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Mechanism and Steric Course of Octahedral Aquation. XVII.¹ Acid and Base Hydrolysis of *trans*-Dichloro(1,9-diamino-3,7-dithianonane)cobalt(III) Cations

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The kinetics and steric course of the acid and base hydrolysis of *trans*-[Co(ETE)Cl₂]⁺ are reported (ETE = 1,9-diamino-3,7-dithianonane). For aquation, $k = 4.1 \times 10^{-6} \text{ sec}^{-1}$ at 25°, $\Delta H^\ddagger = 26.1 \text{ kcal/mol}$, and $\Delta S^\ddagger = +4 \text{ cal deg}^{-1} \text{ mol}^{-1}$. The first observed product is β -*cis*-[Co(ETE)ClH₂O]²⁺ but the rapid isomerization of the *trans* isomer of the product, $2.5 \times 10^{-4} \text{ sec}^{-1}$ at 25°, does not permit a direct determination of the steric course. The Hg²⁺-catalyzed aquation proceeds with complete retention of configuration. The complex is reasonably sensitive to base hydrolysis, $k = 1600 \text{ M}^{-1} \text{ sec}^{-1}$ at 13.5°, and the reaction proceeds with complete retention of configuration. The complex is compared with the analogous 1,9-diamino-3,7-diazanonane species and it is concluded that replacement of NH by S causes no great change in reactivity and stereochemistry except in the base hydrolysis reaction.

In part XII of this series² we reported the kinetics and the steric course of the spontaneous and mercury-catalyzed aquation of the *RS* and *RR(SS)* isomers of the *trans*-[Co(2,3,2-tet)Cl₂]⁺ cation (2,3,2-tet = 1,9-diamino-3,7-diazanonane). In these complexes the isomerism arises from the two possible configurations of the secondary nitrogen atoms when coordinated³ and it was shown that the *RS* isomer aquated with complete retention of configuration whereas the *RR(SS)* isomer gave a mixture of the *trans*- and β -*cis*-chloroaquo product initially which then isomerized completely to the β -*cis* form. The entropies of activation of the aquation of the *RS* and *RR(SS)* isomers were +1 and +12 cal deg⁻¹ mol⁻¹, respectively, in agreement with the observation that stereochemical change in the aquation of octahedral amine complexes was generally associated with a significantly higher entropy of activation than retention of configuration.⁴

The cobalt(III) complexes of the ligand 1,9-diamino-3,7-dithianonane (=ETE) have been described by Bosnich, *et al.*⁵ The ligand differs from 2,3,2-tet only in that the NH groups are replaced by S and since the sulfur, on coordination, remains pyramidal, it is possible to envisage *RR*, *RS*, and *SS* isomers analogous to those of 2,3,2-tet with the lone pair on the sulfur taking the place of the amine proton. Only one form of *trans*-[Co(ETE)Cl₂]⁺ was described and despite much effort we have been unable to find any other. The kinetics and steric course of aquation were studied in order to see whether they could throw light upon the configuration of the sulfur atoms. The base hydrolysis was studied in order to see the effect of removing the secondary amine groups which have been shown to be the sites of deprotonation in the base hydrolysis of *trans*-(*RS*)-[Co(2,3,2-tet)Cl₂]⁺.⁶

Experimental Section

trans-Dichloro-1,9-diamino-3,7-dithianonane cobalt(III) perchlorate was prepared and purified by the method of Bosnich, *et al.*⁵ *Anal.* Calcd for C₈H₁₆N₂S₂O₂CoCl₂: C, 19.9; H, 4.3; N, 6.6; Cl, 25.0. Found: C, 19.9; H, 4.4; N, 6.6; Cl, 25.0. Mercuric perchlorate solutions were prepared by diluting a stock solution obtained by

dissolving the required amount of mercuric oxide in a known excess of dilute perchloric acid. All other materials were AR or reagent grade.

