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Structural *trans* Effects in some Bis(ethylenediamine)cobalt(III) Complexes

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Abstract

The crystal structures of seven bis(ethylenediamine)cobalt(III) complexes with monodentate oxalato, azido, nitro, sulfito and thiosulfato ligands have been determined by single-crystal X-ray diffraction methods. The complexes, space groups, cell constants, number of molecules per unit cell, Z, calculated and experimental densities and final reliability factors are as follows: *cis*$[en_2Co(NO_2)(C_2O_4)]\cdot 2H_2O$, $P\bar{1}$, $a = 6.925(3)$, $b = 8.055(3)$, $c = 12.158(4)$ Å, $\alpha = 80.16(2)^\circ$, $\beta = 77.87(2)^\circ$, $\gamma = 87.90(2)^\circ$, $V = 653$ Å^3, $Z = 2$, $\rho_{exp} = 1.78$ g cm^{-3}, $\rho_{calc} = 1.76$ g cm^{-3}, $R_1 = 5.5$, $R_2 = 9.4$; *trans*$[en_2Co(NO_2)(C_2O_4)]\cdot 2H_2O$, $P2_1/n$, $a = 8.218(2)$, $b = 15.613(1)$, $c = 10.694(1)$ Å, $\beta = 101.49(1)^\circ$, $V = 1344$ Å^3, $Z = 4$, $\rho_{exp} = 1.73$ g cm^{-3}, $\rho_{calc} = 1.74$ g cm^{-3}, $R_1 = 3.5$, $R_2 = 5.6$; *cis*$[en_2Co(N_3)(C_2O_4)]\cdot H_2O$, $P2_1/c$, $a = 8.379(1)$, $b = 15.548(4)$, $c = 9.736(3)$ Å, $\beta = 97.44(2)^\circ$, $V = 1258$ Å^3, $Z = 4$, $\rho_{exp} = 1.73$ g cm^{-3}, $\rho_{calc} = 1.69$ g cm^{-3}, $R_1 = 4.3$, $R_2 = 4.8$; *trans*$[en_2Co(N_3)(C_2O_4)]\cdot 2H_2O$, $I4_1/a$, $a = 26.684(2)$, $c = 7.625(2)$ Å, $V = 5429$ Å^3, $Z = 16$, $\rho_{exp} = 1.69$ g cm^{-3}, $\rho_{calc} = 1.69$ g cm^{-3}, $R_1 = 6.6$, $R_2 = 7.9$; *cis*-$NH_4[en_2Co(S_2O_3)(SO_3)]\cdot 3H_2O$, $P2_1/n$, $a = 10.094(9)$, $b = 12.205(12)$, $c = 13.358(3)$ Å, $\beta = 90.19(4)^\circ$, $V = 1646$ Å^3, $Z = 4$, $\rho_{exp} = 1.79$ g cm^{-3}, $\rho_{calc} = 1.78$ g cm^{-3}, $R_1 = 7.6$, $R_2 = 9.2$; *cis*$[en_2Co(N_3)(SO_3)]\cdot 1.5H_2O$, $P2_1/n$, $a = 7.749(1)$, $b = 10.701(2)$, $c = 15.101(4)$ Å, $\beta = 102.80(2)^\circ$, $V = 1221$ Å^3, $Z = 4$, $\rho_{exp} = 1.78$ g cm^{-3}, $\rho_{calc} = 1.78$ g cm^{-3}, $R_1 = 3.2$, $R_2 = 4.0$; *cis*$[en_2Co(NO_2)(SO_3)]\cdot 1H_2O$, $P2_1/c$, $a = 6.629(2)$, $b = 11.429(4)$, $c = 15.156(4)$ Å, $\beta = 93.27(2)^\circ$, $V = 1146$ Å^3, $Z = 4$, $\rho_{exp} = 1.87$ g cm^{-3}, $\rho_{calc} = 1.86$ g cm^{-3}, $R_1 = 3.5$, $R_2 = 4.4$. Additionally, the previously reported structure of *cis*$[en_2Co(N_3)_2]NO_3$ has been redetermined: *Pnma*, $a = 11.903(3)$, $b = 23.566(6)$, $c = 8.877(2)$ Å, $V = 2493$ Å^3, $Z = 8$, $\rho_{exp} = 1.73$ g cm^{-3}, $\rho_{calc} = 1.73$ g cm^{-3}, $R_1 = 4.8$, $R_2 = 5.9$.

