

59042-80-7;  $\text{Co}^{13}\text{CN}(\text{CN})_4\text{OH}_2^{2-}$ , 59091-67-7;  $\text{Co}^{13}\text{CN}(\text{CN})_4\text{OH}^{2-}$ , 59091-68-8.

## References and Notes

- (1) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions", 2d ed, Wiley, New York, N.Y., 1967, Chapters 3 and 4.
- (2) D. A. Buckingham, I. I. Olsen, and A. M. Sargenson, *Aust. J. Chem.*, **20**, 597 (1967).
- (3) D. A. Buckingham, I. I. Olsen, and A. M. Sargenson, *J. Am. Chem. Soc.*, **89**, 5129 (1967).
- (4) J. Halpern, R. A. Palmer, and L. M. Blakley, *J. Am. Chem. Soc.*, **88**, 2877 (1966).
- (5) A. Haim and W. K. Wilmarth, *Inorg. Chem.*, **1**, 573, 583 (1962).
- (6) A. Haim, R. V. Crassi, and W. K. Wilmarth, *Adv. Chem. Ser.*, No. 49 (1965).
- (7) H. H. Chen, M. S. Tsao, R. W. Gaver, P. H. Tewari, and W. K. Wilmarth, *Inorg. Chem.*, **5**, 1913 (1966).
- (8) P. H. Tewari, R. W. Gaver, H. K. Wilcox, and W. K. Wilmarth, *Inorg. Chem.*, **6**, 611 (1967).
- (9) J. E. Byrd and W. K. Wilmarth, *Inorg. Chim. Acta, Rev.*, **7** (1971).
- (10) M. Wrighton, G. S. Hammond, and H. B. Gray, *J. Am. Chem. Soc.*, **93**, 5254 (1971).
- (11) A. W. Adamson, A. Chiang, and E. Zinato, *J. Am. Chem. Soc.*, **91**, 5467 (1969).
- (12) M. Wrighton, H. B. Gray, G. S. Hammod, and V. Miskowski, *Inorg. Chem.*, **12**, 740 (1973).
- (13) M. Wrighton and D. Bredeson, *Inorg. Chem.*, **12**, 1707 (1973).
- (14) P. R. Ray, *Z. Anorg. Allg. Chem.*, **208**, 392 (1932).
- (15) G. Levy, *J. Magn. Reson.*, **6**, 143 (1972).
- (16) H. Hirota, Y. Koite, H. Ishizuki, and A. Yamasaki, *Chem. Lett.*, **8**, 853 (1973).
- (17) See ref 31 in P. R. Hoffman and K. G. Caulton, *J. Am. Chem. Soc.*, **97**, 4221 (1975).
- (18) J. P. Birk and J. Halpern, *J. Am. Chem. Soc.*, **90**, 305 (1968).

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## Conformational Dissymmetry. Circular Dichroism and Stereospecificity Induced by Skew Six-Membered Chelate Rings

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A series of complexes of the type  $[\text{Co}(\text{R,R-dmtn})_2\text{X}_2]^{n+}$ , where R,R-dmtn is the optically active 2,4-pentanediamine ligand, have been prepared and characterized. It is found that, unlike the five-membered chelate ring analogues, these six-membered skew rings give consistent patterns for the d-d circular dichroism of their trans complexes and, in addition, the circular dichroism is insensitive to variations in the solvent. The stereospecificity of the *cis*- $[\text{Co}(\text{R,R-dmtn})_2(\text{NH}_3)_2]^{3+}$  complexes is found to be small; the *l*el to *o*b ratio is about 4:1 in liquid ammonia. The circular dichroism of the diammine complexes show a number of unusual features, the more interesting of which are the lack of conformational additivity of the circular dichroism and the apparently large transition magnetic moments carried by the  $^1\text{A}_{1g} \rightarrow ^1\text{T}_{2g}$  manifolds. Possible reasons for these are adumbrated.

The ligand 2,4-pentanediamine (dmtn) is the six-membered chelate ring analogue of 2,4-diaminobutane (bn) which forms five-membered chelate rings, but unlike the latter, the former stabilizes two distinct chelate conformations. Conformational energy calculations<sup>1,2</sup> predict and experimental studies confirm<sup>3,4</sup> that the most stable chelate ring conformation for the meso dmtn (R,S-dmtn) ligand is the chair and that for the racemic ligand (R,R:S,S-dmtn) is the skew conformation. In both conformations the methyl groups are equatorially disposed. These essential conformations seem to persist even when there is considerable interaction between neighboring chelate rings.<sup>3-6</sup> This paper is concerned with the conformational isomers and the optical activity of the  $[\text{Co}(\text{R,R-dmtn})_2\text{X}_2]^{n+}$  complexes; a following paper describes the isomers of the  $(\text{R,S-dmtn})_2\text{Co}^{\text{III}}$  complexes.

There are two aspects of  $(\text{R,R-dmtn})_2$  complexes which are of peculiar interest. The first is that the conformationally induced d-d circular dichroism in complexes containing linear quadridentate amines which incorporate the R,R-dmtn moiety is relatively strong and, at the same time, consistent patterns are observed for a related series of complexes.<sup>7</sup> This is in marked contrast with the bewildering diversity of patterns observed when only five-membered chelate rings are the major source of dissymmetry.<sup>8</sup> Complexes of the type *trans*- $[\text{Co}(\text{R,R-dmtn})_2\text{X}_2]^{n+}$  provide the simplest series of compounds where the d-d circular dichroism of the skew six-membered chelate ring can be investigated.

The second aspect relates to the configurational stereospecificity of octahedral complexes containing two or more R,R-dmtn ligands. Unlike the substituted ethylenediamine cobalt(III) complexes where diastereomeric equilibration can be achieved without appreciable decomposition,<sup>9</sup> the dmtn cobalt(III) complexes are decomposed by the presence of cobalt(II) catalysts. The isomers of  $[\text{Co}(\text{R,R-dmtn})_2$

$(\text{NH}_3)_2]^{3+}$ , however, can be prepared under equilibrium conditions with negligible decomposition.

Figure 1 shows the two possible *cis* isomers of the  $[\text{Co}(\text{R,R-dmtn})_2\text{X}_2]^{n+}$  system. Conformational energy calculations<sup>1,10</sup> predict that the *l*el-*cis*- $\Delta$  diastereomer should be more stable than the *o*b-*cis*- $\Lambda$ -isomer. In all three isomers, the chelate ring is assumed to be in the basic skew<sup>11</sup> conformation.

### 1. Preparations

The original preparations<sup>12,13</sup> of *trans*- $[\text{Co}(\text{R,R-dmtn})_2\text{Cl}_2]^+$  give poor yields of the pure compound. Aerial oxidation of a methanolic solution of partially neutralized R,R-dmtn-2HCl together with cobalt chloride and sodium nitrite affords the  $[\text{Co}(\text{R,R-dmtn})_2(\text{NO}_2)_2]^+$  ion in high yield, which is then converted quantitatively into the (-)-*trans*- $[\text{Co}(\text{R,R-dmtn})_2\text{Cl}_2]\text{ClO}_4$  salt. This dichloro complex is conveniently labile for preparation of other *trans*- $[\text{Co}(\text{R,R-dmtn})_2\text{X}_2]^{n+}$  species (X =  $\text{N}_3^-$ ,  $\text{NCS}^-$ ,  $\text{NO}_2^-$ ,  $\text{NH}_3$ ) provided the anation is carried out in methanol solutions. In other dipolar solvents, solvolysis occurs rapidly and is accompanied by the formation of *cis*-solvento species which give *cis* complexes upon anation. The *trans*-diazido species rapidly undergoes solvolysis and isomerization in all polar solvents, including methanol in which it is the most stable.

The reaction of *trans*- $[\text{Co}(\text{R,R-dmtn})_2\text{Cl}_2]^+$  with disodium oxalate produces the (+)-*cis*- $\Lambda$ - and (-)-*cis*- $\Delta$ - $[\text{Co}(\text{R,R-dmtn})_2\text{ox}]^+$  ions in roughly equal proportions and both isomers have been obtained pure. These proportions are probably largely kinetically controlled but our attempts at equilibrating them in aqueous solutions were frustrated by their decomposition in the presence of charcoal or base. The same rapid decomposition occurs with the (three)  $[\text{Co}(\text{R,R-dmtn})_2(\text{NH}_3)_2]^{3+}$  isomers in the presence of charcoal or base.

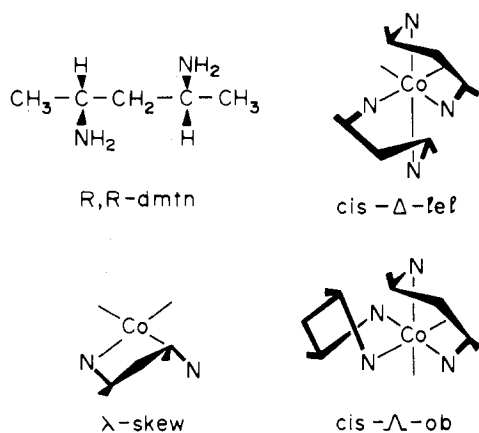
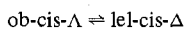


Figure 1. Absolute configuration of *R,R*-dmtn and the stable  $\lambda$ -skew chelate ring it forms. On the right are shown the two *cis*-(*R,R*-dmtn)<sub>2</sub> diastereomers, the more open *cis*- $\Delta$ - $\ell\ell$  isomer and the more crowded *cis*- $\Lambda$ -ob isomer.