Kinetics. (a) **Slow Spectrophotometric Studies.** Solutions were prepared by adding a known amount of the appropriate solvent mixture, previously brought to the reaction temperature, to a weighed amount of the complex. The solutions were placed in a 4-cm silica cell which was kept in the constant-temperature compartment of a Unicam SP 800 spectrophotometer and the spectrum within the range 700–325 nm was scanned at appropriate times. The temperature of the solution was determined by inserting a small thermometer in the cell at the end of the reaction. For half-lives in the range 0.5–10 min the reaction was followed at a single wavelength, the recorder bed moving at a constant rate.

(b) **Fast Spectrophotometric Studies.** Reactions between solutions of the complex and sodium hydroxide or the more concentrated mercuric perchlorate solutions were followed using a Durrum-Gibson stopped-flow apparatus in the recommended fashion. In order to prevent fogging of the mirrors at the relatively low temperatures used, dry air was passed through the mirror housing.

(c) **Titrimetric Studies of Chloride Release.** Potentiometric titration of the ionic chloride was not possible in the presence of the complex cation since the emf vs. titer curve did not take up the normal sigmoid form. It is possible that there was interaction between the Ag⁺ and the sulfur of the ligand but no direct evidence has been obtained in support of this idea. It was therefore necessary to separate the complex cation from the ionic chloride before analysis. The reaction mixture was prepared in the same way as for the spectrophotometric experiments. Samples of 1.00 ml were withdrawn at appropriate times, cooled rapidly to 0°, and passed down a cation-exchange resin in the acid form and eluted with ice-cold water. The eluent was diluted with acetone (20 ml) acidified with nitric acid and titrated with 10⁻³ M AgNO₃ solution using a Radiometer PHM26, TTT11, ABU11, TTA3, SBR2 automatic titration assembly with a silver billet electrode and a Hg-Hg₂SO₄ reference electrode.

(d) **Spectrophotometric Studies of Isomerization.** The required amount of *trans*-[Co(ETE)Cl₂]ClO₄ was weighed into a small volumetric flask and dissolved in the minimum volume of water, and the solution was cooled to 0°. One milliliter of 0.01 M NaOH solution was added and, after 1–2 sec, sufficient perchloric acid was added to neutralize the excess base and hydroxo complex and bring the free acid concentration to the predetermined value on final dilution. The solution of *trans*-[Co(ETE)H₂OCl]²⁺ thus formed was made up to the required volume by water previously brought to a temperature sufficiently in excess of that at which the isomerization was to be studied so that the final diluted solution was within 1° of the reaction temperature. The changes were followed spectrophotometrically in the usual way.

Results

The spectrum of an acidified aqueous solution of *trans*-[Co(ETE)Cl₂]ClO₄ changes slowly, with the maintenance of isosbestic points at 614 (55), 465 (120), 425 (170) and 384 (350) nm, to a new spectrum with a peak at 518 (275) nm and a shoulder at 386 (350) nm (extinction coefficients,

(1) Part XVI: T. P. Dasgupta and M. L. Tobe, *Inorg. Chem.*, **11**, 2046 (1972).

(2) R. Nithyananthan and M. L. Tobe, *Inorg. Chem.*, **8**, 1589 (1969).

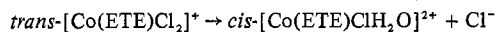
(3) H. G. Hamilton, Jr., and M. D. Alexander, *J. Amer. Chem. Soc.*, **89**, 5065 (1967).

(4) M. L. Tobe, *Inorg. Chem.*, **7**, 1260 (1968).

(5) B. Bosnich, W. R. Kneen, and A. T. Phillip, *Inorg. Chem.*, **8**, 2567 (1969).

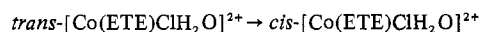
(6) G. Marangoni, M. Panayotou, and M. L. Tobe, *J. Chem. Soc., Dalton Trans.*, in press.

