measured at 510 nm and were found to be biphasic and first order in the complex concentration. The fast rate was attributed to aquation with loss of chloride, and the slower rate, to cleavage into mononuclear fragments. The rate constants were calculated by a nonlinear least-squares fitting procedure: $k_{fast} = (6 \pm 2) \times 10^{-5}$ s^{-1} (hydrolysis of Cl$^-$) and $k_{slow} = (1.4 \pm 0.9) \times 10^{-6}$ s^{-1} (cleavage into monomers).

Conclusions

This work focuses on the initial step of the alkaline hydrolysis of **1** and the isolation of **2** as the anation product **3**, whose crystal structure has been determined by X-ray diffraction. Deprotonation of an NH_3 ligand (but not of the μ-NH_2 bridge) of **1**, followed by rapid elimination of one NH_3 ligand (presumably on the Co(III) center carrying the deprotonated ammine ligand), leads to a pentacoordinated intermediate (reactions 1–3). Interestingly, this intermediate scavenges not only water but also ammonia to restore the deprotonated reactant although ammonia is a poor nucleophile. For the first time, *retardation* of base hydrolysis in the presence of an excess of the leaving group has been observed. This is taken as strong evidence for the D_{cb} mechanism. Bridge cleavage was not detected at this stage.

The fast rate of NH_3 release ($k_{-NH_3} = 4.6 \times 10^{-2}$ s^{-1}) relative to that of mononuclear analogues, e.g. $Co(NH_3)_6{}^{3+}$, is due to steric acceleration. The pK_a of $Co(en)_3{}^{3+}$ was estimated[35] as 14.9. We assume that the pK_a of $Co(NH_3)_6{}^{3+}$ is approximately equal or lower, e.g. ~14. On the basis of the published[36] second-order rate constant for base hydrolysis of $Co(NH_3)_6{}^{3+}$, $k_{OH} = 9.6 \times 10^{-7}$ M^{-1} s^{-1}, we estimate k_{-NH_3} for this complex as $\sim 10^{-6}$ s^{-1}. This value is smaller than the corresponding value of **1** by a factor of ~50 000. Such a large steric acceleration may indicate that an ammonia ligand cis to the μ-NH_2 bridge is eliminated. The isolated chloride anation product of **2**, $[(NH_3)_5CoNH_2CoCl(NH_3)_4]Cl_4 \cdot H_2O$, is also present in the cis configuration. The enhanced acidity of **1** (pK_a = 11.7) compared to e.g. that of $Co(NH_3)_6{}^{3+}$ is due to the high charge of **1**.

The dimer **1** resembles the ($\pm$)-*cis,cis*-$(en)_2(NH_3)CoNH_2Co(NH_3)(en)_2{}^{5+}$ ion in its reactivity, but the en compound reacts in base with only 10–25% ammonia release to give the corresponding μ-amido–erythro compound. The major part of the starting material is cleaved into monomers. It may be speculated that the cleavage pathway occurs via the species where deprotonation is at the most acidic site, presumably the NH_3 ligand. The resulting coordinated NH_2 cannot act as a leaving group, and an $(en)_2(NH_3)CoNH_2$ moiety is substituted, as the en nitrogens are even poorer leaving groups. The amount of NH_3 release would thus arise from deprotonation of a somewhat less acidic en–NH_2 function.

Both **1** and the acid rhodochromium ion undergo fast ammonia release. However, the mechanism of activation is different: the Cr(III) compound is deprotonated at the bridge and can thereby adopt a linear Cr–O–Cr geometry that gives rise to special electronic effects. Ammonia is released from the compound in this configuration. In contrast, the cobalt compound is deprotonated at one ammonia ligand (presumably because the filled d_π orbitals of Co(III) cannot stabilize p orbitals of the bridge). The pK_a of **1** is much higher, but the resulting conjugate base is very reactive due to steric acceleration.

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Registry No. **1**·$5NO_3{}^-$, 15363-12-9; **1**·$5ClO_4$, 31151-80-1; **2**, 110795-80-7; **3**·$4Cl^- \cdot H_2O$, 110795-81-8; $(NH_3)_4Co(OH)_2{}^+$, 38467-93-5; $(NH_3)_5CoOH^{2+}$, 16632-75-0; *trans*-$(NH_3)_4Co(OH_2)_2{}^{3+}$, 19394-99-1; *cis*-$(NH_3)_5Co(OH_2)_2{}^{3+}$, 18460-36-1; $(NH_3)_5Co(OH_2)^{3+}$, 14403-82-8; $Co(NH_3)_6{}^{3+}$, 14695-95-5.

Supplementary Material Available: Table S2, listing anisotropic thermal parameters (1 page); Table S1, listing observed and calculated structure factors (20 pages). Ordering information is given on any current masthead page.

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Ligand Substituent Contributions to the Rotational Strengths in Cyano(ethylenediamine-*N*,*N*,*N'*-triacetato)cobaltate(III) Type Complexes. Crystal Structures of Rb-$(-)_{546}$-*cis*-*eq*-$[Co(ed3a)CN] \cdot 2H_2O$ and K-$(-)_{546}$-*cis*-*eq*-$[Co(hed3a)CN] \cdot 1.5H_2O$

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Circular dichroism spectra are reported for K-*cis-eq*-[Co(ed3a)CN], K-*cis-eq*-[Co(med3a)CN], K-*cis-eq*-[Co(hed3a)CN], and K-*trans-eq*-[Co(ed3a)CN]. Structures and absolute configurations were determined for Rb-$(-)_{546}$-*cis-eq*-$[Co(ed3a)CN] \cdot 2H_2O$ (**1**) (orthorhombic, $C222_1$, with the cell dimensions a = 6.600 (7) Å, b = 14.243 (8) Å, and c = 30.76 (1) Å; eight molecules in the unit cell) and K-$(-)_{546}$-*cis-eq*-$[Co(hed3a)CN] \cdot 1.5H_2O$ (**2**) (monoclinic, $C2$, with the cell dimensions a = 14.546 (7) Å, b = 7.219 (1) Å, c = 19.78 (1) Å, and β = 130.09 (3)°; four molecules in the unit cell). For the *cis-eq*-$[Co(ed3a)CN]^-$ type complexes an alkyl substituent on the ethylenediamine nitrogen, compared to the case of the unsubstituted ed3a, reverses the sign of the circular dichroism peaks in the region of the lower energy absorption band. As for the corresponding nitro complexes, *cis-eq*-$[Co(ed3a)CN]^-$ and *trans-eq*-$[Co(ed3a)CN]^-$ show very similar CD curves.