However, a fairly clean equilibration of the diammine complexes occurs in dry liquid ammonia. Thus, when the green *trans*-[Co(*R,R*-dmtn)<sub>2</sub>Cl<sub>2</sub>]Cl complex is dissolved in anhydrous liquid ammonia, the solution turns a golden yellow at once. The orange residue obtained after evaporation of the ammonia contains the three [Co(*R,R*-dmtn)<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub>]Cl<sub>3</sub> isomers in about 98% yield, the remainder consisting of Co(II) species which were presumably involved in the catalytic equilibration. The three isomers can be isolated pure in very high total yield (>90%) by fractional crystallization.

The equilibrium mixture consists of *trans*-[Co(*R,R*-dmtn)<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub>]<sup>3+</sup> (46.2%),  $\ell\ell$ -*cis*- $\Delta$ -[Co(*R,R*-dmtn)<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub>]<sup>3+</sup> (42.5%) and *ob-cis*- $\Lambda$ -[Co(*R,R*-dmtn)<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub>]<sup>3+</sup> (11.3%). Two aspects of these results are of interest. The first is that more *cis* than *trans* complex exists at equilibrium despite the fact that the interligand interactions are probably greater in the former. This may be because the solvation of the *cis* complexes is greater than that of the *trans* species, a suggestion which is supported by the general observation that tripositively charged cobalt(III) complexes have a strong tendency to adopt the *cis* topology in highly polar solvents. The unipositively charged species, when other factors allow, give *trans* complexes. We have prepared the [Co(*R,R*-dmtn)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]<sup>3+</sup> ion; it is exclusively *cis* in water solution. The other feature is that the equilibrium constant for



is approximately 4, indicating that the stereospecificity is small. This value is obtained at about -33 °C and is probably even less at higher temperatures and, as well, it could be dependent on the nature of the solvent if significant hydrogen bonding between the amino protons and the solvent is involved.

## 2. Circular Dichroism of *Trans* Complexes

Figures 2-4 show the absorption and circular dichroism spectra of the complexes *trans*-[Co(*R,R*-dmtn)<sub>2</sub>X<sub>2</sub>]<sup>+</sup>, where X<sup>-</sup> = N<sub>3</sub><sup>-</sup>, NCS<sup>-</sup>, and NO<sub>2</sub><sup>-</sup>, in a variety of solvents. In a previous paper<sup>7</sup> we showed that for analogous complexes containing a quadridentate ligand with two terminal *R,R*-dmtn rings linked by a dimethylene bridge (*R,R,R,R*-sk-3,2,3) the A band of the <sup>1</sup>T<sub>1g</sub> manifold was negative for all of the complexes except the *trans*-dinitro species. The E component was generally positive although there were cases where a couplet was observed. A similar pattern is observed for the *trans*-[Co(*R,R*-dmtn)<sub>2</sub>Cl<sub>2</sub>]<sup>+</sup> ion.<sup>8</sup>

Inspection of Figures 2-4 reveals that the circular dichroism is relatively strong as compared to other conformational isomers and that for all of the complexes, the A band, at 20 500 cm<sup>-1</sup> (N<sub>3</sub><sup>-</sup>), 22 000 cm<sup>-1</sup> (NCS<sup>-</sup>), and 21 000 cm<sup>-1</sup> (NO<sub>2</sub><sup>-</sup>),

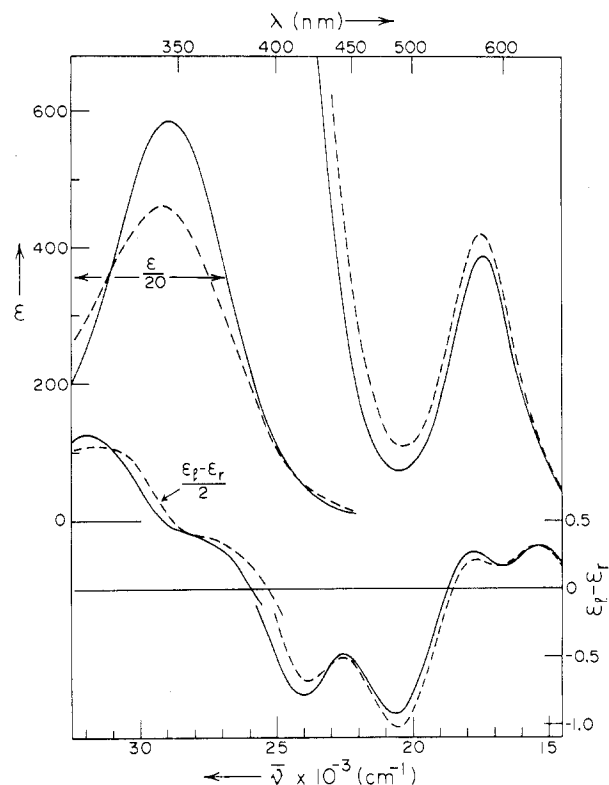


Figure 2. Absorption and circular dichroism spectra of (-)-*trans*-[Co(*R,R*-dmtn)<sub>2</sub>(N<sub>3</sub>)<sub>2</sub>]ClO<sub>4</sub> in methanol (—) and acetonitrile (---).

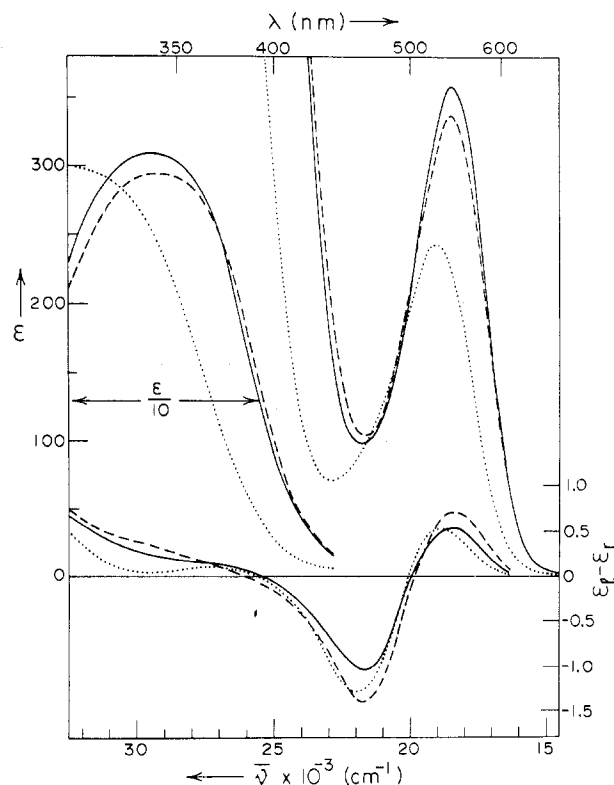


Figure 3. Absorption and circular dichroism spectra of (+)-*trans*-[Co(*R,R*-dmtn)<sub>2</sub>(NCS)<sub>2</sub>]ClO<sub>4</sub> in methanol (—), acetonitrile (---), and water (···).

is negative, and the E bands are residually positive. (The sense of the splitting for the A and E bands of the NO<sub>2</sub><sup>-</sup> species is reversed compared with the other two.<sup>8</sup>) Unlike the circular dichroism associated with conformational isomers where the

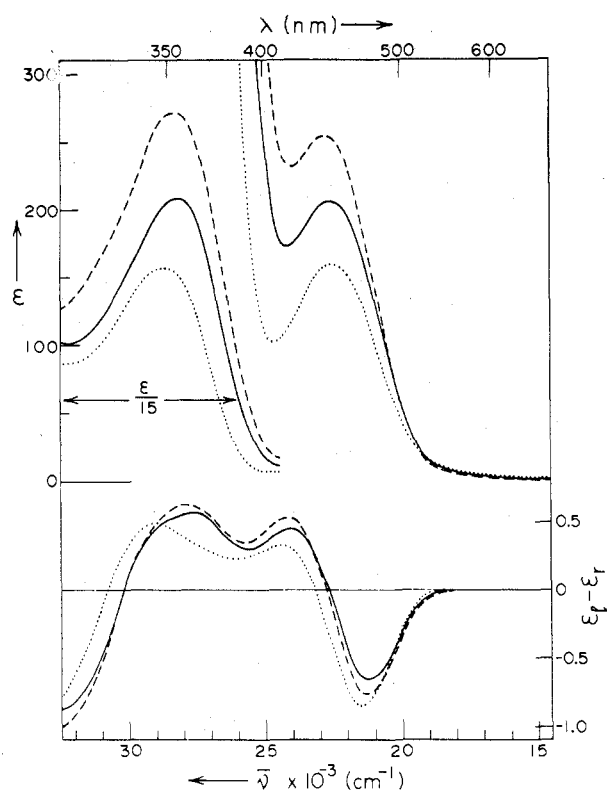


Figure 4. Absorption and circular dichroism spectra of (+)-*trans*-[Co(*R,R*-dmtn)<sub>2</sub>(NO<sub>2</sub>)<sub>2</sub>]ClO<sub>4</sub> in methanol (—), acetonitrile (---), and water (···).

major source of dissymmetry is the puckering of five-membered rings, the circular dichroism of the present complexes is relatively insensitive to solvent variations. It should be noted, however, that these solvent variations are of the same order of magnitude as is observed for the five-membered ring systems, but because the circular dichroism is so much more intense for these six-membered ring systems, the solvent variations do not appear as spectacular variations in sign and intensity. The large changes in the linear absorption band with changes in solvent are due to shifts in the charge-transfer band, which, as it moves to the red, "lifts" the <sup>1</sup>T<sub>1g</sub> envelope and vice versa.