The structural *trans* effect, *STE*, the difference between the Co–N(en) bond length *trans* to a ligand and the average of the two Co–N(en) bond lengths that are both *cis* to that ligand and *trans* to each other, decreases in the series SO_3^{2-}[0.059(7) Å] > SSO_3^{2-}[0.036(9) Å] > NO_2^-[0.019(10) Å] > N_3^- [0.005(6) Å] > $C_2O_4^{2-}$[0.000(6) Å].

Introduction

Kinetic and structural *trans* effects have been well documented for Co(III) complexes containing thio ligands, such as sulfito, SO_3^{2-} [1–3], and thiosulfato, $S_2O_3^{2-}$ [4, 5]. Specifically, the length of a bond between the central Co(III) and a ligand, T, *trans* to the thio ligand is significantly greater than the mean length of the two chemically identical T–Co bonds *trans* to each other in the same complex. Correspondingly, substitution reactions of Co(III) complexes are characteristically faster at ligand sites *trans* to these thio-ligands. Similar, though less pronounced, structural and kinetic *trans* effects have also been noted for Co(III) complexes containing the non-thio ligand nitrito-N, NO_2^- [6–10]. A small structural *trans* effect has been reported for azido, N_3^- [11], although there is no evidence for a kinetic *trans* effect in the aquation of $[Co(en)_2N_3Cl]^+$ [12].

In general, the kinetic evidence for *trans* labilization by some ligands is relatively well-documented, but data for the structural *trans* effect, *STE*, particularly for the weakly *trans*-affecting ligands are subject to considerable scatter. The *STE* in cobalt complexes has been reported predominantly with reference to lengths of the Co–ammine bonds *trans* to the labilizing ligand, X, in complexes such as $(NH_3)_5CoX^{2+,+}$. By this measure, the *STE*s for ligands mentioned above are as follows: SO_3^{2-}-[0.089(4) Å]; $S_2O_3^{2-}$[0.020(8) Å]; NO_2^-[0.021(6) Å]; N_3^-[0.014(6) Å].

The structure of the sulfito-S ligand in complexes of bis(ethylenediamine)cobalt(III) with the *trans* geometry [13] has been repeatedly characterized and *cis*$[(en)_2Co(SO_3)_2]^-$ [14] has been reported. The lengthening [13, 15] of bonds *trans* to this ligand has been well characterized as has the extraordinary *trans*-labilizing ability of the sulfito ligand [16, 17]; a correlation between the structural and kinetic *trans* effects has been noted [4]. With such strongly labilizing ligands, the reactivity of

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the pentaammine complexes makes their crystallization and characterization difficult.

Recently, we have sought a more general measure of the *STE* of ligands in the crystallographic characterization of a series of cobalt(III) complexes of the general formula *cis*[en$_2$CoXX′]. Bis(ethylenediamine) complexes provide a relatively less labile ligand, N(en), *trans* to the labilizing ligand and the three *trans*-Co axes in *cis*[(en)$_2$CoXX′] contain the *trans* ligand pairings: N(en)–N(en), N(en)–X, and N(en)–X′. The N(en)–N(en) pair provides an internal standard of structural reference, the unperturbed N(en)–Co bond, for comparison with the N(en)–Co bonds that are *trans* to the affecting ligands. The structures of six *cis*[en$_2$CoXX′] complexes are reported here. *cis*[en$_2$Co(NO$_2$)(C$_2$O$_4$)], *cis*[en$_2$Co(N$_3$)(C$_2$O$_4$)] and *cis*[en$_2$Co(SO$_3$)(SSO$_3$)]$^-$ have not been previously reported. *cis*[en$_2$Co(NO$_2$)(SO$_3$)] and *cis*[en$_2$Co(N$_3$)(SO$_3$)] are also under investigation elsewhere and preliminary results have been recently published [18]. The published structure of *cis*[en$_2$Co(N$_3$)$_2$]$^+$ [19] reported azido geometries that differed widely from those usually found for non-bridging azido [11, 20] ligands. Further, the reported density was inconsistent with the unit cell parameters and formula weight. These and other anomalies prompted us to redetermine this structure.