Introduction

Absorption spectra of transition-metal complexes are insensitive to changes in stereochemistry except for great effects such as for cis and trans isomers involving ligands differing greatly in field strength. Circular dichroism (CD) spectra reveal smaller splittings in energy levels and often reflect the true molecular symmetry. For chelate complexes the contributions to the rotational strength (or CD intensity) are the chirality and conformation of the chelate rings and the vicinal effect of asymmetric ligand atoms. These contributions have been shown to be additive.[2] Generally, the

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contribution from ring chirality is dominant. Complexes of ethylenediamine-*N,N,N′,N′*-tetraacetic acid (edta for the anion) and related ligands have been studied widely[3] because of the possibilities for variation in stereochemistry. The fixed ring stereochemistry of cobalt(III) complexes of the tetradentate ligand ethylenediaminediacetic acid (edda for the anion) results in little change in the CD spectra even for significant changes in the ligands occupying the other two coordination sites.[4-6] Greater changes result for different substituents (H or alkyl) on the coordinated asymmetric nitrogen atoms.[7] Similarly, large contributions to the rotational strength were observed for the asymmetric donor in the *cis-eq*-nitro(ethylenediaminetriacetato)cobaltate ion.[7] The ethylenediaminetriacetato (ed3a) complexes are of particular interest because the six-coordinate complexes have no net chirality, based on chelate ring pairs, so the asymmetric donor makes a dominant contribution to the rotational strength. Absolute configurations for correlation of CD spectra require X-ray diffraction analysis.

The corresponding chloro and bromo complexes of pentadentate edta and N-substituted ed3a show smaller effects of substitution on the asymmetric donor atom.[8] The results raise questions as to whether the nitro complexes are unique because NO_2^- is the only strong-field ligand studied or because there is some preferred orientation of coordinated NO_2^-. Cyanide ion is of interest as a strong-field ligand with cylindrical symmetry. Complexes of the $[Co(ed3a)CN]^-$ type are reported with different N substituents and for cis-equatorial and trans-equatorial isomers. X-ray structures and absolute configurations of two complexes are presented.

Experimental Section

Preparation of Ethylenediamine-*N,N,N′*-triacetic Acid and Its Complexes. The ed3a ligand and its aqua complex were prepared by procedures given by Maricondi and Maricondi,[7] Bernhard,[9] Blackmer et al.,[10] and Douglas et al.[11,12] The cis-equatorial and trans-equatorial isomers of K[Co(ed3a)CN] were prepared from the aqua complex by the modified published procedure[13] as reported separately.[12]

Resolution of K-*cis-eq*-[Co(ed3a)CN]·2H$_2$O. A mixture of $(-)_D$-$[Co(en)_2(C_2O_4)]Br\cdot H_2O$ (0.365 g, 1.00×10^{-3} mol) and silver acetate (0.167 g, 1.00×10^{-3} mol) in 40 mL of water was warmed with constant stirring at 50 °C for 10 min. The AgBr was separated by filtration and washed with 2 mL of warm water, and to the filtrate was added 0.783 g (2.00×10^{-3} mol) of K-*cis-eq*-$[Co(ed3a)CN]\cdot 2H_2O$. After overnight refrigeration, crystals of the less soluble diastereoisomer, $(-)_D$-$[Co(en)_2(C_2O_4)]$-$(-)_D$-$[Co(ed3a)CN]\cdot 3H_2O$, were removed by filtration, washed with ethanol and then ether, and air-dried. Yield: 0.55 g. The diastereoisomer was recrystallized from hot water to constant optical rotation: $[\alpha]_D = -630°$, $[M]_D = -4015°$; $[\alpha]_{546} = -1100°$, $[M]_{546} = -7010°$. Anal. Calcd for $[Co(en)_2(C_2O_4)][Co(ed3a)CN]\cdot 3H_2O = Co_2C_{15}H_{33}O_{13}N_7$ (fw 637.33): C, 28.26; H, 5.21; N, 15.38. Found: C, 27.37; H, 5.01; N, 15.36.

The optical isomer was obtained as the potassium or ammonium salt by ion-exchange chromatography. The eluate was evaporated to dryness at room temperature. Optical rotation: $[\alpha]_D = -312°$ and $[\alpha]_{546} = -914°$ for the potassium salt; $[\alpha]_D = -350°$ and $[\alpha]_{546} = -960°$ for the ammonium salt. Anal. Calcd for $K[Co(ed3a)CN]\cdot 2H_2O = KCoC_9H_{15}O_8N_3$ (fw 391.26): C, 27.62; H, 3.86; N, 10.74. Found: C, 27.54; H, 3.77; N, 11.00. Calcd for $NH_4[Co(ed3a)CN]\cdot H_2O = CoC_9H_{17}O_7N_4$ (fw 352.19): C, 30.69; H, 4.86; N, 15.90. Found: C, 30.11; H, 4.77; N, 16.05. The opposite enantiomer was isolated by the same procedure using $(+)_D$-$[Co(en)_2(C_2O_4)]I$ as the resolving agent. Crystals suitable for X-ray analysis were not obtained for the potassium salt. Crystals of Rb-$(-)_{546}$-*cis-eq*-$[Co(ed3a)CN]\cdot 2H_2O$ (**1**) were obtained by slow evaporation of a solution of the potassium salt in 0.1 M RbCl solution. A small beaker of the solution was allowed to stand in a larger covered beaker containing methanol.

Resolution of Potassium *trans-eq*-Cyano(ethylenediamine-*N,N,N′*-triacetato)cobaltate(III) Monohydrate. The complex (1.00×10^{-3} mol) was resolved by the same procedure described for the *cis-eq*-isomer using $(-)_D$-$[Co(en)_2(C_2O_4)]Br\cdot H_2O$ (5.00×10^{-4} mol) as the resolving agent. Yield before recrystallization: 0.25 g. Optical rotation after recrystallization to constant rotation: $[\alpha]_D = -510°$, $[M]_D = -2975°$; $[\alpha]_{546} = -210°$, $[M]_{546} = -1225°$. Anal. Calcd for $(-)_D$-$[Co(en)_2(C_2O_4)]$-$(-)_D$-$[Co(ed3a)CN] = Co_2C_{15}H_{27}O_{10}N_7$ (fw 583.28): C, 30.88; H, 4.66; N, 16.80. Found: C, 30.65; H, 4.72; N, 16.40.

The optical isomer was converted to the potassium and ammonium salts as described above. Optical rotations: $[\alpha]_D = -122°$ and $[\alpha]_{546} = +658°$ for the potassium salt; $[\alpha]_D = -120°$ and $[\alpha]_{546} = +620°$ for the ammonium salt. Anal. Calcd for $K[Co(ed3a)CN] = KCoC_9H_{11}O_6N_3$ (fw 355.24): C, 30.43; H, 3.12; N, 11.83. Found: C, 29.78; H, 4.05; N, 11.50. Calcd for $NH_4[Co(ed3a)CN]\cdot H_2O = CoC_9H_{17}O_7N_4$ (fw 352.19): C, 30.69; H, 4.86; N, 15.90. Found: C, 30.40; H, 4.53; N, 16.60. The opposite enantiomer was isolated by the same procedure using $(+)_D$-$[Co(en)_2(C_2O_4)]I$ as the resolving agent.