There is an interesting feature associated with the E band of the diazido species where the circular dichroism appears to consist of three transitions, two positive bands at either side of a trough which might be interpreted as indicating the presence of a negative component. That a negative component is present rather than just two contiguous positive bands appears plausible because, otherwise, the E band would be split by some 2500 cm<sup>-1</sup>. This seems to us unlikely, even if  $\pi$  bonding arising from a unique orientation of the N<sub>3</sub><sup>-</sup> ligands were invoked. We suggest that a strong, broad positive band is present, slightly displaced from a weaker (and perhaps somewhat narrower) negative band and that the observed spectrum is the resultant, where the positive component is seen as the two lateral wings.

### 3. Circular Dichroism of the Diammines

Figure 5 shows the absorption and circular dichroism spectrum of the [Co(*R,R*-dmtn)<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub>]Cl<sub>3</sub> complexes in water solutions. As expected, the linear absorptions are very similar but the circular dichroism is diagnostic in distinguishing the isomerism.

The geometrical and absolute configurations of the three isomers are assigned by <sup>13</sup>C NMR, which unambiguously distinguishes *cis* from *trans* complexes, and by circular dichroism. The circular dichroism and (absolute) crystal

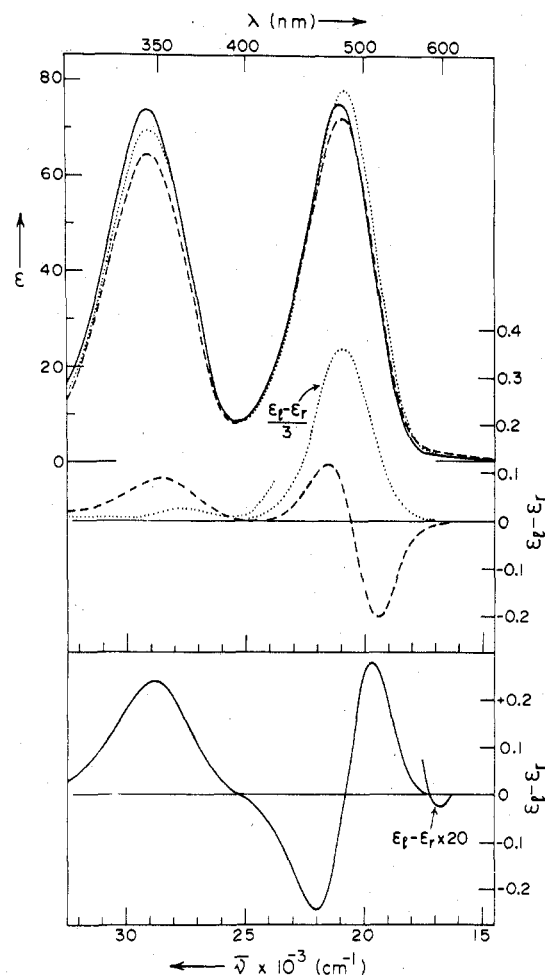


Figure 5. Top: absorption and circular dichroism spectra of *cis*- $\Delta$ -[Co(*R,R*-dmtn)<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub>]Cl<sub>3</sub> (---) and *cis*- $\Lambda$ -[Co(*R,R*-dmtn)<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub>]Cl<sub>3</sub> (···) in water solutions. Bottom: circular dichroism spectrum for the *trans*-[Co(*R,R*-dmtn)<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub>]Cl<sub>3</sub> in water solution; the corresponding absorption for the *trans* form is shown (—) in the top diagram.

structures of the  $\Delta$  and  $\Lambda$  diastereomers of the [Co(*R,R*-dmtn)<sub>3</sub>]<sup>3+</sup> ions have been reported.<sup>3,13</sup> The (+)- $\Lambda$ -[Co(*R,R*-dmtn)<sub>3</sub>]<sup>3+</sup> ion shows<sup>13</sup> a single, strong positive circular dichroism band under the <sup>1</sup>T<sub>1g</sub> manifold, and hence the less abundant *cis*-(+)-[Co(*R,R*-dmtn)<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub>]<sup>3+</sup> ion, which also shows a single positive band for this transition, is assigned the same,  $\Lambda$ , absolute configuration. The more abundant *cis*-(+)-[Co(*R,R*-dmtn)<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub>]<sup>3+</sup> ion is therefore assigned the  $\Delta$  absolute configuration (Figures 1 and 5). These assignments are consistent with the equilibrium proportions of the two *cis* isomers, in that we expect the more crowded  $\Lambda$ -ob isomer to occur in lower proportions compared to the more open-structured  $\Delta$ -lel diastereomer (Figure 1). The circular dichroism under the <sup>1</sup>T<sub>1g</sub> manifold of *cis*- $\Delta$ -[Co(*R,R*-dmtn)<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub>]Cl<sub>3</sub>, which is concentration independent (10<sup>-2</sup>–10<sup>-3</sup> M in water), is similar to that observed<sup>13</sup> for the  $\Delta$ -[Co(*R,R*-dmtn)<sub>3</sub>]Cl<sub>3</sub> in water solution, although the ClO<sub>4</sub><sup>-</sup> salt of the latter shows only a single negative band.

The *trans*-[Co(*R,R*-dmtn)<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub>]<sup>3+</sup> ion shows a unique circular dichroism spectrum for a dissymmetric hexaminecobalt(III) complex; three components are observed under the <sup>1</sup>T<sub>1g</sub> manifold. Moreover, the magnetic dipole forbidden <sup>1</sup>T<sub>2g</sub> manifold carries circular dichroism of the same order of magnitude as that observed under the magnetic dipole allowed <sup>1</sup>A<sub>1g</sub> → <sup>1</sup>T<sub>1g</sub> transition.

Moffitt's<sup>14</sup> original argument that, because the linear absorption spectra of hexamine complexes are very similar

whether or not dissymmetrically disposed aliphatic chelate rings are present, the zero-order ( $O_h$ ) d-d selection rules will be largely retained in dissymmetric hexaamine complexes has been supported by numerous examples with five-membered chelate rings.<sup>15</sup> It is therefore surprising that in these six-membered chelate ring complexes, whose spectra are almost superimposable on those observed for other hexaamine systems, the rule should break down, presumably because of strong mixing between the appropriate states of the  $^1T_{2g}$  manifold and other magnetic dipole allowed states of the system. We note that the  $[\text{Co}(R,R\text{-dmtn})(\text{NH}_3)_4]^{3+}$  and  $\Delta\text{-}[\text{Co}(R,R\text{-dmtn})_3]^{3+}$  ions<sup>13</sup> as well as the present trans complex all show strong circular dichroism under the  $^1A_{1g} \rightarrow ^1T_{2g}$  transition but that the  $\Delta\text{-}[\text{Co}(R,R\text{-dmtn})_3]^{3+}$  ion<sup>13</sup> and the two *cis*- $[\text{Co}(R,R\text{-dmtn})_2(\text{NH}_3)_2]^{3+}$  diastereomers show "normal" patterns. We suspect that particular donor atom distortions away from the octahedral positions may be a factor in causing the extensive mixing although the argument cannot be pursued without structural data. The crystal structures of the  $\Delta$ - and  $\Delta\text{-}[\text{Co}(R,R\text{-dmtn})_3]^{3+}$  ions,<sup>3</sup> however, confirm that greater distortions of the octahedron occur with the  $\Delta$ -ob complex which, unlike the  $\Delta$ -lel isomer, shows strong circular dichroism under the  $^1T_{2g}$  band.

The assignments of the d-d circular dichroism components are suggested by the effects observed in the presence of selenite ions.<sup>16,17</sup> The effect of added selenite ions on either the *trans*- or *cis*- $\Delta\text{-}[\text{Co}(R,R\text{-dmtn})_2(\text{NH}_3)_2]^{3+}$  ions is negligible, but a pronounced effect is seen in the case of the *cis*- $\Delta\text{-}[\text{Co}(R,R\text{-dmtn})_2(\text{NH}_3)_2]^{3+}$  ion (Figure 6). This specific behavior has been observed before for five-membered chelate rings<sup>18</sup> and suggests a similar explanation. We assume that the selenite ion pair forms a cap centered along the helical axis of the *cis*- $\Delta$ -lel ion, the bidentate ligands of which provide two amino protons oriented parallel to the helical axis to hydrogen bond to the oxygen atoms of the selenite ion; a third hydrogen bond may be formed by a coordinated ammonia ligand. Neither of the other two isomers has this particular amino proton arrangement. Thus,<sup>16,18</sup> we assign the ion pair sensitive (positive) circular dichroism band at  $21\,500\text{ cm}^{-1}$  of the *cis*- $\Delta$  complex to the "A" transition, and hence the lower energy negative component at  $19\,500\text{ cm}^{-1}$  is the "E" band. Since the *cis*- $\Delta$  complex has the opposite configurational dissymmetry, the single positive band at  $21\,000\text{ cm}^{-1}$  is assigned to the "E" transition. The bands under the  $^1T_{1g}$  manifold of the trans complex (Figure 5) are difficult to assign except that it is clear that the E band is split, and we think that the very weak negative band at low energies and the one adjacent to it represent this transition. This splitting may indicate that the four donor nitrogen atoms of the bidentate ligands are twisted to an unusual extent. The donor atom distortion, if real, may partly account for the lack of additivity observed in the contribution to the circular dichroism.