$M^{-1} \text{ cm}^{-1}$, in parentheses). Independent titrimetric studies under identical conditions indicate that ionic chloride is being released and that the act of spectrophotometric change is associated with the release of one of the coordinated chlorines. The spectrum of the product is similar in form to that of the cis isomers of $[\text{Co}(\text{L}_4)\text{XY}]^{n+}$, where X and Y (which may be the same) are taken from the group F, Cl, Br, and H_2O , and L_4 is any of a number of ligands providing four amine nitrogen donors. It has already been shown⁵ that, apart from a marked increase in the extinction coefficient, there is no drastic change in the form of the spectrum on replacing one or more NH groups by S. It is concluded therefore that the spectrophotometric change corresponds to the reaction



It is presumed that this is the β -cis form but there is no firm evidence at this stage. The kinetics of aquation were followed spectrophotometrically and the rate constants were determined from the slope of the plot of $\log(D_\infty - D_t)$ against time, where D_t and D_∞ are the optical densities of the reacting solution at 520 nm (the wavelength of maximum change) at time t and after 10 half-lives, respectively. Good first-order plots were obtained over at least 3 half-lives. A parallel titrimetrically followed solvolysis gave the same rate constant. These values are collected in Table I.

The displacement of the coordinated chloride from $\text{trans-}[\text{Co}(\text{ETE})\text{Cl}_2]^+$ is much faster in basic solution and can be complicated by irreproducible side reactions that lead to a general breakdown of the ligand and the complex. The standard methods of using noncoordinating buffers and following the reaction over a pH region where the standard slow reaction techniques can be employed gave unsatisfactory results but it was possible to obtain clean and consistent behavior when excess alkali was used. Preliminary studies, in which a solution of the dichloro complex at 0° was mixed with excess alkali and then acidified within a few seconds with perchloric acid, indicated that the first chloride was released rapidly and the second much more slowly. The spectrum of a solution that has been acidified 2 sec after the base has been added has the form expected for $\text{trans-}[\text{Co}(\text{ETE})\text{ClH}_2\text{O}]^{2+}$. It is similar in general shape to that of the trans -dichloro complex but with a peak at 610 (67) nm, a shoulder at 456 (150) nm (molar extinction coefficients in parentheses), and a diminished absorbance in the near-ultraviolet region. With time, this spectrum changes to one identical with that found at the end of the aquation of $\text{trans-}[\text{Co}(\text{ETE})\text{Cl}_2]^+$ and it is presumed that the spectrum change corresponds to the isomerization



the kinetics of which are reported below.

If the alkaline solution is allowed to stand for more than 10 min and then acidified, the resultant solution has a spectrum that is still "trans-like" but without clearly defined peaks. Chloride analysis indicates that the second chloride is being released and the acidified solution undergoes absorption changes that could be consistent with isomerization to a cis species. However, it is during this second stage that side reactions occur. These are characterized by a general increase in absorbance that becomes more marked as the wavelength becomes shorter, an observation consistent with light scattering by small particles. A black precipitate can often be observed in the reaction vessel.

The kinetics of base hydrolysis were followed by a stopped-flow technique, the rate constants being obtained spectro-

Table I. Rate Constants for the Aquation of $\text{trans-}[\text{Co}(\text{ETE})\text{Cl}_2]^+$ in $10^{-2} M \text{ HNO}_3$ ^a

Temp, °C	$10^4 k_{\text{obsd}}$, sec ⁻¹	Method	Temp, °C	$10^4 k_{\text{obsd}}$, sec ⁻¹	Method
39.0	0.31	Spec	58.0	3.9	Spec
47.0	0.96 ^b	Spec	65.0	10.2	Spec
47.0	0.93 ^b	Tit	73.9	21	Spec
48.8	1.25	Spec	83.9	79	Spec

^a $\Delta H^\ddagger = 26.1 \text{ kcal mol}^{-1}$; $\Delta S^\ddagger = +4 \text{ cal deg}^{-1} \text{ mol}^{-1}$. ^b Average of four independent runs.

Table II. Rate Constants for the First Stage of the Base Hydrolysis of $\text{trans-}[\text{Co}(\text{ETE})\text{Cl}_2]^+$ ^a

Temp, °C	$10^3 [\text{OH}^-]$, M	k_{obsd} , ^b sec ⁻¹	k_2 , M ⁻¹ sec ⁻¹
13.5	2.5	4.1	1600
	3.0	5.1	
	4.0	8.1	
	5.0	10.8	
	10.0	15.5	
	15.0	21	
16.8	20.0	34	2800
	25.0	41	
	2.5	6.7	
	3.0	8.5	
	4.0	11.2	
	5.0	14.0	

^a $[\text{Complex}] = 2.5 \times 10^{-4} M$; $\mu = 0.05 (\text{NaNO}_3)$. ^b Average of at least three independent kinetic runs (agreement better than $\pm 8\%$).

photometrically. The ionic strength was held constant with NaClO_4 (0.05 M), first-order kinetics were ensured by using sodium hydroxide concentrations that were much greater than those of the complex, and the rate constants were obtained in the usual way from the change in absorbance at 520 nm. These are collected in Table II.

