both before and after intercalation, the *h0l* series shows alternately sharp and broad lines (sharp when *l* = 2*n*) which can be attributed to this type of disorder. Finally, Jellinek has reported that stacking faults frequently occur in TaS$_2$.[21] Nevertheless, the disorder must be understood more fully before precise structural information about the intercalated molecules can be obtained.

Our studies of TiS$_2 \cdot$NH$_3$ were undertaken to determine the position of the N atom of the intercalated NH$_3$ molecule. We have found a best fit by placing N on the midplane between the layers in the center of the trigonal prism. This position was predicted by Silbernagel and Gamble[5] from their studies of the anisotropy of the proton spin–lattice relaxation time in single crystals of TaS$_2 \cdot$NH$_3$, which indicate the molecular threefold symmetry axis is parallel to the layers. This suggests that the N should reside at the midplane. From our data, no strong inference can be drawn regarding the NH$_3$ orientation, but the midplane location of the nitrogen is firmly established for TiS$_2 \cdot$NH$_3$.

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Contribution from the Department of Chemistry,
Kent State University, Kent, Ohio 44242

Electron Transfer through Organic Structural Units. XX. Reductions at High Ionic Strength[1]

JEAN C. THOMAS, JOHN W. REED, and EDWIN S. GOULD*

The reductions of acetato- and propionatopentaamminecobalt(III) with chromium(II), vanadium(II), and europium(II) (25°, $\mu = 4.0$) are strongly retarded as (H$^+$) is increased from 0.10 to 4.0 M, with the observed dependencies being far too steep to be attributed reasonably to medium effects. The reactions conform to a rate law (eq 2) consistent with partition of the cobalt(III) complex into a nonprotonated and a more slowly reacting protonated form. Acidity constants for the protonated forms of both oxidants have been evaluated, as have the specific rates for the reactions of the two forms of these oxidants with V^{2+} and Eu^{2+}. We have been unable to detect the protonated path for reduction of the protonated acetato complex with Cr^{2+}, and the specific rate for the protonated propionato derivative is marginal. The nonprotonated reduction paths are predominantly (although not entirely) inner sphere, but the k_V/k_{Eu} ratios calculated for the protonated paths correspond closely to the ratios observed for known outer-sphere series (and differ markedly from inner-sphere ratios). This correspondence confirms the reality of the protonated specific rates and indicates that the protonated path is outer sphere, with the carbonyl oxygen blocked off by protonation. The specific rates for the protonated paths are 10^2 times those calculated for the (minor) outer-sphere components for the nonprotonated route, this ratio being in accord with the stipulation that electron withdrawal from coordinated Co(III) accelerates outer-sphere reduction of that metal center.

Acetatopentaaminecobalt(III) was one of the original oxidants used to demonstrate electron transfer through an organic ligand.[2] Although an approximate specific rate was reported in 1955 for the reaction of this species with Cr^{2+} in 0.1 M HClO$_4$,[2] 16 years elapsed before an acid dependency was established.[3] In 1971, Barrett and coworkers[3a] presented rate data closely following eq 1, an expression consistent with

$$\text{rate} = \frac{k_A(\text{Cr}^{II})(\text{Co}^{III})}{1 + (\text{H}^+)/K_{HA}} \qquad (1)$$

partition of the acetato complex into two forms, an unreactive protonated form (having acidity constant K_{HA}) and a reactive nonprotonated form reduced at specific rate k_A. This system is of particular interest, for, in contrast to many known acid-dependent Co(III)–Cr(II) reactions,[4] there is a strong likelihood that protonation occurs here at the carbonyl oxygen,

tying up the lead-in function[5] and blocking off the inner-sphere path.

Since protonation equilibria involving the oxidant should be independent of the reductant taken, acid dependencies are to be anticipated for other reductions of the acetato complex. In addition, evidence for protonation equilibria would be expected to arise from examination of the reactions of other alkylcarboxylato complexes.

In the present investigation, which pursues these points, many of the measurements have been made at high ionic strength ($\mu = 4.0$), using LiClO$_4$ as the supporting electrolyte. The greater μ allows experiments embracing a wider range of acidity. Moreover, as has been shown for similar equilibria involving this charge type,[3a,6] these dipositive acids are more completely protonated at greater ionic strengths, bringing into sharper focus the trends we seek. Although our data should perhaps be interpreted with some caution, we feel justified in

reporting similar acid dependencies for the reduction of the acetato complex by V(II) and by Eu(II), as well as for the related propionato complex. The measurements described here allow calculation of specific rates for reductions of the protonated forms of both oxidants by V(II) and Eu(II), but the corresponding protonated rates for Cr(II) are marginal.