Figure 6 shows the calculated conformational contribution of one *R,R*-dmtn-Co ring derived from the circular dichroism of the two *cis* complexes. The additivity of the conformational contribution in the five-membered ring systems is precise,<sup>19</sup> but it can be seen that this is not so for the present systems. Apart from possible solvation differences, we think that, in changing from one complex to another, variations in the donor atom distortions and changes in the conformations of these somewhat flexible<sup>1</sup> ring systems may account for the lack of additivity. We perhaps should add that, as yet, no convincing explanation has been given for the additivity in the five-membered ring systems.

#### 4. Circular Dichroism of the Oxalato Diastereomers

A recent report<sup>20</sup> described the isolation of  $\Delta\text{-}[\text{Co}(S,S\text{-dmtn})_2\text{Ox}]\text{ClO}_4\cdot\text{H}_2\text{O}$ . We find, however, that the solubility characteristics reported are at variance with our observations,

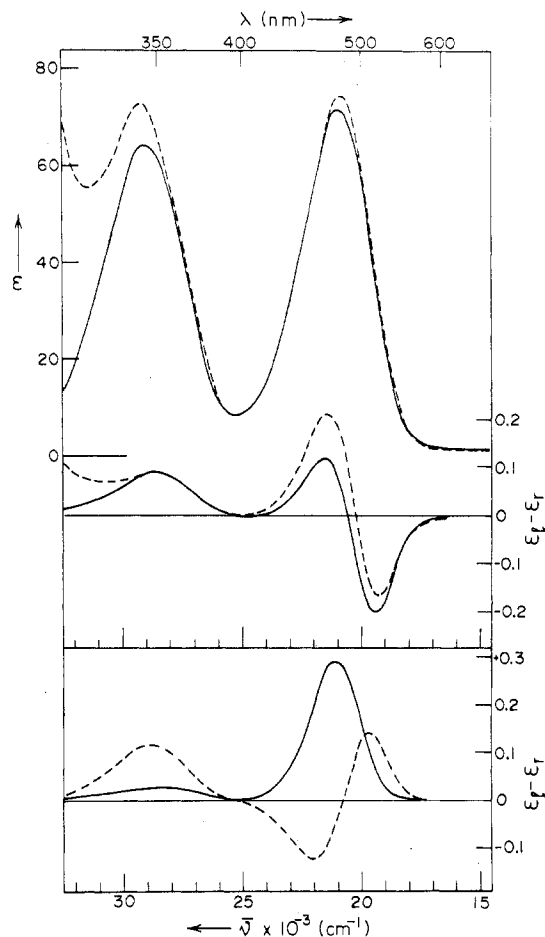


Figure 6. Top: absorption and circular dichroism spectra of *cis*- $\Delta\text{-}[\text{Co}(R,R\text{-dmtn})_2(\text{NH}_3)_2]\text{Cl}_3$  ( $5 \times 10^{-3}$  M) in water solution, without  $\text{SeO}_3^{2-}$  ions (—) and in the presence of  $\text{SeO}_3^{2-}$  ions ( $5 \times 10^{-3}$  M) (---). Bottom: conformational contribution of one *R,R*-dmtn chelate ring to the circular dichroism calculated from the spectra of the two *cis* diastereomers (—) and the circular dichroism of the *trans*- $[\text{Co}(R,R\text{-dmtn})_2(\text{NH}_3)_2]^{3+}$  ion divided by 2 (---).

and the reported absorption and circular dichroism spectra are not the same as for the corresponding diastereomer, which is not a hydrate. The circular dichroism and absorption spectra of the two pure diastereomers,  $\Delta$ - and  $\Delta\text{-}[\text{Co}(R,R\text{-dmtn})_2\text{Ox}]^+$ , are shown in Figure 7. It will be seen that the circular dichroism under the  $^1T_{1g}$  absorption for each isomer consists of a single band and that the intensities are nearly equal in magnitude. These are ascribed to "E" bands. The assignment of the configurational isomerism is based on the assumption that the signs of the "E" bands of the oxalato and diammine complexes will be the same for the same absolute configuration. In fact the circular dichroism is similar in form to that observed<sup>21</sup> for the  $[\text{Co}(\text{en})_2\text{Ox}]^+$  ions, the absolute configurations of which have been established by x-ray diffraction.<sup>22</sup>

#### 5. Stereochemistry

The isomerism of the complexes is readily established by NMR. Table I records the chemical shifts of the methyl protons for the complexes. These, of course, occur as doublets; and, as expected, the trans species all show a single sharp doublet by virtue of the environmental equivalence of the methyl groups. The *cis* complexes, which have two environmentally distinct methyl groups reveal this in their NMR spectra although the chemical shifts are such that not all the peaks are clearly resolved (Table I). The  $^{13}\text{C}$  spectra, however,

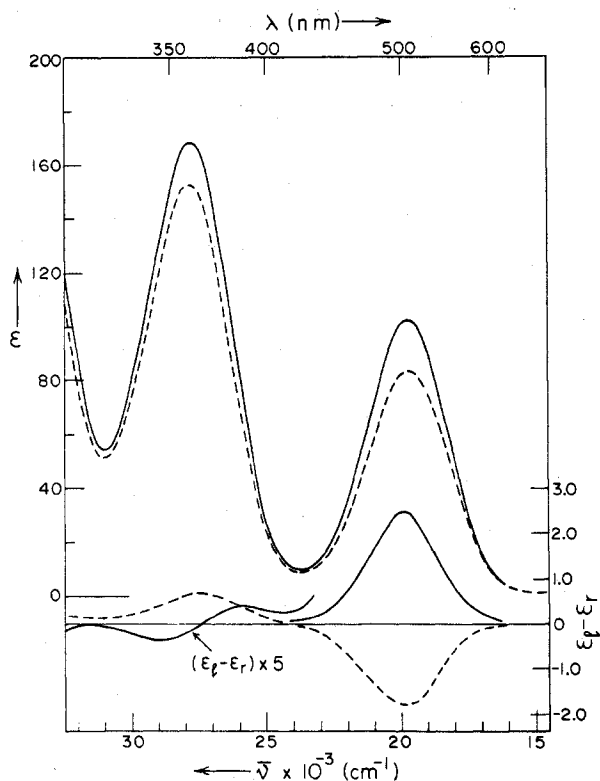


Figure 7. Absorption and circular dichroism spectra of (+)-*cis*- $\Delta$ -[Co(*R,R*-dmtn)<sub>2</sub>Ox]Cl (—) and (-)-*cis*- $\Delta$ -[Co(*R,R*-dmtn)<sub>2</sub>Ox]ClO<sub>4</sub> (---) in water solutions.

Table I. Methyl Proton Resonances of (*R,R*-dmtn)<sub>2</sub> Complexes<sup>a</sup>

Compd	Solvent	$\delta$ , ppm
(+)- <i>trans</i> -[Co( <i>R,R</i> -dmtn) <sub>2</sub> (NO <sub>2</sub> ) <sub>2</sub> ]Cl	D <sub>2</sub> O <sup>b</sup>	1.15, 1.21
(+)- <i>trans</i> -[Co( <i>R,R</i> -dmtn) <sub>2</sub> (NCS) <sub>2</sub> ]ClO <sub>4</sub>	DMSO- <i>d</i> <sub>6</sub> <sup>c</sup>	1.26, 1.33
(-)- <i>trans</i> -[Co( <i>R,R</i> -dmtn) <sub>2</sub> (N <sub>3</sub> ) <sub>2</sub> ]BPh <sub>4</sub>	Acetone- <i>d</i> <sub>6</sub> <sup>c</sup>	1.32, 1.38
(+)- <i>trans</i> -[Co( <i>R,R</i> -dmtn) <sub>2</sub> (NH <sub>3</sub> ) <sub>2</sub> ]Cl <sub>3</sub>	D <sub>2</sub> O <sup>b</sup>	1.32, 1.40
(+)- <i>cis</i> - $\Delta$ -[Co( <i>R,R</i> -dmtn) <sub>2</sub> (NH <sub>3</sub> ) <sub>2</sub> ]Cl <sub>3</sub> ·H <sub>2</sub> O	D <sub>2</sub> O <sup>b</sup>	1.35, <sup>d</sup> 1.41, 1.42
(+)- <i>cis</i> - $\Delta$ -[Co( <i>R,R</i> -dmtn) <sub>2</sub> (NH <sub>3</sub> ) <sub>2</sub> ]Cl <sub>3</sub> ·H <sub>2</sub> O	D <sub>2</sub> O <sup>b</sup>	1.31, <sup>e</sup> 1.34 <sup>e</sup>
(+)- <i>cis</i> - $\Lambda$ -[Co( <i>R,R</i> -dmtn) <sub>2</sub> (C <sub>2</sub> O <sub>4</sub> )]Cl·5H <sub>2</sub> O	D <sub>2</sub> O <sup>b</sup>	1.34, 1.36, 1.40, 1.42

<sup>a</sup> At 100 MHz and 30 °C. <sup>b</sup> Solvent acidified with DCl; internal DSS. <sup>c</sup> Internal TMS. <sup>d</sup> Resonance has an unresolved shoulder. <sup>e</sup> Unresolved resonance.

are quite unambiguous as far as structural assignments are concerned (Table II).