The isomerization of $\text{trans-}[\text{Co}(\text{ETE})\text{H}_2\text{OCl}]^{2+}$ was followed spectrophotometrically after generating the complex by acidifying the first product of base hydrolysis of the trans -dichloro complex. The changing spectra generated isosbestic points at 613 (48), 473 (128), and 440 (133) nm, and the plot of $\log(D_\infty - D_t)$ at 524 nm (the wavelength of maximum change) against time was linear for at least 3 half-lives. The rate constants are reported in Table III. An attempt was made to determine the rate of isomerization of the trans -aquo-chloro complex which is generated in the Hg^{2+} -catalyzed aquation of the dichloro complex. This reaction follows a course that resembles the catalyzed aquation of $\text{trans-}[\text{Co}(\text{trien})\text{Cl}_2]^+$ ⁷ or, to a lesser extent, that of $\text{trans-}(\text{RR}, \text{SS})\text{-}[\text{Co}(2,3,2\text{-tet})\text{Cl}_2]^+$,² the spectroscopic changes being quite dissimilar from those observed during the spontaneous aquation. For mercuric perchlorate concentrations in the range 0.003–0.01 M, the spectra start to cross at 616 (56) and 453 (111) nm, but, as the second stage of the reaction takes over, well-formed isosbestic points develop at 597 (53), 464 (123), and 425 (143) nm. The rate constant for the first step (which was a first-order process at any particular $[\text{Hg}^{2+}]$) was determined from the change in optical density at 597 nm before the isosbestic point developed, while the rate constant for the second step was obtained from the change in optical density at 520 nm, ignoring the data relating to reaction times before the isosbestic points developed. The rate constants are listed in Table IV where it will be seen that the first stage has a first-order dependence on the total mercuric ion concentration. There is no evidence for any approach to a Hg^{2+} -independent rate for the first step at high mercuric

(7) A. M. Sargeson and G. H. Searle, *Inorg. Chem.*, 6, 2172 (1967).

Table III. Rate Constants for the Trans-Cis Isomerization of *trans*-[Co(ETE)ClH₂O]²⁺ in 1.0 M perchloric acid^a

Temp, °C	20.5	30.8	40.0
10 ⁴ <i>k</i> , sec ⁻¹	1.12	4.35	13.7

^a Complex generated by the acidification of the first product of the base hydrolysis of the *trans*-dichloro complex. $\Delta H^\ddagger = 23.0$ kcal mol⁻¹; $\Delta S^\ddagger = +1$ cal deg⁻¹ mol⁻¹.

Table IV. Rate Constants for the Mercuric Ion Catalyzed Aquation of *trans*-[Co(ETE)Cl₂]⁺ in 0.01 M Perchloric Acid at 25.0°

[Hg ²⁺], M	First step		Second step
	10 ⁴ <i>k</i> , sec ⁻¹	<i>k</i> /[Hg ²⁺], sec ⁻¹ M ⁻¹	10 ⁴ <i>k</i> , sec ⁻¹
0.003	5.0 ^a	0.17	1.2 ^a
0.004	6.0 ^a	0.15	1.4 ^a
0.005	7.6 ^a	0.15	1.6 ^a
0.006	10.0 ^a	0.15	2.0 ^a
0.008	13 ^a	0.16	2.1 ^a
0.009	14 ^a	0.16	1.9 ^a
0.010			1.5 ^a
0.018			1.5 ^a
0.020			1.4 ^a
0.030			1.6 ^a
0.040			2.1 ^a
0.050	175 ^b	0.35	
0.100	290 ^b	0.29	1.9 ^a
0.200	240 ^b	0.21	
0.250	560 ^b	0.22	