Experimental Section

Materials. Solutions of Cr(II),[7] Eu(II),[8] and V(II)[6b,9] were prepared and analyzed as described. Cobalt complexes were available from a previous study.[6b] Lithium perchlorate was prepared as described.[10] Methanol and ethanol for kinetic runs in mixed solvents were refluxed with chromium(II) perchlorate solution under N_2 and then fractionally distilled, again under N_2.

Rate Measurements. Rates were estimated from measurements of absorbance decreases on the Cary 14 recording spectrophotometer as described.[6-8] Measurements were made near 502 nm. Reactions were first order each in Co(III) and in reductant, but rate measurements were carried out under pseudo-first-order conditions with at least a tenfold excess of reductant. Ionic strengths were adjusted using twice-recrystallized $LiClO_4$. To minimize volume changes resulting from mixing reagents, the solution containing the Co(III) complex, perchloric acid, and lithium perchlorate was made up to the appropriate volume, and a small known volume of a concentrated solution of the reductant was added using a calibrated microsyringe. Reactions were followed for at least 5 half-lives. Rate constants evaluated from successive half-life values within a single run generally agreed to within 4%. No trends indicative of systematic errors were noted, and average values did not differ significantly from those obtained from least-squares treatment of logarithmic plots of absorbance differences against reaction time. Temperatures were kept at 25.0 ± 0.2° during the entire series of experiments.[11]

Treatment of Data. Specific rates at $\mu = 4.0$, but at the various acidities, were fitted to eq 2 by an iterative nonlinear least-squares

$$\text{rate} = (Co^{III})(Red)\frac{k_A K_{HA} + k_{HA}[H^+]}{K_{HA} + [H^+]} \quad (2)$$

refinement. Preliminary values of k_A and k_{HA}, the specific rates for the nonprotonated and protonated paths, for Cr^{2+} were obtained by extrapolation of plots of k^{-1} vs. $[H^+]$ and k vs. $[H^+]^{-1}$. Preliminary values for K_{HA}, the acidity constants of the acetato and propionato complexes, were obtained by plotting the ratio $(k_A - k_{obsd})/(k_{obsd} - k_{HA})$ derived from the Cr(II) data against $[H^+]$. Preliminary estimates of k_A and k_{HA} for the V^{2+} and Eu^{2+} reductions were made by plotting the function $k_{obsd}(K_{HA} + [H^+])$ against $[H^+]$. In the refinement, observed specific rates were weighted in inverse proportion to the squares of their relative standard deviations. Individual values of k_{HA} and k_A for the various systems were allowed to vary, but the stipulation was made that K_{HA} for a given oxidant was independent of the reductant taken. The refinement converged after six cycles.

Results and Discussion

Typical kinetic data for reduction of the acetato complex at various acidities with Cr(II), V(II), and Eu(II) are given in Table I, and those for reductions of the corresponding propionato derivative appear in Table II. Table III lists representative values from the limited number of related experiments, carried out in this laboratory and elsewhere, at high ionic strengths, and includes, for comparison, some entries in which acidity was varied at unit ionic strength. Except for the formato complex, for which variation in the Cr^{2+} rate is marginal, the reductions in Table III appear to be independent of $[H^+]$ at high acidities. The generally good agreement between values at various acidities bolsters the implication arising from the study by Lavallee and Deutsch[12] that kinetic medium effects associated with substitution of Li^+ for H^+ in aqueous perchlorate media are slight for the reductions of saturated carboxylatocobalt(III) complexes.[13] The variations in specific rates of reduction of the acetato and propionato complexes with acidity may then be taken as kinetically significant.