All of the *trans* complexes show three ("noise" decoupled) <sup>13</sup>C resonances, one each for the carbon atoms associated with the methyl, methylene, and methine groups of the system. Since in the *cis* complexes the two ends of each (dmtn) bidentate chelate are environmentally different, the methyl and methine carbon atoms experience different chemical shifts (Table II). Allowing the <sup>13</sup>C nuclei to couple with their respective protons unambiguously establishes the assignments, since the multiplicity of the <sup>13</sup>C resonances is given as one more than the number of attached protons. This was observed in all cases. It is perhaps of interest that the <sup>13</sup>C resonance of coordinated oxalate is easily observed under the conditions used for the detection of the resonances associated with the dmtn ligands. The reasons for this are not immediately apparent since the <sup>13</sup>C resonance for the coordinated NCS<sup>-</sup> ligand is not observed under the same conditions.

Table II. <sup>13</sup>C NMR of (*R,R*-dmtn)<sub>2</sub> Complexes (100 MHz)

Compd	Solvent	$\delta$ , <sup>d</sup> ppm		
		CH <sub>3</sub>	CH <sub>2</sub>	CH
(-)- <i>trans</i> -[Co( <i>R,R</i> -dmtn) <sub>2</sub> (N <sub>3</sub> ) <sub>2</sub> ]BPh <sub>4</sub>	Acetone- <i>d</i> <sub>6</sub> <sup>b</sup>	+23.57	+39.01	+43.79
(+)- <i>trans</i> -[Co( <i>R,R</i> -dmtn) <sub>2</sub> (NCS) <sub>2</sub> ]BPh <sub>4</sub>	Acetone- <i>d</i> <sub>6</sub> <sup>b</sup>	+23.47	+39.19	+44.94
(+)- <i>trans</i> -[Co( <i>R,R</i> -dmtn) <sub>2</sub> (NO <sub>2</sub> ) <sub>2</sub> ]Cl	H <sub>2</sub> O <sup>a</sup>	-43.94	-28.99	-22.98
(+)- <i>trans</i> -[Co( <i>R,R</i> -dmtn) <sub>2</sub> (NH <sub>3</sub> ) <sub>2</sub> ]Cl <sub>3</sub>	H <sub>2</sub> O <sup>a</sup>	-43.205	-29.25	-23.15
(+)- <i>cis</i> - $\Lambda$ -[Co( <i>R,R</i> -dmtn) <sub>2</sub> (NH <sub>3</sub> ) <sub>2</sub> ]Cl <sub>3</sub> ·H <sub>2</sub> O	H <sub>2</sub> O <sup>a</sup>	-42.91	-29.47	-22.27
(+)- <i>cis</i> - $\Delta$ -[Co( <i>R,R</i> -dmtn) <sub>2</sub> (NH <sub>3</sub> ) <sub>2</sub> ]Cl <sub>3</sub> ·H <sub>2</sub> O	H <sub>2</sub> O <sup>a</sup>	-43.14	-29.36	-22.74
(+)- <i>cis</i> - $\Delta$ -[Co( <i>R,R</i> -dmtn) <sub>2</sub> (NH <sub>3</sub> ) <sub>2</sub> ]Cl <sub>3</sub> ·H <sub>2</sub> O	H <sub>2</sub> O <sup>a</sup>	-43.00	-29.36	-22.18
(+)- <i>cis</i> - $\Lambda$ -[Co( <i>R,R</i> -dmtn) <sub>2</sub> (C <sub>2</sub> O <sub>4</sub> )]Cl·5H <sub>2</sub> O <sup>c</sup>	H <sub>2</sub> O <sup>a</sup>	-43.63	-28.88	-22.37
		-44.29		-23.85

<sup>a</sup> External reference dioxane in D<sub>2</sub>O, lock D of D<sub>2</sub>O. <sup>b</sup> Internal TMS reference, lock D of acetone-*d*<sub>6</sub>. <sup>c</sup>  $\delta$  of C<sub>2</sub>O<sub>4</sub> at +102.15 ppm. <sup>d</sup> "Noise" decoupled.

## 6. Experimental Section

(a) **Physical Measurements.** Proton magnetic resonance spectra were obtained using a Varian HA-100 instrument. The <sup>13</sup>C spectra were collected on a Varian SP-100 instrument. In general, the (<sup>1</sup>H-decoupled) <sup>13</sup>C NMR were recorded at a spectral width of 5000 Hz. Concentrations of the complexes were approximately 0.1 M and the acquisition time was 0.8 s. Usually, 2000–3000 pulses were required to give a clean spectrum with a noise level of less than a few percent. A number of the complexes were converted into more soluble salts (Tables I and II) by well-known procedures. However, no suitable salt, among the four we prepared of the *cis*- $\Delta$ -[Co(*R,R*-dmtn)<sub>2</sub>(C<sub>2</sub>O<sub>4</sub>)]<sup>+</sup> ion, was sufficiently soluble to give a spectrum in a reasonable time. All of the rotations are corrected for the density of the solvent and are at 25 °C.

(b) **Preparations.** (-)-*trans*-[Co(*R,R*-dmtn)<sub>2</sub>Cl<sub>2</sub>]ClO<sub>4</sub>. To *R,R*-dmtn·2HCl (10.0 g;  $\alpha_D +17.0^\circ$ , 1 M HCl)<sup>8</sup> partly neutralized with sodium hydroxide (3.44 g) in water (30 ml) at 5 °C were successively added sodium nitrite (5.9 g) in water (25 ml) at 5 °C, cobalt chloride hexahydrate (6.8 g) in water (10 ml) at 5 °C, and methanol (200 ml) at 5 °C. The mixture was maintained at 5 °C and aerated for 6 h. The clear yellow-brown solution was reduced to 50 ml under vacuum, and then urea (3 g) followed by HCl (30 ml; 12 M) was added. Vigorous evolution of NO<sub>2</sub> occurred at 20 °C, and, after 30 min, a red solution of the chloronitro complex was formed. This was then heated on a steam bath, and when the volume had reached ~20 ml, bright green crystals formed. Addition of HClO<sub>4</sub> (15 ml; 12 M) and heating the solution for 15 min caused transformation to the deep green crystals of the perchlorate salt. The mixture was allowed to cool and the crystals were collected. These were washed with water, then with ethanol-ether (1:2), and finally with ether. The crude product (11.1 g) was dissolved in water (240 ml; 100 °C), the hot solution was filtered, HCl (40 ml; 12 M) was added, and the solution was refluxed for 10 min and then filtered again. Perchloric acid (2.5 ml; 12 M) was added to the hot solution which, after standing at 25 °C for 5 h, deposited long bright green needles of the pure (-)-*trans*-[Co(*R,R*-dmtn)<sub>2</sub>Cl<sub>2</sub>]ClO<sub>4</sub> complex (8.4 g). A further 1.7 g was obtained after slow evaporation of the filtrate;  $\alpha_D -316 \pm 2^\circ$ ,  $(\epsilon_l - \epsilon_r)_{477} = -0.826$  (0.2% in methanol),  $\Delta_M = 88.5 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$  (10<sup>-3</sup> M in methanol, 23 °C). Anal. Calcd for [Co(C<sub>3</sub>H<sub>14</sub>N<sub>2</sub>)<sub>2</sub>Cl<sub>2</sub>]ClO<sub>4</sub>: C, 27.7; H, 6.5; N, 12.9; Cl, 24.5. Found: C, 27.8; H, 6.6; N, 13.0; Cl, 24.7.

(+)-*trans*-[Co(*R,R*-dmtn)<sub>2</sub>(NO<sub>2</sub>)<sub>2</sub>]ClO<sub>4</sub>. A solution of sodium nitrite (1.70 g) in methanol (10 ml) and water (5 ml) was added to *trans*-[Co(*R,R*-dmtn)<sub>2</sub>Cl<sub>2</sub>]ClO<sub>4</sub> (3.50 g) in boiling methanol (250 ml). The solution immediately turned a rust brown color, and after it was refluxed for 30 min, the resulting clear orange solution was pumped to dryness. The residue was crystallized from boiling water (275 ml) by the addition of sodium perchlorate (5.3 g). After cooling of the solution at 5 °C for 12 h, the crystals were collected and were washed with 40% aqueous ethanol (30 ml) and then with ether. Recrystallization from boiling water (250 ml) by the addition of sodium perchlorate (4.0 g) in water (5 ml) gave the pure product as bright yellow flakes (2.6 g);  $\alpha_D +65 \pm 2^\circ$ ,  $(\epsilon_l - \epsilon_r)_{472} = -0.66$  (0.1% in methanol),  $\Delta_M = 89 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$  (10<sup>-3</sup> M in methanol, 23 °C).