Preparation of *N*-Methylethylenediamine-*N,N′,N′*-triacetic Acid and Its Cobalt(III) Aqua Complex. *N*-Methylethylenediamine was obtained by the method of Aspinall.[14] The corresponding *N*-methylethylenediamine-*N,N′,N′*-triacetic acid ligand (med3a) was prepared by the method of Van Saun and Douglas.[8] The $[Co(med3a)(H_2O)]\cdot 0.5H_2O$ complex reported by Bause[15] was prepared as described for the corresponding ed3a complex.[7,9,10] A portion of the med3a preparation solution (5.0×10^{-2} mol, assuming 100% yield), 8.42 g (0.15 mol) of KOH, and 14.55 g (5.00×10^{-2} mol) of $Co(NO_3)_2\cdot 6H_2O$ yielded 8.0 g (~48%) of $[Co(med3a)(H_2O)]\cdot 0.5H_2O$.

Preparation and Resolution of Potassium *cis-eq*-Cyano(*N*-methylethylenediamine-*N,N′,N′*-triacetato)cobaltate(III) Hemihydrate. This complex was prepared from the corresponding aqua complex by the published method[13] modified as follows: To a solution of $[Co(med3a)(H_2O)]\cdot 0.5H_2O$ (1.65 g, 5.00×10^{-3} mol) in 150 mL of DMSO was added KCN (0.49 g, 7.5×10^{-3} mol). The mixture was warmed at 70 °C for 4 h, and the resulting solution was introduced into a column (5 cm × 40 cm) containing Dowex 1-X8 (200–400 mesh) anion-exchange resin in the Cl^- form. The column was washed with water, and the dark red band (with anions of −1 charge) was eluted with 0.1 M KCl. The eluate was evaporated under vacuum and desalted by using a G-10 Sephadex column (2.5 cm × 40 cm). The eluate was evaporated to a volume of 2 mL and was refrigerated overnight. Brick red crystals of K-*cis-eq*-$[Co(med3a)CN]\cdot 0.5H_2O$ were separated by filtration, washed with ethanol and then ether, and air-dried. Yield: 0.85 g (~45%). Anal. Calcd for $KCoC_{10}H_{13}O_6N_3\cdot 0.5H_2O$ (fw 378.26): C, 31.75; H, 3.73; N, 11.11. Found: C, 31.07; H, 3.74; N, 11.47.

The complex was resolved as described for the corresponding ed3a complex. The less soluble diastereoisomer (0.50 g), $(-)_D$-$[Co(en)_2(C_2O_4)]$-$(+)_D$-$[Co(med3a)CN]\cdot xH_2O$, was recrystallized from hot water to constant optical rotation: $[\alpha]_D = -305°$, $[\alpha]_{546} = -566°$. The diastereoisomer was converted to the potassium salt by ion-exchange chromatography. The eluate, evaporated to 2 mL, crystallized after 2 days in a desiccator containing methanol. The crystals of K-*cis-eq*-$(+)_D$-$[Co(med3a)CN]\cdot 0.5H_2O$ were isolated as described above, giving $[\alpha]_D = +298°$ and $[\alpha]_{546} = +72°$. Anal. Calcd for $KCoC_{10}H_{13}O_6N_3\cdot 0.5H_2O$ (fw 378.26): C, 31.75; H, 3.73; N, 11.11. Found: C, 31.83; H, 3.76; N, 11.24. The $(-)_D$ enantiomer was isolated by the same procedure using $(+)_D$-$[Co(en)_2(C_2O_4)]I$ as the resolving agent.

Preparation of *N*-(Hydroxyethyl)ethylenediamine-*N,N′,N′*-triacetic Acid and Its Cobalt(III) Aqua Complex. The method used for the preparation of *N*-methylethylenediamine-*N,N′,N′*-triacetic acid[8] was also used for the preparation of *N*-(hydroxyethyl)ethylenediamine-*N,N′,N′*-triacetic acid. The corresponding cobalt(III) aqua complex reported by Bause[15] was prepared by using the method for the preparation of $[Co(ed3a)(H_2O)]\cdot 1.5H_2O$.[13-15] A portion of the hed3a preparation solution (5.0×10^{-2} mol, assuming 100% yield), 8.42 g (0.15 mol) of KOH, and 14.55 g (5.00×10^{-2} mol) of $Co(NO_3)_2\cdot 6H_2O$ yielded 15.5 g (~80%) of $[Co(hed3a)H_2O]\cdot 2H_2O$.

Preparation and Resolution of Potassium *cis-eq*-Cyano(*N*-(hydroxyethyl)ethylenediamine-*N,N′,N′*-triacetato)cobaltate(III) Monohydrate.

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This complex was prepared from the corresponding aqua complex as described for *cis-eq*-[Co(med3a)CN]$^-$. The reaction of 1.94 g (5.00 × 10^{-3} mol) of [Co(hed3a)(H_2O)]·$2H_2O$ and 0.49 g (7.5 × 10^{-3} mol) of KCN after 12 h yielded 0.80 g (~40%) of K-*cis-eq*-[Co(hed3a)CN]·H_2O. Anal. Calcd for $KCoC_{11}H_{17}O_8N_3$ (fw 417.28): C, 31.66; H, 4.10; N, 10.07. Found: C, 32.02; H, 4.01; N, 9.30.

The complex was resolved as described for the corresponding ed3a complex. The less soluble diastereoisomer, $(-)_D$-[Co(en)$_2$(C_2O_4)]-$(+)_D$-[Co(hed3a)CN]·xH_2O (0.55 g), was recrystallized to constant optical rotation: $[\alpha]_D = -315°$, $[\alpha]_{546} = -674°$. The diastereoisomer was converted to the potassium salt by ion-exchange chromatography. The eluate was evaporated to a small volume and was left to stand in a desiccator containing methanol for 2 days. The crystals of K-$(+)_{546}$-*cis-eq*-[Co(hed3a)CN]·$1.5H_2O$ (**2**) were filtered out, washed with methanol and then ether, and air-dried. $[\alpha]_D = +185°$ and $[\alpha]_{546} = -247°$. Anal. Calcd for $KCoC_{11}H_{15}O_7N_3$·$1.5H_2O$ (fw 426.28): C, 30.99; H, 4.25; N, 9.85. Found: C, 30.85; H, 4.05; N, 9.99. The second enantiomer, K-$(+)_{546}$-*cis-eq*-[Co(hed3a)CN]·$1.5H_2O$, was isolated by the same procedure using $(+)_D$-[Co(en)$_2$(C_2O_4)]I as the resolving agent.

Physical Measurements. The electronic absorption spectra were recorded by using a Varian Super Scan 3 recording spectrophotometer and 3 × 10^{-3} M aqueous solutions. The optical rotations were measured for 0.1% aqueous solutions in a 1-dm tube at 20 °C on a Perkin-Elmer Model 241 polarimeter. The circular dichroism curves were recorded at room temperature with a Jobin-Yvon Dichrographe Mark III using a xenon-arc source.

Analyses. Elemental microanalyses were performed by the Microanalytical Laboratory, Department of Chemistry, Faculty of Science, University of Belgrade.