Protonation, as expected, retards reaction with all three reducing agents, but the apparent patterns of acid dependency

Table I. Kinetic Data for Reductions of Acetatopentaamminecobalt(III) at High Ionic Strengths[a]

Reductant	μ	$(H^+), M$	k_{obsd}[b]	k_{calcd}[c]
Cr^{2+}	4.0	0.10	0.335 ± 0.017	0.358
		0.40	0.237 ± 0.019	0.223
		1.0	0.147 ± 0.003	0.134
		2.0	0.084 ± 0.003	0.087
		2.5	0.075 ± 0.003	0.076
		3.0	0.067 ± 0.002	0.069
		3.5	0.062 ± 0.001	0.063
		3.9	0.053 ± 0.001	0.060
V^{2+}	3.0	0.10	2.52 ± 0.10	
		0.30	2.06 ± 0.03	
		1.0	1.68 ± 0.08	
		2.0	1.60 ± 0.09	
		2.5	1.50 ± 0.06	
		2.95	1.41 ± 0.04	
	4.0	0.10	2.68 ± 0.17	2.71
		0.20	2.47 ± 0.06	2.43
		1.0	1.69 ± 0.04	1.71
		2.0	1.48 ± 0.06	1.50
		3.0	1.43 ± 0.03	1.41
		3.9	1.36 ± 0.06	1.37
Eu^{2+}	4.0	0.10	1.95 ± 0.13	1.95
		0.20	1.61 ± 0.14	1.65
		1.0	0.90 ± 0.06	0.85
		1.12	0.82 ± 0.07	0.81
		2.0	0.63 ± 0.04	0.62
		3.0	0.54 ± 0.02	0.53
		3.82	0.45 ± 0.02	0.49

[a] Specific rates in M^{-1} sec^{-1} at 25°; supporting electrolyte $LiClO_4$. $(Co^{III})_0 = 3 \times 10^{-4}$–$1 \times 10^{-3}$ M; (reductant) = 0.01–0.02 M. Values are averages of two to four replicate runs. [b] k_{obsd} defined as $(-d(Co^{III})/dt)(Co^{III})^{-1}(\text{reductant})^{-1}$. [c] k_{calcd} from eq 2, using parameters listed in Table III.

Table II. Kinetic Data for Reductions of Propionatopentaamminecobalt (III) at $\mu = 4.0$[a]

Reductant	$(H^+), M$	k_{obsd}	k_{calcd}
Cr^{2+}	0.10	0.246 ± 0.004	0.242
	1.0	0.091 ± 0.003	0.084
	2.0	0.061 ± 0.001	0.057
	3.0	0.045 ± 0.001	0.047
	3.64	0.038 ± 0.001	0.044
	3.78	0.039 ± 0.002	0.043
V^{2+}	0.10	2.27 ± 0.11	2.25
	1.0	1.54 ± 0.02	1.56
	2.0	1.46 ± 0.03	1.44
	3.0	1.41 ± 0.03	1.40
	3.96	1.38 ± 0.01	1.37
Eu^{2+}	0.10	1.05 ± 0.04	1.07
	1.0	0.59 ± 0.03	0.53
	2.0	0.47 ± 0.01	0.44
	3.0	0.40 ± 0.01	0.41
	3.70	0.39 ± 0.01	0.39
	3.85	0.36 ± 0.03	0.39
	3.96	0.33 ± 0.02	0.39

[a] Reaction conditions are similar to those listed in Table I.

are not precisely the same. Specific rates with Cr(II) (k_{Cr} values) approach, but do not reach, proportionality to $[H^+]^{-1}$ at high acidities, whereas with V(II) they clearly level off. The inference here is that the protonated path constitutes the predominant route for reduction by V(II) at high acidity, whereas with Cr(II), only a minor reduction component proceeds through this path. The acidity pattern for k_{Eu}, the specific rates for reduction with Eu^{2+}, lies between these extremes.

We have applied the general rate law[3a,4b] represented by eq 2 to these systems. Here the specific rates k_A and k_{HA} refer to the nonprotonated and protonated paths, and K_{HA} is the acidity constant for the protonated oxidant.[15] With the aid of an iterative nonlinear least-squares procedure, values of k_A, k_{HA}, and K_{HA} giving the closest fit to the observed rates have been calculated. These appear in Table IV. Rates calculated

Table III. Reductions of Various Carboxylatopentaamminecobalt(III) Complexes, $RCo(NH_3)_5{}^{2+}$