Anal. Calcd for  $[\text{Co}(\text{C}_5\text{H}_{14}\text{N}_2)_2(\text{NO}_2)_2]\text{ClO}_4$ : C, 26.4; H, 6.2; N, 18.5; Cl, 7.8. Found: C, 26.4; H, 6.3; N, 18.6; Cl, 7.8.

(-)-*trans*- $[\text{Co}(\text{R,R-dmtn})_2(\text{N}_3)_2]\text{ClO}_4$ . Sodium azide (0.46 g) in water (1 ml) and methanol (10 ml) was added to *trans*- $[\text{Co}(\text{R,R-dmtn})_2\text{Cl}_2]\text{ClO}_4$  (1.0 g) in boiling methanol (40 ml). The solution was refluxed for 5 min and then the volume was reduced under vacuum until crystallization began, when sodium perchlorate (4.9 g) was added. After cooling of the mixture at 5 °C for 2 h, the resultant deep blue, almost black, blocks were collected and washed with water (10 ml), absolute ethanol-ether (1:3; 10 ml), and ether. The product was recrystallized four times from acetonitrile (~45 ml) by the slow addition of ether (~150 ml). Green-brown needles of the pure product were obtained (0.40 g);  $\alpha_{578} = -771 \pm 4^\circ$ ,  $(\epsilon_1 - \epsilon_r)_{565} = +0.271$ ,  $(\epsilon_1 - \epsilon_r)_{483} = -0.932$  (0.04% in methanol),  $\Delta_M = 90 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$  ( $10^{-3} \text{ M}$  in methanol, 23 °C). Anal. Calcd for  $[\text{Co}(\text{C}_5\text{H}_{14}\text{N}_2)_2(\text{N}_3)_2]\text{ClO}_4$ : C, 26.9; H, 6.3; N, 31.4; Cl, 8.0. Found: C, 26.9; H, 6.2; N, 31.6; Cl, 8.2.

(+)-*trans*- $[\text{Co}(\text{R,R-dmtn})_2(\text{NCS})_2]\text{ClO}_4$ . A solution of *trans*- $[\text{Co}(\text{R,R-dmtn})_2\text{Cl}_2]\text{ClO}_4$  (0.6 g) and sodium thiocyanate (0.33 g) in methanol (35 ml) was refluxed for 1.75 h, and the resulting red solution was taken to dryness under vacuum. The residue was precipitated three times from methanol (50 ml/g) by the addition of lithium perchlorate (7 g/g of complex) and then recrystallized from boiling methanol (40 ml/g) by the addition of hot aqueous lithium perchlorate (1.5 g/g of complex) to give large red needles (0.5 g);  $\alpha_D + 370 \pm 2^\circ$ ,  $\alpha_{436} + 608 \pm 3^\circ$ ,  $(\epsilon_1 - \epsilon_r)_{542} = +0.537$  (0.05% in methanol),  $\Delta_M = 81 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$  ( $10^{-3} \text{ M}$  in methanol, 23 °C). Anal. Calcd for  $[\text{Co}(\text{C}_5\text{H}_{14}\text{N}_2)_2(\text{NCS})_2]\text{ClO}_4$ : C, 30.1; H, 5.9; N, 17.5; Cl, 7.4. Found: C, 30.1; H, 5.9; N, 17.2; Cl, 7.5.

(+)- and (-)- $[\text{Co}(\text{R,R-dmtn})_2\text{C}_2\text{O}_4]^+$ . *trans*- $[\text{Co}(\text{R,R-dmtn})_2\text{Cl}_2]\text{ClO}_4$  (5.0 g) and lithium oxalate (prepared from oxalic acid (1.52 g) and lithium carbonate (0.85 g)) were taken up in water (150 ml), heated at 80 °C for 10 min, and then refluxed for 10 min. The solution was evaporated to dryness under vacuum. The pink residue was stirred in water (40 ml) at 80 °C for 15 min, and the mixture was allowed to cool to 25 °C. It was then filtered and was washed with water (10 ml), then ethanol, and finally ether. The filtrate and washings were taken to dryness, the residue was extracted as above with water (20 ml), and a second crop of the purple (-) diastereomer was collected. It was set aside with the first crop.

(+)- $[\text{Co}(\text{R,R-dmtn})_2\text{C}_2\text{O}_4]\text{Cl}$ . The red filtrate remaining was reduced to 2 ml under vacuum (any purple solid which separated was removed and discarded). Addition of absolute ethanol (50 ml) and ether (200 ml) to this reduced filtrate caused the separation of the (+) diastereomer as an oil. This was twice dissolved in absolute ethanol (5 ml) and precipitated with ether (as a powder) to remove Co(II) impurities. The powder was taken up in water (3 ml) at 70 °C, and after the solution was allowed to cool, the pure (+) diastereomer deposited as long, thin red rods of the chloride salt (0.70 g). Fractional crystallization of this material did not alter its optical rotation. The product effloresces on extensive vacuum-drying at 25 °C;  $\alpha_D + 555 \pm 3^\circ$ ,  $(\epsilon_1 - \epsilon_r)_{505} = +2.47$  (0.04% in water),  $\Delta_M = 80 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}$  ( $10^{-3} \text{ M}$  in water, 25 °C). Anal. Calcd for (+)- $[\text{Co}(\text{C}_5\text{H}_{14}\text{N}_2)_2\text{C}_2\text{O}_4]\text{Cl}$ : C, 37.3; H, 7.3; N, 14.5; Cl, 9.2. Found: C, 37.3; H, 7.3; N, 14.8; Cl, 9.7.

(-)- $[\text{Co}(\text{R,R-dmtn})_2\text{C}_2\text{O}_4]\text{ClO}_4$ . The combined solid residues of the crude (-) diastereomer obtained from the extractions were dissolved in boiling water (70 ml) and perchloric acid (1 ml; 12 M) was added. After the solution was allowed to cool, large purple, almost black, blocks of the pure diastereomer formed (2.3 g). Fractional crystallization did not alter the optical activity;  $\alpha_D - 276 \pm 4^\circ$ ,  $(\epsilon_1 - \epsilon_r)_{504} = -1.81$  (0.07% in water),  $\Delta_M = 86 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$  ( $10^{-3} \text{ M}$  in water, 25 °C). Anal. Calcd for (-)- $[\text{Co}(\text{C}_5\text{H}_{14}\text{N}_2)_2\text{C}_2\text{O}_4]\text{ClO}_4$ : C, 32.0; H, 6.2; N, 12.4; Cl, 7.9. Found: C, 32.1; H, 6.3; N, 12.5; Cl, 8.0.

*cis*- $\Delta$ -, *cis*- $\Delta$ -, and *trans*- $[\text{Co}(\text{R,R-dmtn})_2(\text{NH}_3)_2]^{3+}$ . *trans*- $[\text{Co}(\text{R,R-dmtn})_2\text{Cl}_2]\text{ClO}_4$  (10.0 g) was converted to the chloride salt by shaking three times a methanol solution of the complex with Dowex 2-X8 anion-exchange resin (Cl<sup>-</sup> form). The resultant solution was reduced to dryness under vacuum; the residue was collected and washed with acetone until the washings were colorless. It was then washed with ether and thoroughly dried.

Addition of the complex (8.4 g) to anhydrous liquid ammonia (500 ml) caused immediate reaction to form soluble, orange species. After the ammonia was allowed to evaporate, the last traces of ammonia were removed by slurrying two times the residue with methanol and removing the liquid under vacuum.

*trans*- $[\text{Co}(\text{R,R-dmtn})_2(\text{NH}_3)_2]\text{Cl}_3$ . The residue was taken up in water (50 ml) acidified with 1 drop of HCl (concentrated), and then absolute ethanol (500 ml) was added. After 2 days at 5 °C, the solution deposited bright orange crystals of the *trans* isomer which were collected, the filtrate was set aside, and the crystals were washed first with 95% ethanol and then with ether (3.0 g). Addition of absolute ethanol (100 ml) to the filtrate caused, after 2 days at 5 °C, the deposition of both the *trans* complex (orange powder) and the *cis*- $\Delta$  isomer (orange blocks). The two were collected and the filtrate was set aside. These were separated mechanically. The 3.0 g of *trans* isomer and the powder were combined and recrystallized twice from acidified water (0.4 ml/g) containing absolute ethanol (0.8 ml/g) by the careful portionwise addition of acetone. The pure *trans* isomer formed thin orange plates which readily effloresced in air;  $\alpha_D + 146 \pm 2^\circ$ ,  $(\epsilon_1 - \epsilon_r)_{508} = +0.277$ ,  $(\epsilon_1 - \epsilon_r)_{453} = -0.244$ ,  $(\epsilon_1 - \epsilon_r)_{347} = +0.234$  (0.5% in water),  $\Delta_M = 305 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$  ( $10^{-3} \text{ M}$  in water, 25 °C). Anal. Calcd for  $[\text{Co}(\text{C}_5\text{H}_{14}\text{N}_2)_2(\text{NH}_3)_2]\text{Cl}_3$ : C, 29.8; H, 8.4; N, 20.8; Cl, 26.4. Found: C, 30.0; H, 8.6; N, 20.7; Cl, 26.6.