^a Ionic strength variable, no added salts. [Complex] = (1-2) × 10⁻³ M. ^b Measured by stopped-flow techniques; ionic strength = 2.0 M. [Complex] = 2.5 × 10⁻⁴ M.

ion concentrations of the sort found in the analogous studies with α -*cis*-[Co(EEE)Cl₂]⁺⁸ (EEE = 1,8-diamino-3,6-dithiaoctane); indeed the second-order rate constant is larger at the highest [Hg²⁺], presumably due to the higher ionic strength. This difference between *cis* and *trans* isomers has already been noted in the catalyzed reaction of the [Co(en)₂Cl₂]⁺ species.⁹ The second stage appears to be essentially independent of the concentration of mercuric perchlorate. In the presence of a sufficient excess of Hg²⁺, the first recorded spectrum is characterized by a peak at 610 (55) nm and a shoulder at 460 (125) nm.

Although the rate constants for the mercuric-independent process and the isomerization of the acidified first product of the base hydrolysis of the dichloro complex are very similar, there are inconsistencies in the observed spectrophotometric changes. The differences can, in part, be explained by incomplete removal of the first coordinated chloride in the base hydrolysis during the time allowed for the reaction. The final spectrum, which is virtually identical with that observed in the spontaneous aquation of the dichloro complex, is only achieved after rather excessive reaction times and does not pass through the isobestic points of the isomerization. No such trouble is observed at the lower [Hg²⁺] but on increasing its concentrations sufficiently, the final spectrum shifts toward shorter wavelengths and the shoulder at 386 nm becomes resolved into a second peak. Although this may be accounted for by the removal of the second chlorine, no indication of another mercury-dependent step appears in the kinetics. An alternative possibility is that interaction between Hg²⁺ and the remaining lone pair on the ligand sulfur atoms leads to a significant change in absorption spectrum. While this does not appear to have been observed for cobalt(III)-thioether complexes, a shift in the spectrum of N-bonded

(8) J. H. Worrell and C. R. Fortuni, *J. Inorg. Nucl. Chem.*, **33**, 3571 (1971).

(9) C. Bifano and R. G. Linck, *Inorg. Chem.*, **7**, 908 (1968).

Table V. Comparison of Kinetic and Stereochemical Data for Reactions of *trans*-[Co(L₄)Cl₂]⁺

	L ₄		
	(RS)-2,3,2-tet	(RR,SS)-2,3,2-tet	ETE
Aquation			
<i>k</i> _{25.0} , sec ⁻¹	1.5 × 10 ⁻⁵ ^a	2.9 × 10 ⁻⁴ ^a	4.1 × 10 ⁻⁶ ^b
<i>H</i> [‡] , kcal mol ⁻¹	24.3 ^a	25.9 ^a	26.1 ^b
<i>S</i> [‡] , cal deg ⁻¹ mol ⁻¹	+1 ^a	+12 ^a	+4 ^b
Product compn	100% <i>RS</i> - <i>trans</i> ^a	50 ± 20% <i>RR,SS</i> <i>trans</i> , rest β - <i>cis</i> ^a	?
Base Hydrolysis			
<i>k</i> _{13.50} , M ⁻¹ sec ⁻¹	13,600 ^c	29,600 ^c	1600 ^{b,d}
Product compn	100% <i>RS</i> - <i>trans</i>	100% <i>RS</i> - <i>trans</i> ^c	100% <i>trans</i>
Hg ²⁺ -Catalyzed Aquation			
<i>k</i> _{25.0} , M ⁻¹ sec ⁻¹	0.24 ^a	3.6 ^a	0.17 ^b
Product compn	100% <i>RS</i> - <i>trans</i> ^a	70% <i>RR,SS</i> - <i>trans</i> + 30% β - <i>cis</i> ^a	100% <i>trans</i>

^a Reference 2. ^b This work (extrapolated from data at higher temperatures). ^c M. L. Tobe and M. L. Tucker, to be submitted for publication. ^d *k*_{13.50} for *trans*-[Co(en)₂Cl₂]⁺ is 670 M⁻¹ sec⁻¹ [interpolated from data in S. C. Chan and M. L. Tobe, *J. Chem. Soc.*, 4531 (1962)].