Ligand, R	Reductant	μ	$(H^+), M$	k^a
Formato[b]	Cr^{2+}	4.0	0.1	8.8
			1.0	8.4
			3.9	6.1
Maleato[c]			1.0	210
			4.0	230
Benzoato[d]		1.2	0.02	0.15
			1.20	0.15
Malonato[e]		4.0	1.00	4.1
			3.95	4.0
Dimethylmalonato[e]			1.00	0.325
			3.75	0.310
Trimethylacetato	Cr^{2+}	2.0	f	0.0070
	Eu^{2+}	4.0	0.10	0.23[j]
			3.72	0.23[j]
Furoato	Cr^{2+}	3.0	0.16	0.38[g]
			2.3	0.44[g]
	Eu^{2+}	1.0	0.01	3.3[h]
			1.0	3.5[h]
2-Thiophenecarboxylato	Cr^{2+}	3.0	0.16	0.25[g]
			2.3	0.29[g]
Glycolato[h]	Eu^{2+}	1.0	0.01	87
			1.0	88
Salicylato	Eu^{2+}		0.01	0.82[h]
			1.0	0.86[h]
	V^{2+}		0.10	1.13[i]
			1.0	1.15[i]
Pyruvato[i]	V^{2+}		0.10	10.2
			1.0	10.8

[a] Specific rates in M^{-1} sec^{-1} at 25°. Supporting electrolyte is $LiClO_4$ unless otherwise noted. [b] J. R. Barber, Jr., Ph.D. Thesis, Kent State University, 1973. [c] E. S. Gould, *J. Am. Chem. Soc.*, **88**, 2983 (1966). [d] See ref 4b. [e] See ref 12. [f] Reaction reported to be independent of acidity in the range $(H^+) = 0.1–1.1$ *M*. See ref 3a. [g] E. S. Gould and H. Taube, experiments at Stanford University, 1962. Supporting electrolyte is $NaClO_4$. [h] F.-R. F. Fan, M.Sc. Thesis, Kent State University, 1975. [i] J. C. Thomas, Ph.D. Thesis, Kent State University, 1975. [j] This work.

Table IV. Calculated Kinetic Parameters for Reductions of Acetato- and Propionatopentaamminecobalt(III) Complexes[a]

|	K_{HA}, M	Reductant	k_A	k_{HA}
Acetato	0.35 ± 0.07	Cr^{2+}	0.46 ± 0.08	0.024 ± 0.019
		V^{2+}	3.15 ± 0.12	1.22 ± 0.03
		Eu^{2+}	2.43 ± 0.11	0.31 ± 0.05
Propionato	0.24 ± 0.04	Cr^{2+}	0.33 ± 0.02	0.025 ± 0.010
		V^{2+}	2.66 ± 0.10	1.30 ± 0.02
		Eu^{2+}	1.39 ± 0.06	0.33 ± 0.01

[a] Reactions at 25°, $\mu = 4.0$. Specific rate, in M^{-1} sec^{-1}, calculated by minimization of the function $(k_{calcd} - k_{obsd})^2$, where values of k_{calcd} are obtained eq 2.

using these parameters are compared to observed rates in Tables I and II.

The estimated acidity constant 0.35 ± 0.07 *M* for the acetato complex is in reasonable agreement with the value 0.48 ± 0.11 obtained spectrophotometrically.[3] As anticipated, the degree of protonation of this complex in water is greater at $\mu = 4.0$ ($pK_A = 0.46$) than at $\mu = 1.0$ ($pK_{HA} = -0.60$).[3a] The magnitude of this effect is astonishingly large, for the apparent change in basicity is proportionately far greater than the change in μ, whereas variation in thermodynamic salt effects within this range of ionic strengths is generally much less steep than that corresponding to a direct proportionality.[16] The sharpness of this dependence appears to be responsible, at least in part, for the slight *decrease* in some of the k_V values when μ is raised from 3.0 to 4.0 *M* (Table I); here rate increases resulting from the kinetic salt effects are offset by the greater degree of conversion to the less reactive form of the oxidant at the higher μ.