*cis*- $\Delta$ - $[\text{Co}(\text{R,R-dmtn})_2(\text{NH}_3)_2]\text{Cl}_3 \cdot \text{H}_2\text{O}$ . The filtrate remaining after the isolation of the crude *trans* isomer was reduced to dryness under vacuum. Addition of absolute ethanol (50 ml) and acetone (160 ml) to a solution of the residue in acidified water (25 ml) resulted in the slow (2 days at 5 °C) formation of large dark orange blocks of the *cis*- $\Delta$  isomer (2.3 g). These and the mechanically separated *cis*- $\Delta$  isomer obtained from the isolation of the *trans* complex were combined and crystallized as for the *trans* isomer. The product effloresces on extensive vacuum-drying;  $\alpha_D + 40 \pm 1^\circ$ ,  $(\epsilon_1 - \epsilon_r)_{516} = -0.202$ ,  $(\epsilon_1 - \epsilon_r)_{464} = +0.117$ ,  $(\epsilon_1 - \epsilon_r)_{352} = +0.090$  (0.5% in water),  $\Delta_M = 316 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$  ( $10^{-3} \text{ M}$  in water, 25 °C). Anal. Calcd for  $[\text{Co}(\text{C}_5\text{H}_{14}\text{N}_2)_2(\text{NH}_3)_2]\text{Cl}_3 \cdot \text{H}_2\text{O}$ : C, 28.5; H, 8.5; N, 19.9. Found: C, 28.8; H, 8.6; N, 20.0. Anal. Calcd for the vacuum-dried material at 25 °C,  $[\text{Co}(\text{C}_5\text{H}_{14}\text{N}_2)_2(\text{NH}_3)_2]\text{Cl}_3$ : C, 29.7; H, 8.4; N, 20.8. Found: C, 29.7; H, 8.5; N, 20.7.

*cis*- $\Delta$ - $[\text{Co}(\text{R,R-dmtn})_2(\text{NH}_3)_2]\text{Cl}_3 \cdot \text{H}_2\text{O}$ . The filtrate remaining after the isolation of the crude *cis*- $\Delta$  isomer was pumped to dryness. The orange residue consisted of small amounts of the two isomers previously isolated, a pink decomposition product, and the remaining isomer. This was taken up in acidified water (2 ml) and forced out with absolute ethanol (100 ml) and acetone (300 ml) to give a flocculent, hygroscopic orange powder which was collected and washed well with acetone and ether. Reprecipitation as above gave a clean orange powder (0.85 g). Careful recrystallization (as for the *trans* isomer) allowed the simultaneous crystallization of all three isomers in their distinctive morphologies. These are easily separated mechanically and each was recrystallized. The pure *cis*- $\Delta$  isomer formed bright orange square plates;  $\alpha_D + 161 \pm 1^\circ$ ,  $(\epsilon_1 - \epsilon_r)_{480} = +1.09$ ,  $(\epsilon_1 - \epsilon_r)_{362} = +0.026$  (0.5% in water),  $\Delta_M = 315 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$  ( $10^{-3} \text{ M}$  in water, 25 °C). Anal. Calcd for  $[\text{Co}(\text{C}_5\text{H}_{14}\text{N}_2)_2(\text{NH}_3)_2]\text{Cl}_3 \cdot \text{H}_2\text{O}$ : C, 28.5; H, 8.5; N, 19.9; Cl, 25.2. Found: C, 28.5; H, 8.9; N, 20.4; Cl, 25.2.

In order to obtain the isomer proportions, each of the various filtrates and solid complexes were worked up until all of the isomers were pure and no diammine species remained.

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**Registry No.** (-)-*trans*- $[\text{Co}(\text{R,R-dmtn})_2\text{Cl}_2]\text{ClO}_4$ , 39018-05-8; (+)-*trans*- $[\text{Co}(\text{R,R-dmtn})_2(\text{NO}_2)_2]\text{ClO}_4$ , 39001-45-1; (-)-*trans*- $[\text{Co}(\text{R,R-dmtn})_2(\text{N}_3)_2]\text{ClO}_4$ , 58866-07-2; (+)-*trans*- $[\text{Co}(\text{R,R-dmtn})_2(\text{NCS})_2]\text{ClO}_4$ , 58866-09-4; (+)-*cis*- $\Delta$ - $[\text{Co}(\text{R,R-dmtn})_2\text{C}_2\text{O}_4]\text{Cl}$ , 58894-32-9; (-)-*cis*- $\Delta$ - $[\text{Co}(\text{R,R-dmtn})_2\text{C}_2\text{O}_4]\text{ClO}_4$ , 58894-34-1; (+)-*trans*- $[\text{Co}(\text{R,R-dmtn})_2(\text{NH}_3)_2]\text{Cl}_3$ , 58866-10-7; (+)-*cis*- $\Delta$ - $[\text{Co}(\text{R,R-dmtn})_2(\text{NH}_3)_2]\text{Cl}_3$ , 58894-35-2; (+)-*cis*- $\Delta$ - $[\text{Co}(\text{R,R-dmtn})_2(\text{NH}_3)_2]\text{Cl}_3$ , 58894-36-3; (+)-*trans*- $[\text{Co}(\text{R,R-dmtn})_2(\text{NO}_2)_2]\text{Cl}$ , 58866-11-8; (-)-*trans*- $[\text{Co}(\text{R,R-dmtn})_2(\text{N}_3)_2]\text{BPh}_4$ , 58866-12-9; (+)-*trans*- $[\text{Co}(\text{R,R-dmtn})_2(\text{NCS})_2]\text{BPh}_4$ , 58866-13-0;  $\text{SeO}_3^{2-}$ , 14124-67-5;  $^{13}\text{C}$ , 14762-74-4.

## References and Notes

- (1) S. R. Niketic and F. Woldbye, *Acta Chem. Scand.*, **27**, 621 (1973).
- (2) L. J. De Hayes and D. H. Busch, *Inorg. Chem.*, **12**, 1505 (1973).
- (3) A. Kobayashi, F. Marumo, and Y. Saito, *Acta Crystallogr., Sect. B*, **28**, 3591 (1972); **29**, 2443 (1973).
- (4) N. C. Payne, private communication.
- (5) B. Bosnich and J. MacB. Harrowfield, *Inorg. Chem.*, **14**, 836, 853 (1975).

- (6) I. Oonishi, S. Sato, and Y. Saito, *Acta Crystallogr., Sect. B*, **30**, 2256 (1974).
- (7) B. Bosnich and J. MacB. Harrowfield, *Inorg. Chem.*, **14**, 861 (1975).
- (8) B. Bosnich and J. MacB. Harrowfield, *J. Am. Chem. Soc.*, **94**, 3425 (1972); *Inorg. Chem.*, **14**, 828, 847 (1975).
- (9) A. M. Sargeson, *Transition Metal Chem.*, **3**, 303 (1967), and references therein.
- (10) R. J. Geue and M. R. Snow, *J. Chem. Soc. A*, 2981 (1971).
- (11) There is general agreement on the names of two of the basic conformations of the trimethylenediamine chelate ring, namely, the chair and the boat, but the one shown in Figure 1 has been called either skew or twist or skew boat or twist boat. The cyclohexane analogy notwithstanding, it seems to us that either of the last two names is better reserved for the conformation which is intermediate between the skew (twist) and the boat. This conformation becomes important when two or more six-membered chelate rings are (linearly) linked (see, D. A. House, P. R. Ireland, I. E. Maxwell, and W. T. Robinson, *Inorg. Chim. Acta*, **5**, 397 (1971)).
- (12) C. J. Dippel and F. M. Jaeger, *Recl. Trav. Chim. Pays-Bas*, **50**, 547 (1931).
- (13) F. Mizukami, H. Ito, J. Fujita, and K. Saito, *Bull. Chem. Soc. Jpn.*, **45**, 2129 (1972); R. Kuroda, J. Fujita, and Y. Saito, *Chem. Lett.*, **225** (1975).
- (14) W. Moffitt, *J. Chem. Phys.*, **25**, 467 (1956).
- (15) C. J. Hawkins, "Absolute Configuration of Metal Complexes", Interscience, New York, N.Y., 1971.
- (16) S. F. Mason and B. J. Norman, *Proc. Chem. Soc. London*, 339 (1964).
- (17) H. L. Smith and B. E. Douglas, *J. Am. Chem. Soc.*, **86**, 3885 (1964).
- (18) S. F. Mason and B. J. Norman, *J. Chem. Soc. A*, 307 (1966).
- (19) B. E. Douglas, *Inorg. Chem.*, **4**, 1813 (1965); S. F. Mason, A. M. Sargeson, R. Larsson, B. J. Norman, A. J. McCaffery, and G. M. Searle, *Inorg. Nucl. Chem. Lett.*, **2**, 333 (1966); *J. Chem. Soc.*, 1304, 1310 (1968); K. Ogino, K. Murano, and J. Fujita, *Inorg. Nucl. Chem. Lett.*, **4**, 351 (1968).
- (20) F. Mizukami, H. Ito, J. Fujita, and K. Saito, *Bull. Chem. Soc. Jpn.*, **46**, 2410 (1973).
- (21) A. J. McCaffery, S. F. Mason, and B. J. Norman, *J. Chem. Soc.*, 5094 (1965).
- (22) T. Aoki, K. Matsumoto, S. Ooi, and H. Kuroya, *Bull. Chem. Soc. Jpn.*, **46**, 159 (1973).