X-ray Crystallography. X-ray crystallographic data collection and analysis were carried out by using the Nicolet R3m crystallographic system. This includes the SHELXTL version 4.0, which was used in solving and refining the structures.

Graphite-monochromated X-ray data were collected at room temperature by using a four-circle diffractometer. Preliminary rotation and oscillation photographs taken on the diffractometer were used to determine the crystal systems and to assess the overall crystal quality. More precise unit cell parameters were obtained by using a least-squares procedure on a set of carefully centered reflections. The respective crystallographic space groups were determined from an inspection of the data set collected. In the case of K[Co(hed3a)CN], the lattice was observed to be an A-centered cell. The cell parameters and the reflection indices were transformed to correspond to the monoclinic *C*-centered cell. The data given in the tables refer to the transformed cell.

A unique set of X-ray data was collected for each crystal. Radiation decay was monitored by periodically measuring three standard reflections. Absorption correction factors were calculated on the basis of transmission data from a set of azimuthal scans. These data were collected from a list of reflections with $290° < \chi > 250°$. The structures were solved by the heavy-atom method and refined by a least-squares procedure using a "blocked cascade" algorithm. The weights used were based on counting statistics corrected for instrumental instabilities. The latter were represented by a factor that was varied in the final cycles of the refinement. The absolute configurations were determined by refining the chirality/polarity parameter η.[16] This parameter refined to final values of 1.01 (4) for the hed3a complex and 0.96 (6) for the ed3a complex.

All non-hydrogen atoms were refined with anisotropic temperature factors. For K[Co(hed3a)CN] the positions of the hydrogen atoms were determined from difference Fourier maps and were refined isotropically. The methylene hydrogens on C(5) were refined by using a riding model assuming idealized bond lengths and angles and fixed temperature factors.

The structure determination of Rb[Co(ed3a)CN] used a combination of Patterson and electron density map refinement procedures. Hydrogens were generated by assuming idealized geometry and were refined by using a riding model attached to the atoms to which they are bonded. The temperature factors were fixed to approximately 1.2 times the heavy atoms to which they are bonded. There are three sites for water molecules of crystallization. One site is fully occupied, and two others, related by a 2-fold axis, are half-occupied.

Results

The absolute configurations from X-ray diffraction studies for Rb-$(-)_{546}$-*cis-eq*-[Co(ed3a)CN] and K-$(-)_{546}$-*cis-eq*-[Co(hed3a)CN] are shown in Figure 1. The complexes have opposite absolute configurations. Tables I–VII list the relevant crystallographic data.

Table I. Crystallographic Parameters

formula	$C_9H_{11}N_3O_6CoRb$·$2H_2O$ (**1**)	$C_{11}H_{15}N_3O_7CoK$·$1.5H_2O$ (**2**)
cryst system	orthorhombic	monoclinic
space group	$C222_1$	$C2$
a, Å	6.600 (5)	14.546 (7)
b, Å	14.243 (8)	7.219 (1)
c, Å	30.76 (1)	19.78 (1)
β, deg	90	130.09 (3)
Z	8	4
d_{calcd}, g/cm^3	2.01	1.73
cryst size, mm	0.35 × 0.15 × 0.13	0.38 × 0.38 × 0.25
radiation	Mo Kα	Mo Kα
scan type	ω, bisecting	$\theta/2\theta$, bisecting
2θ range	4–50	4–50
scan speed, deg/min	12	12
μ, cm^{-1}	47.57	13.72
no. of unique reflcns	1465	1529
no. of obsd reflcns	1103	1468
R (R_w)	0.06 (0.05)	0.027 (0.028)

Table II. Atomic Coordinates (×10^4) and Isotropic Thermal Parameters (Å^2 × 10^3) for Rb-$(-)_{546}$-*cis-eq*-[Co(ed3a)CN]·$2H_2O$

	x	y	z	U^a
Rb	8028 (2)	3514 (1)	4932 (1)	34 (1)
Co	9745 (3)	3077 (1)	6114 (1)	19 (1)
O(1)	8092 (15)	3222 (6)	6612 (3)	29 (3)
C(1)	8406 (22)	2581 (11)	6922 (4)	30 (5)
O(2)	7429 (18)	2600 (10)	7260 (3)	66 (5)
C(2)	9931 (22)	1837 (9)	6812 (4)	29 (4)
N(1)	11 264 (18)	2191 (7)	6458 (3)	24 (3)
C(3)	13 142 (25)	2665 (10)	6622 (4)	36 (5)
C(4)	12 568 (19)	3675 (10)	6716 (3)	23 (4)
N(2)	11 594 (16)	4060 (8)	6314 (3)	25 (4)
C(5)	10 305 (22)	4898 (10)	6371 (4)	36 (5)
C(6)	8595 (17)	4883 (10)	6049 (4)	23 (4)
O(4)	7597 (15)	5599 (7)	5968 (3)	36 (3)
O(3)	8355 (16)	4091 (6)	5850 (3)	27 (3)
C(7)	13 136 (22)	4241 (10)	5962 (4)	27 (4)
C(8)	12 912 (22)	3524 (11)	5602 (3)	28 (4)
O(6)	14 114 (16)	3530 (8)	5300 (3)	43 (4)
O(5)	11 447 (13)	2931 (6)	5631 (3)	25 (3)
C(9)	8010 (25)	2157 (9)	5867 (3)	23 (4)
N(3)	6951 (23)	1631 (8)	5698 (4)	45 (4)
W(1)^b	11 168 (22)	5000	5000	61 (6)
W(2)	3302 (26)	5223 (10)	2279 (4)	88 (6)
W(3)	5000	733 (16)	7500	124 (12)

^{a} Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor. ^{b} W = water oxygen.

Table III. Bond Lengths (Å) for Rb-$(-)_{546}$-*cis-eq*-[Co(ed3a)CN]·$2H_2O$

Rb–O(3)	2.949 (8)	Rb–O(5)	3.226 (9)
Rb–W(1)^a	2.970 (10)	Rb–O(4)	3.057 (9)
Rb–O(6)	2.821 (10)	Rb–O(6)	3.082 (12)
Rb–O(5)	2.885 (9)	Co–O(1)	1.892 (9)
Co–N(1)	1.928 (11)	Co–N(2)	1.956 (11)
Co–O(3)	1.894 (9)	Co–O(5)	1.874 (9)
Co–C(9)	1.899 (14)	O(1)–C(1)	1.336 (16)
C(1)–O(2)	1.224 (17)	C(1)–C(2)	1.502 (20)
C(2)–N(1)	1.487 (17)	N(1)–C(3)	1.500 (20)
C(3)–C(4)	1.515 (20)	C(4)–N(2)	1.499 (15)
N(2)–C(5)	1.475 (18)	N(2)–C(7)	1.508 (17)
C(5)–C(6)	1.503 (18)	C(6)–O(4)	1.239 (16)
C(6)–O(3)	1.293 (16)	C(7)–C(8)	1.513 (18)
C(8)–O(6)	1.222 (16)	C(8)–O(5)	1.286 (17)
C(9)–N(3)	1.150 (19)		

^{a} W = water oxygen.

