
15. Harnung, S. E., Kallesøe, S., Sargeson, A. M. and Schäffer, C. E. *Acta Chem. Scand. A* 28 (1974) 385.
16. Keene, F. R. and Searle, G. H. *Inorg. Chem.* 11 (1972) 148.
17. Bjerrum, J. and Rasmussen, S. E. *Acta Chem. Scand.* 6 (1952) 1265.
18. Sen, D. and Fernelius, W. C. *J. Inorg. Nucl. Chem.* 10 (1959) 269.

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