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## Oxygen Exchange and Acid Hydrolysis Reactivity of Bis(ethylenediamine)oxalatorhodium(III) Ion<sup>1</sup>

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The reactivity of  $\text{Rh}(\text{en})_2\text{C}_2\text{O}_4^+$  toward oxygen exchange with solvent and aquation to  $\text{cis-Rh}(\text{en})_2(\text{H}_2\text{O})_2^{3+}$  has been examined in aqueous  $\text{HNO}_3/\text{NaNO}_3$  media at ionic strength 0.50 M. There are two kinetically distinct types of coordinated oxygen, the slower exchange being attributed to inner/outer oxygen interchange which we presume must occur before inner oxygens can exchange with solvent. Over the temperature range studied, rate constants for inner/outer oxygen interchange and for exchange of outer oxygens with solvent differ only slightly. Both processes are first order in  $[\text{H}^+]$ . Rate parameters, calculated on the basis that there are two outer oxygens and two inner oxygens, are as follows: for inner/outer oxygen interchange, per mole of complex,  $k_{12} (=k_{11}/[\text{H}^+]) = 4.5 \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$  at 35.0 °C,  $\Delta H^\ddagger_{12} = 26.0 (\pm 1.2) \text{ kcal mol}^{-1}$ ,  $\Delta S^\ddagger_{12} = +5.8 (\pm 4.0) \text{ cal mol}^{-1} \text{ K}^{-1}$ ; for outer oxygen exchange with solvent, per mole of complex,  $k_{o2} (=k_{o1}/[\text{H}^+]) = 9.6 \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$  at 35.0 °C,  $\Delta H^\ddagger_{o2} = 17.1 (\pm 0.3) \text{ kcal mol}^{-1}$ ,  $\Delta S^\ddagger_{o2} = -21.6 (\pm 1.0) \text{ cal mol}^{-1} \text{ K}^{-1}$ .  $\text{Rh}(\text{en})_2\text{C}_2\text{O}_4^+$  also equilibrates in acidic solution in accord with the stoichiometry:  $\text{Rh}(\text{en})_2\text{C}_2\text{O}_4^+ + 2\text{H}_3\text{O}^+ \rightleftharpoons \text{cis-Rh}(\text{en})_2(\text{H}_2\text{O})_2^{3+} + \text{H}_2\text{C}_2\text{O}_4$ . Thermodynamic parameters for this reaction are  $K = 2.1 (\pm 0.2) \times 10^{-3} \text{ M}^{-1}$  at 35.0 °C,  $\Delta H^\circ = 4.5 (\pm 0.4) \text{ kcal mol}^{-1}$ , and  $\Delta S^\circ = 2.4 (\pm 1.2) \text{ cal mol}^{-1} \text{ K}^{-1}$ . The forward hydrolysis rate proceeds according to a two-term rate law:  $R = \{k_{a2}[\text{H}^+] + k_{a3}[\text{H}^+]^2\}[\text{Rh}(\text{en})_2\text{C}_2\text{O}_4^+]$ . At 35.0 °C,  $k_{a2} = 4.3 \times 10^{-6} \text{ M}^{-1} \text{ s}^{-1}$  and  $k_{a3} = 8.8 \times 10^{-6} \text{ M}^{-2} \text{ s}^{-1}$ ; also  $\Delta H^\ddagger_{a2} = 24.1 (\pm 2.0) \text{ kcal mol}^{-1}$ ,  $\Delta S^\ddagger_{a2} = -5.0 (\pm 6.0) \text{ cal mol}^{-1} \text{ K}^{-1}$ ,  $\Delta H^\ddagger_{a3} = 18.0 (\pm 2.5) \text{ kcal mol}^{-1}$ , and  $\Delta S^\ddagger_{a3} = -23.4 (\pm 8.0) \text{ cal mol}^{-1} \text{ K}^{-1}$ . Rate and equilibrium data for the hydrolysis reaction provide values of the kinetic parameters for the anation reaction. Mechanistic interpretations for the oxygen-exchange, hydrolysis, and anation data are provided. The behavior of  $\text{Rh}(\text{en})_2\text{C}_2\text{O}_4^+$  is contrasted to that of  $\text{Co}(\text{en})_2\text{C}_2\text{O}_4^+$ , which in acidic solution is notably less reactive toward inner oxygen exchange and hydrolysis.

### Introduction

The reactivities of  $\text{Co}(\text{en})_2\text{C}_2\text{O}_4^+$ ,<sup>3,4</sup>  $\text{Co}(\text{C}_2\text{O}_4)_3^{3-}$ ,<sup>5-7</sup> and  $\text{Rh}(\text{C}_2\text{O}_4)_3^{3-}$ <sup>8-10</sup> in aqueous acidic solution have all been examined in some detail. Results obtained for these complexes indicated that a study of the reactivity of  $\text{Rh}(\text{en})_2\text{C}_2\text{O}_4^+$  would be of interest. Substitution at the Rh(III) center generally occurs at comparable or lower rates than substitution in corresponding Co(III) complexes.<sup>11</sup> Comparison between  $\text{Rh}(\text{C}_2\text{O}_4)_3^{3-}$  and  $\text{Co}(\text{C}_2\text{O}_4)_3^{3-}$  is complicated, however, by the relatively rapid internal redox decomposition reaction of the latter complex in acidic solution.<sup>5-7</sup> On the other hand,  $\text{Co}(\text{en})_2\text{C}_2\text{O}_4^+$  shows no tendency to undergo internal redox decomposition in aqueous solution; further, this complex is notably unreactive toward exchange of inner oxygens with solvent water<sup>3</sup> and toward aquation.<sup>4</sup> These observations on  $\text{Co}(\text{en})_2\text{C}_2\text{O}_4^+$  might lead one to suppose that  $\text{Rh}(\text{en})_2\text{C}_2\text{O}_4^+$  would also be extremely unreactive toward the inner oxygen exchange and aquation reactions. Contrary to this simplistic view, we find  $\text{Rh}(\text{en})_2\text{C}_2\text{O}_4^+$  to be moderately reactive toward these processes.

### Experimental Section

**Materials.** Bis(ethylenediamine)oxalatorhodium(III) nitrate was prepared as described earlier<sup>12</sup> from cis or cis/trans mixtures of

$[\text{Rh}(\text{en})_2\text{Cl}_2]\text{NO}_3$ .<sup>13</sup> The purity of a sample was checked by elemental analysis. Anal.<sup>14</sup> Calcd for  $[\text{Rh}(\text{N}_2\text{C}_2\text{H}_8)_2\text{C}_2\text{O}_4][\text{NO}_3 \cdot \text{H}_2\text{O}]$ : C, 18.4; H, 4.64; N, 17.9. Found: C, 18.6; H, 4.52; N, 18.0. Other samples were checked by comparison of visible-uv spectra with that for the analyzed sample ( $\lambda_{\text{max}} 325 \text{ nm}$ ,  $\epsilon 260 \text{ M}^{-1} \text{ cm}^{-1}$ ).<sup>12</sup>

*cis*-Bis(ethylenediamine)dihydroxorhodium(III) ion was prepared in solution by reaction of *cis*- $\text{Rh}(\text{en})_2\text{Cl}_2^+$  with potassium or sodium hydroxide.<sup>15,16</sup> *cis*-Diaquobis(ethylenediamine)rhodium(III) ion was prepared in solution by acidifying, with perchloric or nitric acid, solutions containing *cis*- $\text{Rh}(\text{en})_2(\text{OH})_2^+$ , prepared as described above.

All solutions for kinetic and equilibrium studies utilized water, obtained from ordinary distilled water which was refluxed with alkaline potassium permanganate in a Barnstead S-1 water still and redistilled.

A nitric acid/sodium nitrate aqueous medium was chosen for the studies because of the very low solubility of the oxalato complex in perchlorate media. Nitrate absorbs in the uv region; at the complex absorption maximum at 325 nm,  $\epsilon \approx 2.5 \text{ M}^{-1} \text{ cm}^{-1}$  for nitrate which was too large for us to handle in spectrophotometric studies of the hydrolysis. However, such studies could be carried out at 340 nm where for nitrate  $\epsilon$  is  $\approx 0.1 \text{ M}^{-1} \text{ cm}^{-1}$ . A stock 2 M nitric acid solution was prepared from reagent grade acid which had been boiled for 20 min to remove oxides of nitrogen.<sup>17</sup> After standardization the stoppered solution was stored in the dark. A stock 2 M sodium nitrate solution, prepared from recrystallized reagent grade material, was standardized and stored in a refrigerator.

**Acid Hydrolysis Studies.** In acidic solution  $\text{Rh}(\text{en})_2\text{C}_2\text{O}_4^+$  slowly releases coordinated oxalate. The stoichiometry and equilibrium for