The k_A values in Table IV are comparable to specific rates reported for a host of aliphatic $(NH_3)_5Co^{III}$ complexes[3a,6a,8a] and require no further comment. Assuming, however, that protonation of the acetato and propionato complexes rules out inner-sphere reduction, the k_{HA} values may be taken as outer-sphere specific rates. Note that the ratio k_V/k_{Eu} for the protonated route is 3.9 for both oxidants. This ratio falls in the range 3–4 which has been found to apply to outer-sphere reductions of N-bound $(NH_3)_5Co^{III}$ derivatives of heterocyclic ligands at $\mu = 1.0$[8a] and is, at the same time, well removed from the ratios appropriate to reductions through carboxylato bridges, for which, in the absence of complicating effects,[4a] values of k_V and k_{Eu} are nearly equal.[8b] The k_{Cr} value for the protonated acetato complex is not statistically real, but the (relatively uncertain) k_{Eu}/k_{Cr} ratio for the protonated propionato derivative is 13 ± 5, thus falling in the range set by a wide variety of outer-sphere oxidants.[8b] In short, those k_{HA} values which we can determine adhere to the linear free energy relationships which have been found[5,6b,8a] to correlate measured outer-sphere rates of reduction with these dipositive centers. This fit confirms the view that the k_{HA}'s resulting from our treatment are real (i.e., that they are not artifacts reflecting medium effects) and that they indeed represent outer-sphere specific rates. Further, Marcus' prediction that relative rates of outer-sphere reduction of a given oxidant by two or more reductants should be independent of the oxidant (and vice versa)[17] is seen to extend to these protonated oxidants.

Specific rates for the protonated acetato complex exceed, by a factor of about 10^2, the estimated[8a] outer-sphere components for reduction of the nonprotonated oxidant and are 50 times the k_{Cr} and k_V values measured by Scott and Sykes[5] for the μ-acetato complex **1**. The structural environment about

1
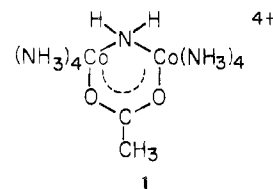
the two Co^{III} centers in **1** is very similar to that about Co^{III} in the mononuclear complex, but **1** cannot undergo inner-sphere reduction because the carbonyl group is blocked off by coordination. These striking rate increases resulting from protonation add to a growing body of evidence[8a,18] that electron withdrawal from Co^{III} enhances reduction rates, provided that the structural modification is not made in a bridging ligand.[19]

Will other carboxylatocobalt(III) complexes exhibit acidity patterns of the type described here? Protonation of the oxidant (under present conditions) should be negligible if an electron-withdrawing substituent such as halogen, a second carboxyl, or a benzene ring is incorporated into the coordinated carboxylato group. However, measurable acid dependencies should be observable for complexes of at least some of the higher straight-chain fatty acids, and possibly for some branched-chain derivatives as well, although appreciable shift of the region of variation to higher pH's is not to be expected. Finally, since inner-sphere rates are known to be much more sensitive than outer-sphere rates to the degree of branching in the carboxylato group,[8a] we would not be astonished to encounter at least one Co(III) derivative of a branched ligand which is reduced more rapidly (mainly via the outer-sphere path) at high acidity than at low. Convincing data pointing to such a reversal have not been obtained, but we are examining several likely candidates.

Registry No. Acetatopentaamminecobalt(III), 16632-78-3; propionatopentaamminecobalt(III), 19173-62-7; Cr(II), 22541-79-3; V(II), 15121-26-3; Eu(II), 16910-54-6; trimethylacetatopentaamminecobalt(III), 33887-25-1.

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(11) In addition to the measurements in aqueous media at high ionic strengths, a series of preliminary experiments was carried out in methanol–water and ethanol–water mixtures at ionicities in the range 0.1–0.2 *M* (LiClO₄). In all cases, specific rates were, as expected, lower than those in water, but differences in acidity patterns were evident. The V(II) and Cr(II) reductions of the formatopentaammine complex, the V(II) reduction of the pyruvato complex, I, and the Cr(II) and Eu(II) reductions of the N,N-dimethylnicotinamide complex, II, are each very nearly independent of added acid in the range (H⁺) = 0.005–0.10 *M*, both in 80% methanol and 80% ethanol (v/v). On the other hand, the V(II) reductions of the aquopentaammine complex, the pyridine complex, III, and the dimethylnicotinamide complex, as well as the Eu(II) reduction of the

pyridine complex, each in 80% methanol, proceed more rapidly at low acidity than at high, but the acid dependence is less sensitive to (H⁺) than inverse first order. At present, we see no direct correlation of these patterns, either with reaction mechanism or with the structures of the reactants.