The CD and absorption spectra for these complexes, for K-$(+)_{546}$-*cis-eq*-[Co(med3a)CN], and for K-$(+)_{546}$-*trans-eq*-[Co(ed3a)CN] are shown in Figure 2. The spectral data are given in Table VIII. These are the enantiomers isolated from the less soluble diastereoisomers formed by using $(-)_D$-[Co(en)$_2$(C_2O_4)]$^+$

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[16] Rogers, D. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1981**, *A37*, 734.

Table IV. Bond Angles (deg) for Rb-$(-)_{546}$-*cis-eq*-$[Co(ed3a)CN]\cdot 2H_2O$

O(1)–Co–N(1)	85.8 (4)	O(1)–Co–N(2)	91.5 (4)
N(1)–Co–N(2)	88.4 (5)	O(1)–Co–O(3)	89.1 (4)
N(1)–Co–O(3)	170.6 (4)	N(2)–Co–O(3)	83.8 (4)
O(1)–Co–O(5)	178.4 (4)	N(1)–Co–O(5)	92.9 (4)
N(2)–Co–O(5)	87.4 (4)	O(3)–Co–O(5)	92.0 (4)
O(1)–Co–C(9)	92.9 (5)	N(1)–Co–C(9)	94.6 (5)
N(2)–Co–C(9)	174.8 (4)	O(3)–Co–C(9)	93.6 (5)
O(5)–Co–C(9)	88.2 (5)	Co–O(1)–C(1)	114.5 (8)
O(1)–C(1)–O(2)	120.7 (14)	O(1)–C(1)–C(2)	115.2 (11)
O(2)–C(1)–C(2)	124.1 (13)	C(1)–C(2)–N(1)	108.8 (10)
Co–N(1)–C(2)	108.4 (8)	Co–N(1)–C(3)	108.7 (8)
C(2)–N(1)–C(3)	113.2 (10)	N(1)–C(3)–C(4)	106.6 (12)
C(3)–C(4)–N(2)	107.3 (10)	Co–N(2)–C(4)	105.4 (8)
Co–N(2)–C(5)	104.9 (8)	C(4)–N(2)–C(5)	116.4 (9)
Co–N(2)–C(7)	108.5 (7)	C(4)–N(2)–C(7)	111.4 (10)
C(5)–N(2)–C(7)	109.7 (10)	N(2)–C(5)–C(6)	110.1 (11)
C(5)–C(6)–O(4)	121.3 (12)	C(5)–C(6)–O(3)	114.6 (11)
O(4)–C(6)–O(3)	124.0 (11)	Co–O(3)–C(6)	113.8 (8)
N(2)–C(7)–C(8)	110.1 (11)	C(7)–C(8)–O(6)	119.2 (13)
C(7)–C(8)–O(5)	117.8 (11)	O(6)–C(8)–O(5)	123.0 (12)
Co–O(5)–C(8)	115.6 (8)	Co–C(9)–N(3)	176.2 (11)

Table V. Atomic Coordinates ($\times 10^4$) and Isotropic Thermal Parameters for K-$(-)_{546}$-*cis-eq*-$[Co(hed3a)CN]\cdot 1.5H_2O$

	x	*y*	*z*	U^a
Co	9944 (1)	7500	7454 (1)	15 (1)
C(9)	11557 (3)	6702 (6)	8039 (2)	23 (2)
N(3)	12509 (3)	6211 (7)	8376 (3)	49 (2)
O(1)	9789 (2)	8376 (4)	6481 (2)	21 (1)
C(1)	10220 (3)	9996 (6)	6575 (2)	21 (2)
O(2)	10249 (3)	10735 (4)	6029 (2)	31 (2)
C(2)	10767 (3)	10953 (6)	7441 (2)	22 (2)
N(1)	10403 (2)	10087 (4)	7917 (2)	16 (1)
C(10)	11411 (3)	10232 (6)	8901 (2)	22 (2)
C(11)	11889 (3)	12158 (6)	9270 (2)	25 (2)
O(7)	11106 (3)	13211 (4)	9309 (2)	31 (1)
C(3)	9276 (3)	10975 (5)	7652 (2)	20 (2)
C(4)	8198 (3)	10213 (5)	6778 (2)	22 (2)
N(2)	8265 (2)	8166 (4)	6846 (2)	18 (1)
C(7)	7990 (3)	7489 (6)	7418 (2)	22 (2)
C(8)	9060 (3)	6614 (5)	8273 (2)	22 (2)
O(6)	8945 (3)	5955 (5)	8781 (2)	39 (2)
O(5)	10054 (2)	6620 (4)	8405 (2)	22 (1)
O(3)	9260 (2)	5191 (4)	6848 (2)	23 (1)
C(6)	8103 (3)	5261 (6)	6183 (3)	26 (2)
O(4)	7513 (3)	3893 (4)	5731 (2)	42 (2)
C(5)	7547 (3)	7158 (6)	6003 (2)	24 (2)
K(1)	10000	3041 (2)	10000	40 (1)
K(2)	10000	7808 (2)	5000	40 (1)
W(1)[b]	10000	−638 (9)	10000	84 (5)
W(2)	10253 (4)	4725 (5)	5928 (3)	46 (2)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor. [b] W = water oxygen.

Table VI. Bond Lengths (Å) for K-$(-)_{546}$-*cis-eq*-$[Co(hed3a)CN]\cdot 1.5H_2O$

Co–C(9)	1.918 (4)	Co–O(1)	1.896 (4)
Co–N(1)	1.996 (3)	Co–N(2)	1.965 (3)
Co–O(5)	1.892 (4)	Co–O(3)	1.916 (3)
C(9)–N(3)	1.140 (6)	O(1)–C(1)	1.283 (5)
C(1)–O(2)	1.229 (7)	C(1)–C(2)	1.513 (6)
C(2)–H(3)	0.868 (46)	C(2)–H(2)	0.957 (37)
C(2)–N(1)	1.485 (7)	N(1)–C(3)	1.506 (6)
N(1)–C(10)	1.507 (4)	C(10)–H(13)	1.011 (57)
C(10)–H(14)	0.967 (64)	C(10)–C(11)	1.515 (6)
C(11)–H(15)	0.955 (30)	C(11)–H(16)	0.928 (57)
C(11)–O(7)	1.413 (6)	O(7)–H(17)	0.607 (49)
C(3)–C(4)	1.502 (4)	C(4)–H(6)	0.973 (51)
C(4)–N(2)	1.482 (5)	C(4)–H(7)	1.029 (55)
N(2)–C(7)	1.506 (7)	N(2)–C(5)	1.469 (5)
C(7)–H(11)	1.077 (59)	C(7)–H(12)	0.894 (42)
C(7)–C(8)	1.513 (4)	C(8)–O(6)	1.216 (7)
C(8)–O(5)	1.293 (6)	O(3)–C(6)	1.309 (4)
C(6)–C(5)	1.512 (6)	C(6)–O(4)	1.234 (5)
C(5)–H(9)	0.970 (58)	C(5)–H(8)	1.032 (57)