thiocyanate as a result of coordination of mercuric ions to the sulfur is well documented.¹⁰

Discussion

The reactivity of *trans*-[Co(ETE)Cl₂]⁺ toward acid hydrolysis is similar in many respects to that of the complexes of the corresponding tetradentate amine ligand, 2,3,2-tet, indicating that the replacement of NH by S does not greatly affect the rate of acid hydrolysis. The resemblance is particularly close to the *RS* isomer of the tetramine complex. The relevant information is collected in Table V. This relationship has already been noted by Worrell,¹¹ who has remarked upon the similarity of the behavior of the α -*cis*-[Co(EEE)Cl₂]⁺ and α -*cis*-[Co(trien)Cl₂]²⁺.

Owing to the fact that the rate constant for the *trans* to *cis* isomerization of [Co(ETE)H₂OCl]²⁺ is some 50 times larger than the rate constant for the aquation of the *trans*-dichloro complex at 25° at pH 2, it is not possible to say whether the act of aquation takes place with retention of configuration or with stereochemical change. The fact that the mercuric ion catalyzed aquation takes place with complete retention of configuration is not necessarily proof that the spontaneous aquation is also stereoretentive. It is usually the case that the steric course of the aquation is independent of the nature of the leaving group; thus *trans*-[Co(en)₂ClX]ⁿ⁺ gives between 25 and 35% *cis*-[Co(en)H₂OCl]²⁺ when X = Cl,¹² Br,¹³ N₂,¹⁴ and ClHg,¹⁵ *trans*-(*RS*)-[Co(2,3,2-tet)Cl₂]⁺ gives only *trans*-chloroaquo product in the spontaneous and Hg²⁺-catalyzed aquations,² and *trans*-(*RR,SS*)-[Co(2,3,2-tet)Cl₂]⁺ gives 50 ± 20% β -*cis*-chloroaquo product in the spontaneous aquation and 70% β -*cis*-chloroaquo product in the Hg²⁺-catalyzed aquation.² However, there are some significant exceptions to this rule, the most relevant being the aquation of *trans*-(*SS*)-[Co(trien)Cl₂]⁺ where the spontaneous

(10) W. C. Waggener, J. A. Mattern, and G. H. Cartledge, *J. Amer. Chem. Soc.*, **81**, 2958 (1959); L. C. Falk and R. G. Linck, *Inorg. Chem.*, **10**, 215 (1971).

(11) J. A. Worrell and T. A. Jackman, *J. Amer. Chem. Soc.*, **93**, 1044 (1971).

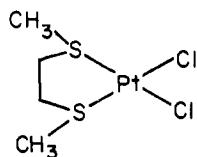
(12) M. L. Tobe, S. C. Chan, and M. E. Baldwin, *J. Chem. Soc.*, 4637 (1961).

(13) S. C. Chan and M. L. Tobe, *J. Chem. Soc.*, 5700 (1963).

(14) D. A. Loeliger and H. Taube, *Inorg. Chem.*, **5**, 1376 (1966).

(15) A. M. Sargeson, *Aust. J. Chem.*, **17**, 385 (1964).

aquation gives 100% of the β -*cis*-chloroaquo complex with the aquo ligand trans to the secondary nitrogen, while the Hg^{2+} -catalyzed reaction gives only trans product.⁷ In the absence of unambiguous stereochemical evidence it is not possible to examine the relationship between the steric course and the entropy of activation, but the activation parameters bear a strong resemblance to those of the *trans*-(*RS*)-[Co-(2,3,2-tet)Cl₂]⁺ complex, which aquates with complete retention of configuration. Although there is good reason to believe that the coordinated sulfur atoms are pyramidal (ψ -tetrahedral with the lone pair occupying the fourth position), care must be taken not to carry the analogy relating NH with S too far. The amine nitrogens are configurationally stable provided the N-H bond remains intact whereas the sulfur atom is capable of inversion without the need for any bond rupture. This may be the reason why we have been unable to isolate more than one form of the *trans*-dichloro complex. However, the rate of inversion of a sulfur atom in a similar situation, *i.e.*



has been shown to be fairly slow.¹⁶ It will probably be

necessary to await an X-ray diffraction study of the crystalline solids to see (a) whether *trans*-[Co(ETE)Cl₂]⁺ has the *RS* configuration as predicted and (b) whether the β -*cis*-chloroaquo product has undergone inversion at the sulfur.