(Ro = "roseo" = (NH₃)₅Co^III)
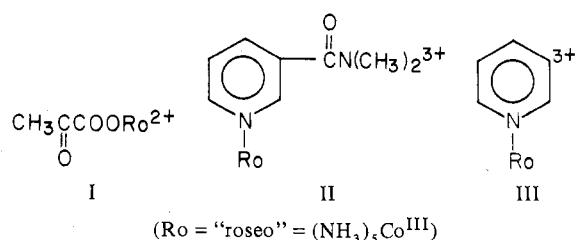
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(13) Such medium effects have been shown to be significant, however, in the reduction, by Cr(II), of (NH₃)₅H₂OCo³⁺ ¹⁴ᵃ and in the reductions of α,β-unsaturated carboxylato complexes of Co(III).¹⁴ᵇ

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Contribution from the Chemistry Department,
The University of South Florida, Tampa, Florida 33620

Kinetics and Stereochemistry of the Spontaneous and Mercury(II)-Catalyzed Acid Hydrolysis for the Symmetrical Cis Isomer of the Dichloro(1,8-diamino-3,6-dithiaoctane)cobalt(III) Cation

JAY H. WORRELL

The spontaneous aquation of *s-cis*-Co(eee)Cl₂⁺ and *s-cis*-Co(eee)ClH₂O²⁺·, where eee is NH₂–CH₂CH₂–S–CH₂CH₂–S–CH₂CH₂NH₂, has been studied under various conditions of temperature and acid concentration. The rate and mechanism of mercury(II)-assisted hydrolysis is also reported for both ions. All reactions proceeded with retention of absolute configuration. Spontaneous aquation of both complex ions obeys the rate law d[Co(III)]/dt = k[Co(III)] where k = 1.77 × 10⁻⁴ sec⁻¹ and 1.10 × 10⁻⁶ sec⁻¹ for the dichloro and aquochloro complexes, respectively, at 50° in 0.10 *M* HClO₄. Activation parameters for the dichloro compound are ΔH‡ = +20.4 kcal/mol and ΔS‡ = −12.6 eu. Mercury(II) forms a binuclear complex with *s-cis*-Co(eee)Cl₂⁺ which aquates according to the rate law −d[Co(eee)Cl₂⁺]/dt = k₁K[Hg²⁺][Co(III)]/1 + K[Hg²⁺] where k₁ = 2.72 × 10⁻² sec⁻¹ and K = 34.4 *M*⁻¹ at 15° in 0.10 *M* HClO₄. The Hg(II)-catalyzed aquation of *s-cis*-Co(eee)ClH₂O²⁺ follows second-order kinetics, the rate law being −d[Co(eee)ClH₂O²⁺]/dt = kₜ[Co(eee)ClH₂O²⁺][Hg²⁺] where kₜ = 8.41 × 10⁻² *M*⁻¹ sec⁻¹ at 50° in 0.10 *M* HClO₄ with ΔH‡ = 22.7 kcal/mol and ΔS‡ = +6.75 eu. These data are discussed and compared to nitrogen donor systems and trans sulfito systems with a view toward contrasting the unique deactivation role thioether donor atoms play when positioned trans to reactive sites within the complex.

Introduction

The recent synthesis of various new quadridentate ligands has resulted in the preparation and isolation of interesting new complexes which because of their multiple sterochemistries,¹⁻¹⁶ donor atom arrangements,²,⁸,⁹ and varied solvation spheres³,⁷,¹⁰,¹²,¹⁵,¹⁶ are ideally suited for meaningful kinetic and mechanistic investigations. To date, such investigations have been limited to the acid and base hydrolysis for a number of cobalt(III) complexes derived from flexible open-chain tetramine ligands¹³,¹⁷,¹⁸ and cyclic tetramines.¹⁹,²⁰

Initially, Sargeson and Searle elegantly characterized and

reported the aquation kinetics and stereochemistry for the D-*s-cis*-, D-*uns-cis*-, and *trans*-Co(S,S-trien)Cl₂⁺ ions.¹⁸ A

s-cis   uns-cis
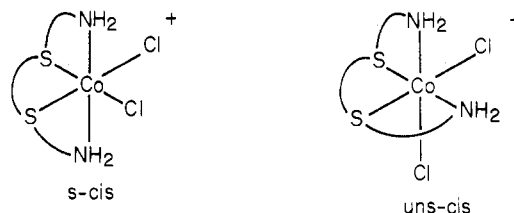
macrocyclic ligand which is directly related to triethylene-