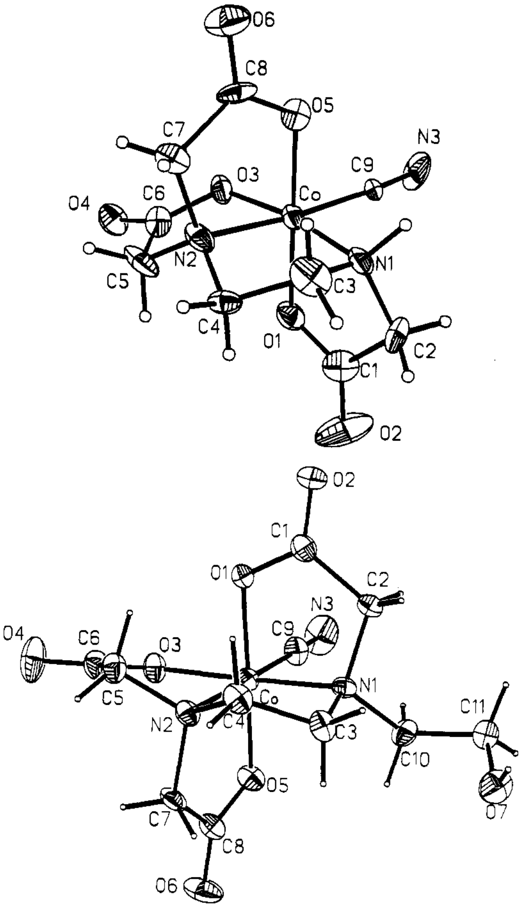

Figure 1. ORTEP diagrams and absolute configurations for Rb-$(-)_{546}$-*cis-eq*-$[Co(ed3a)CN]\cdot 2H_2O$ (**1**) (top) and K-$(-)_{546}$-*cis-eq*-$[Co(hed3a)CN]\cdot 1.5H_2O$ (**2**) (bottom).

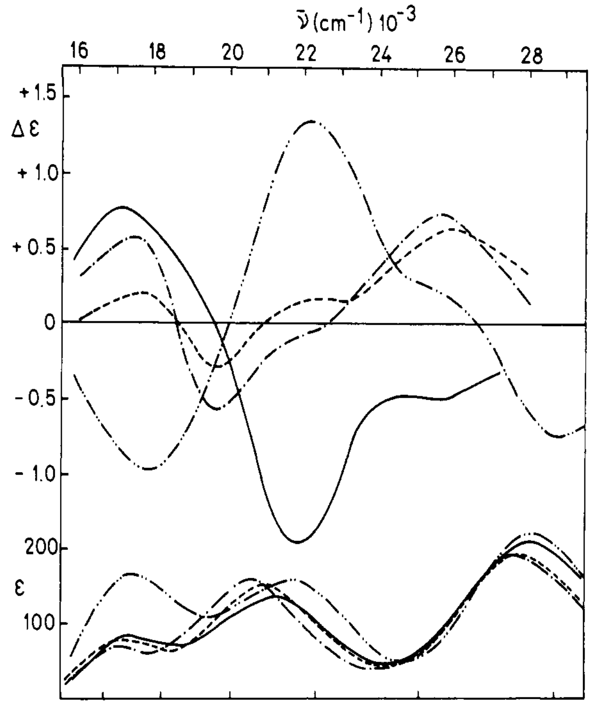

Figure 2. Absorption and circular dichroism curves for K-$(-)_{546}$-*cis-eq*-$[Co(ed3a)CN]\cdot 2H_2O$ (—), K-$(+)_{546}$-*cis-eq*-$[Co(med3a)CN]\cdot 0.5H_2O$ (- - -), K-$(-)_{546}$-*cis-eq*-$[Co(hed3a)CN]\cdot 1.5H_2O$ (–·–), and K-$(+)_{546}$-*trans-eq*-$[Co(ed3a)CN]$ (–··–).

as the resolving agent. The cis-eq and trans-eq stereochemistry has been established by NMR spectroscopy[12] and the characteristic

Table VII. Bond Angles (deg) for K-$(-)_{546}$-*cis-eq*-[Co(hed3a)CN]·$1.5H_2O$

C(9)–Co–O(1)	90.7 (2)	C(9)–Co–N(1)	95.0 (1)
O(1)–Co–N(1)	86.5 (1)	C(9)–Co–N(2)	176.7 (2)
O(1)–Co–N(2)	90.5 (1)	N(1)–Co–N(2)	88.2 (1)
C(9)–Co–O(5)	90.7 (2)	O(1)–Co–O(5)	178.5 (1)
N(1)–Co–O(5)	94.0 (1)	N(2)–Co–O(5)	88.1 (1)
C(9)–Co–O(3)	93.2 (1)	O(1)–Co–O(3)	88.9 (1)
N(1)–Co–O(3)	170.6 (1)	N(2)–Co–O(3)	83.7 (1)
O(5)–Co–O(3)	90.4 (1)	Co–C(9)–N(3)	179.0 (4)
Co–O(1)–C(1)	115.5 (3)	O(1)–C(1)–O(2)	124.0 (4)
O(1)–C(1)–C(2)	115.5 (4)	O(2)–C(1)–C(2)	120.4 (4)
C(1)–C(2)–H(3)	116.2 (27)	C(1)–C(2)–H(2)	102.9 (27)
H(3)–C(2)–H(2)	106.6 (35)	C(1)–C(2)–N(1)	112.6 (3)
H(3)–C(2)–N(1)	109.3 (40)	H(2)–C(2)–N(1)	108.7 (28)
Co–N(1)–C(2)	104.7 (3)	Co–N(1)–C(3)	105.7 (2)
C(2)–N(1)–C(3)	110.7 (3)	Co–N(1)–C(10)	114.7 (2)
C(2)–N(1)–C(10)	110.0 (3)	C(3)–N(1)–C(10)	110.8 (4)
H(13)–C(10)–H(14)	110.3 (43)	H(13)–C(10)–C(11)	111.7 (26)
H(14)–C(10)–C(11)	109.1 (29)	H(13)–C(10)–N(1)	100.0 (22)
H(14)–C(10)–N(1)	108.7 (19)	C(11)–C(10)–N(1)	116.6 (3)
C(10)–C(11)–H(15)	104.6 (27)	C(10)–C(11)–H(16)	112.2 (29)
H(15)–C(11)–H(16)	103.2 (42)	C(10)–C(11)–O(7)	112.5 (4)
H(15)–C(11)–O(7)	109.8 (37)	H(16)–C(11)–O(7)	113.6 (30)
C(11)–O(7)–H(17)	111.1 (62)	N(1)–C(3)–C(4)	109.9 (4)
C(3)–C(4)–H(6)	113.9 (20)	C(3)–C(4)–N(2)	107.6 (3)
H(6)–C(4)–N(2)	103.4 (23)	C(3)–C(4)–H(7)	117.3 (27)
H(6)–C(4)–H(7)	103.5 (40)	N(2)–C(4)–H(7)	110.3 (29)
Co–N(2)–C(4)	106.4 (2)	Co–N(2)–C(7)	106.8 (2)
C(4)–N(2)–C(7)	111.0 (4)	Co–N(2)–C(5)	105.6 (3)
C(4)–N(2)–C(5)	115.7 (3)	C(7)–N(2)–C(5)	110.8 (3)
N(2)–C(7)–H(11)	110.1 (33)	N(2)–C(7)–H(12)	109.9 (38)
H(11)–C(7)–H(12)	113.3 (44)	N(2)–C(7)–C(8)	113.3 (4)
H(11)–C(7)–C(8)	107.9 (20)	H(12)–C(7)–C(8)	102.2 (23)
C(7)–C(8)–O(6)	119.7 (4)	C(7)–C(8)–O(5)	115.9 (4)
O(6)–C(8)–O(5)	124.4 (3)	Co–O(5)–C(8)	115.6 (2)
Co–O(3)–C(6)	114.1 (3)	O(3)–C(6)–C(5)	114.7 (3)
O(3)–C(6)–O(4)	122.8 (4)	C(5)–C(6)–O(4)	122.5 (3)
N(2)–C(5)–C(6)	107.5 (2)	N(2)–C(5)–H(9)	100.7 (32)
C(6)–C(5)–H(9)	118.8 (36)	N(2)–C(5)–H(8)	101.5 (22)
C(6)–C(5)–H(8)	111.0 (30)	H(9)–C(5)–H(8)	114.9 (41)