The results of the base hydrolysis are also of interest because here there is a considerable difference between the reactivity of the ETE and the 2,3,2-tet complexes, the latter being some 8-20 times more reactive than the former. It has already been shown that the dissociatively active conjugate base from the (*RS*)-2,3,2-tet complex has lost a proton from the secondary amine nitrogen⁶ and the lower reactivity of the ETE complex is consistent with the absence of secondary amine protons. The reactivity toward base hydrolysis is closer to that of the *trans*-[Co(en)₂Cl₂]⁺ cation (Table V).¹⁷

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Registry No. *trans*-[Co(ETE)Cl₂]ClO₄, 41777-25-7; *cis*-[Co(ETE)ClH₂O]²⁺, 41777-26-8; *trans*-[Co(ETE)ClH₂O]²⁺, 41777-27-9.

(16) R. J. Cross, I. G. Dalglish, G. J. Smith, and R. Wardle, *J. Chem. Soc., Dalton Trans.*, 992 (1972).

(17) The lone pair on the sulfur does not appear to confer any stabilizing properties upon this donor in its thioether form and the comparison should be made with OH₂, which has a lone pair but no significant stabilizing power, rather than with NH₂⁻ (or NR₂⁻) which has a lone pair and confers considerable lability upon the complex.

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Preparation and Magnetic Properties of Cobalt(II) and Cadmium(II) Complexes of the Dianion of Cyclopentadienedithiocarboxylic Acid

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The disodium salt of cyclopentadienedithiocarboxylic acid reacts with cobalt(II) bromide and cadmium(II) bromide in anhydrous acetonitrile to form 2:1 ligand to metal complexes which can be isolated as the tetraethylammonium salts. The cobalt and cadmium complexes possess *D*_{2h} symmetry at the metal center as indicated by electron spin resonance, optical, and infrared spectroscopy. The unpaired electron in the low-spin cobalt complex is shown to occupy a molecular orbital made up of the d_{yz} metal orbital. When compared to other cobalt(II) dithiolate systems, this further indicates the strong electron-withdrawing nature of the dithiolate ligand.

Introduction

Much recent interest has centered on the chemistry of transition element dithiolate complexes. The recent synthesis of a novel, new dithiolate ligand, the dianion of cyclopentadienedithiocarboxylic acid, and the characterization of its zinc and copper complexes have prompted the syntheses of further metal complexes.¹ It was hoped the unusual electronic effects at the metal center of this ligand might be further substantiated by an investigation of a wider range of complexes. Complexation of cobalt(II) and cadmium(II) to form dianionic 2:1 species has been achieved.

The synthesis of the cobalt complex was undertaken because of the scarcity of 1,1-dithiolate complexes of cobalt in the +2 oxidation state.² Reaction of cobalt(II) with dithiocarbamates leads to oxidation of the metal even under

anhydrous and oxygen-free conditions.³ Since the dithiocarbamates are mononegative species, the dinegative charge on the cyclopentadienedithiocarboxylate ligand was expected to stabilize a cobalt(II) complex.⁴

It was also felt that the electronic and magnetic effects of the ligand might be more fully understood when the properties of the cobalt complex were compared to those of other cobalt(II) dithiolate systems.⁵⁻⁷

(3) J. P. Fackler, Jr., and D. G. Holah, *Inorg. Nucl. Chem. Lett.*, 2, 251 (1966).

(4) Although the cobalt(III) complex of isomaleonitriledithiolate Co[*i*-S₂C₂(CN)₂]₃³⁺ has been prepared, no reference to the synthesis nor attempted synthesis of a cobalt(II) complex exists. One would predict by the same reasoning it should be stable. Attempts are currently under way to prepare a cobalt(II) complex of *i*-S₂C₂(CN)₂²⁻.

(5) K. M. Erck and B. B. Wayland, *Inorg. Chem.*, 11, 1141 (1972).

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