Table VIII. Absorption and Circular Dichroism Data for $[Co(ed3a)CN]^-$ Type Complexes

	absorption		circular dichroism	
complex ion[a]	$\bar{\nu}$, cm^{-1}	ϵ	$\bar{\nu}$, cm^{-1}	$\Delta\epsilon$
$(-)_{546}$-*cis-eq*-$[Co(ed3a)CN]^-$	17 400	85	17 200	+0.76
	21 300	142	21 900	−1.45
	27 900	188	25 600	−0.50
$(+)_{546}$-*cis-eq*-$[Co(med3a)CN]^-$	17 200	73	17 700	+0.20
	20 900	148	19 700	−0.27
			22 100	+0.17
	27 600	185	25 900	+0.61
$(-)_{546}$-*cis-eq*-$[Co(hed3a)CN]^-$	17 000	70	17 500	+0.52
	20 700	157	20 100	−0.52
			22 100 sh	−0.06
	27 600	191	25 700	+0.72
$(+)_{546}$-*trans-eq*-$[Co(ed3a)CN]^-$	17 400	167	17 900	−0.96
	21 600	160	22 200	+1.35
			25 600 sh	+0.20
	28 100	223	28 900	−0.73

[a] The sign refers to the sign of optical rotation at 546 nm.

differences in absorption spectra.[17]

Discussion

The possible geometrical isomers of [Co(ed3a)X] (cis-eq, trans-eq, and cis-polar) have been shown elsewhere.[12,17] The cis-eq and trans-eq isomers of $[Co(ed3a)CN]^-$ and the cis-eq isomers of $[Co(med3a)CN]^-$ and $[Co(hed3a)CN]^-$ are reported here. The corresponding cobalt–cyano complexes of trimethylenediamine-*N*,*N*,*N′*-triacetate ion[18] and the corresponding *N*-methyl ligand[13] were reported to form only polar isomers. The complexes reported in Figures 1 and 2 and Table VIII are the enantiomers isolated by using the same resolving agent, but the absolute configurations of the $(-)_{546}$-cis-equatorial isomers of $[Co(ed3a)CN]^-$ and $[Co(hed3a)CN]^-$ are opposite, as shown in Figure 1. From the close similarities of the CD curves of $(+)_{546}$-$[Co(med3a)CN]^-$ and $(-)_{546}$-$[Co(hed3a)CN]^-$ it is certain that these are the enantiomers with the same absolute configuration. The different signs of rotation at 546 nm for these complexes might suggest that they have opposite configurations. However, 546 nm is very nearly the point of zero CD intensity between two CD peaks of opposite signs for both complexes. These peaks differ significantly in intensities for the complexes, and the signs of rotation might be expected to differ in this region. The molar rotation of $(+)_{546}$-$[Co(med3a)CN]^-$ is very small (+72°) at 546 nm.

For each of the complexes, the lower energy absorption band (~410–650 nm) has two components, suggesting effective tetragonal (D_{4h}) symmetry, with no apparent splitting of the higher energy band (maximum at ~360 nm). The polar isomers of the cobalt–cyano complexes of the trimethylenediamine-*N*,*N*,*N′*-triacetato ligand (and the *N*-methyl derivative) showed no splitting of the lower energy absorption band.[13,18] The CD spectrum of $(-)_{546}$-$[Co(hed3a)CN]^-$ reveals three peaks within the first absorption band region (+) a peak at 17.5×10^3 cm^{-1}, (−) a peak at 20.1×10^3 cm^{-1}, and a (−) shoulder at about 22.0×10^3 cm^{-1}. The first two CD peaks for $(+)_{546}$-$[Co(med3a)CN]^-$ are shifted only slightly relative to those of the hed3a complex but have much lower intensities. The third component is a positive peak at about 22.1×10^3 cm^{-1}. Three components reveal the true lower symmetry of the complexes. Although only one CD peak is seen for the range covered in the region of the higher energy absorption band, the CD maximum is at much lower energy than the absorption maximum, indicating the presence of more than one component in this region also. A higher energy component, not observed in the spectral range covered, is expected.

The great similarity in the CD curves for the cis-equatorial isomers of the med3a and hed3a complexes make it clear that the isomers shown in Figure 2 have the same absolute configuration, as shown for the hed3a complex in Figure 1. Since $(-)_{546}$-*cis-eq*-$[Co(ed3a)CN]^-$ has a configuration (Figure 1) opposite to that of $(-)_{546}$-*cis-eq*-$[Co(hed3a)CN]^-$, it is the $(+)_{546}$ enantiomer of *cis-eq*-$[Co(ed3a)CN]^-$ that has the same absolute configuration as the $(+)_{546}$-med3a and $(-)_{546}$-hed3a complexes, for which the CD curves are shown in Figure 2. This corresponds to the opposite-sign pattern of the CD curve for $(-)_{546}$-*cis-eq*-[Co(ed3a)CN] shown in Figure 2. Compared to the med3a and hed3a complexes, the ed3a complex exhibits only two components of greater intensities in the region of the lower energy absorption band (~410–650 nm). The prominent CD peak at 17.2×10^3 cm^{-1} for the $(+)_{546}$-ed3a complex has a sign opposite to those of the corresponding peaks of the $(+)_{546}$-med3a and $(+)_{546}$-hed3a complexes, all with the same absolute configuration. Thus H as an N substituent compared to alkyl substituents reverses the signs for the CD components in the low-energy absorption band region (16 000–23 000 cm^{-1}). These CD comparisons are strikingly similar to those reported for N-substituted ed3a complexes[7] with NO_2^- replacing CN^-.

In these complexes with no net chirality of chelate rings, the asymmetric N donor and ring conformations are expected to make major contributions to the rotational strengths. In the cyano complexes reported here, as for substituted edda complexes and substituted ed3a complexes with NO_2^- as the sixth ligand, the differences in contributions to CD intensities are small among alkyl substituents but very great for H versus an alkyl group. In these cases the net rotational strength within an absorption band region is small, as might be expected with no net ring chirality. In such cases theoretical models dealing with net rotational strength[19] do not help with substituent effects. As noted by Maricondi and

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(17) Maricondi, C. W.; Maricondi, C. *Inorg. Chem.* **1974**, *13*, 1110.

(18) Doh, M.-K.; Fujita, J.; Ogino, H.; Saito, K. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 469.

(19) Richardson, F. S. *Inorg. Chem.* **1972**, *11*, 2366.

Maricondi,[7] Bosnich and Harrowfield[20] suggested that polar N–H bonds on donor atoms might make contributions of opposite signs to the rotational strength as compared to other N–R bonds.

Since there is no net chirality, the IUPAC rules do not apply the ed3a complexes. The ring pairs are (Δ,Λ). However, $(-)_{546}$-*cis-eq*-[Co(ed3a)CN]$^-$ can be related to Δ- (or $\Delta\Lambda\Delta$-) [Co(edta)]$^-$ since the N–CN unspanned edge, corresponding to the missing acetate arm of edta, when paired with the *R* ring involving N(2) has Δ chirality. Likewise, $(-)_{546}$-*cis-eq*-[Co(hed3a)CN]$^-$ can be related to Λ-[Co(edta)]$^-$ by using the unspanned N–CN edge and the *R* ring involving N(2). The CD curve for $(-)_{546}$-*cis-eq*-[Co(ed3a)CN]$^-$ agrees with that reported[17] for [Co-(*R*)-(−)-(pd3a)NO$_2$]$^-$ (pd3a = 1,2-propanediamine-*N*,*N*,*N'*-triacetate ion). The absolute configuration of the (*R*)-pd3a complex is known from the absolute configuration of the stereospecific ligand. It agrees with the configuration reported here for the ed3a complex.

The splitting of the lower energy absorption band of *trans-eq*-[Co(ed3a)CN]$^-$ is more pronounced than for the cis-equatorial isomers, as might be expected because of the greater strain in the trans isomer. The CD curve for $(+)_{546}$-*trans-eq*-[Co(ed3a)CN]$^-$ is nearly the mirror image of that for the $(-)_{546}$-cis-eq isomer. This close similarity (with sign reversal for one isomer) might not be expected since the ring patterns differ significantly, but it agrees with the results for cis-equatorial and trans-equatorial isomers of [Co-(*R*)-(−)-(pd3a)NO$_2$]$^-$. For the trans-eq isomer there is also no net ring chirality. The great similarity in the CD curves suggests the same major contributions from the asymmetric secondary N and the ethylenediamine ring conformation. The glycinate rings are nearly planar. For $(-)_{546}$-*cis-eq*-[Co(ed3a)CN]$^-$ then en ring conformation is λ and the secondary N has the *S* configuration. Because of the great differences in ring patterns, the chirality of *trans-eq*-[Co(ed3a)CN]$^-$ cannot be related to that of [Co(edta)]$^-$ unambiguously. However, the CD curve for $(+)_{546}$-*trans-eq*-[Co(ed3a)CN]$^-$ agrees remarkably with that[17] for *trans-eq*-[Co-(*R*)-(−)-(pd3a)NO$_2$]$^-$ with known absolute configuration. The same configuration for *trans-eq*-[Co(ed3a)CN]$^-$ gives the *R* configuration for N. The cis-equatorial and trans-equatorial isomers of the nitro complex[17] showed the same nearly mirror image pattern observed here for the cis-equatorial and trans-equatorial isomers with configurations opposite to those of the coordinated secondary nitrogens.

For all of the isomers there is a great similarity for the CD spectra comparing the cyano and nitro complexes and these are very much different from those for the complexes of H$_2$O[15], Cl$^-$, and Br$^-$.[8] CN$^-$ and NO$_2^-$ are very strong field ligands and π-acceptors. Possible effects resulting from preferred orientations of coordinated NO$_2^-$ cannot pertain to the cylindrically symmetrical CN$^-$.

The Co–CN bond lengths are about the same for the ed3a (1.899 Å) and hed3a (1.918 Å) complexes although the Co–NO$_2$ distance in [Co(hed3a)NO$_2$]$^-$ is considerably longer than that in [Co(ed3a)NO$_2$]$^-$.[21] The smaller CN$^-$ ligand is not affected by the hydroxyethyl substituent. The Co–O bond lengths show no significant variation in the cyano complexes. Although the Co–N(1) bond length (1.928 Å) is appreciably shorter than that for Co–N(2) (1.956 Å) for the ed3a complex, the reverse is true for the hed3a complex, 1.996 Å for Co–N(1) and 1.965 Å for Co–N(2). There is little change in the Co–N(2) bond lengths for the two complexes, but the Co–N(1) bond is lengthened appreciably by addition of the hydroxyethyl arm. This is the major change in Co–ligand distances for the two complexes. The same effect of the hydroxyethyl arm is observed for the corresponding nitro complexes.[21] The angles subtended at Co by the chelate rings are slightly less (83.7–88.4°) than the ideal 90°, but they reveal less strain, as expected, than for [Co(edta)]$^-$. There is little effect on these angles resulting from addition of the hydroxyethyl substituent.

The structure of racemic NH$_4$-*cis-eq*-[Co(ed3a)CN] is reported elsewhere.[12] Several samples that proved to be incompletely resolved yielded crystals of the racemic complex. Finally, suitable crystals of the Rb salt of the optically active complex were obtained and the absolute configuration, essential for this study, was established and is reported here. The racemic crystal gave $R = 0.033$ and $R_w = 0.041$ and smaller standard deviations (0.002 Å) for important bond lengths. Although the Co–CN bonds are essentially linear (179°) for *cis-eq*-[Co(hed3a)CN]$^-$ and the corresponding bond angle at carbon for $(-)_{546}$-*cis-eq*-[Co(ed3a)CN]$^-$ was 176.2°, it is 178.8° for racemic *cis-eq*-[Co(ed3a)CN]$^-$. The small apparent deviation from linearity for the resolved complex ion is not significant.

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Supplementary Material Available: Tables SIX–SXIV, giving anisotropic thermal parameters, H atom coordinates, and least-squares planes for **1** and **2** (4 pages); Tables SXV and SXVI, listing observed and calculated structure factors for both compounds (17 pages). Ordering information is given on any current masthead page.

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