Structural determination of both the *cis* and *trans* isomers of [en$_2$CoXX′] complexes allows for the determination of the relative *STE* of X and X′. Recently one of us has reported the synthesis of *cis* and *trans*[en$_2$Co(NO$_2$)(C$_2$O$_4$)] [7], containing the monodentate oxalato ligand. We report here the new syntheses of *cis* and *trans*[en$_2$Co(N$_3$)(C$_2$O$_4$)]. In addition to the structures of the *cis* isomers, we herein report the structures of *trans*[en$_2$Co(N$_3$)(C$_2$O$_4$)] and *trans*[en$_2$Co(NO$_2$)(C$_2$O$_4$)].

The structure of the monodentate oxalato ligand has been previously reported in two structures, *trans*[Pt(SCN)$_2$(C$_2$O$_4$)$_2$]$^{4-}$ [21] in which the planes of the two adjacent carboxylate groups in the oxalato ligands are twisted with respect to each other at a dihedral angle of about 13°, and *trans*[en$_2$Co(H$_2$O)(C$_2$O$_4$)]$^+$ [22] in which the dihedral angle between the adjacent carboxylate groups is 5.3°. Spectroscopic characterization of *cis* and *trans*[en$_2$Co(NO$_2$)(C$_2$O$_4$)] complexes [7] leaves little doubt of their structural identification. However, the exploitation of the ^{13}C NMR data for the characterization of oxalato groups bound as synergistic anions in transferrins [23] makes absolute confirmation of the structural inferences of interest. Kinetic studies on these oxalato complexes, as well as the *cis* and *trans*[en$_2$Co(N$_3$)(C$_2$O$_4$)] complexes, are underway to provide the correlation between the kinetic *trans* effect (*KTE*) and the structural *trans* effect (*STE*) [24].

Experimental

General Data

For chromatographic elutions, concentrated aqueous NaClO$_4$, prepared from the hydrated salt obtained from G. F. Smith Chemical Co., was filtered before diluting. All other materials were commercially available, of reagent grade, and were used without further purification. Chromatographic separations were accomplished by elution from Sephadex cation exchange resins, SP-C25, Na$^+$ form. Vis–UV spectra (700–200 nm) were recorded on a Varian DMS 90 and solution absorptivities (cm^{-1} M^{-1}) were based on total Co concentrations determined by the Kitson method [25]. IR spectra (cm^{-1}) were recorded either on a Perkin-Elmer 337 or a Nicolet 5DXC FT IR in KBr pellets. ^{13}C NMR and ^{1}H were obtained on a Jeol FX90 Q in D$_2$O as previously described [7].

Preparations and Characterizations

(a) cis-(Oxalato)(nitrito-N)bis(ethylenediamine)-cobalt(III), cis-[en$_2$Co(NO$_2$)(C$_2$O$_4$)]·2H$_2$O, abbreviated as cis-NO$_2$(C$_2$O$_4$)

This complex is prepared as previously described [7] and a supersaturated solution is allowed to crystallize overnight at 5 °C. When the crystallization is performed in a borosilicate glass beaker, the crystals are well-formed but show evidence of twinning both under the polarizing microscope and in precession photographs. Crystals suitable for X-ray structural determination, with no evidence of twinning, are obtained when the crystallization is performed in a Nalgene$^{(R)}$ cup.

(b) trans-(Oxalato)(nitrito-N)bis(ethylenediamine)-cobalt(III), trans-[en$_2$Co(NO$_2$)(C$_2$O$_4$)]·2H$_2$O, abbreviated as trans-NO$_2$(C$_2$O$_4$)

The complex is prepared as previously described [7]. Crystals suitable for X-ray structural determination are obtained by recrystallization from a saturated aqueous solution into which a four-fold excess volume of ethanol is allowed to diffuse at 5 °C over a period of two days.

(c) cis-(Azido)(oxalato)bis(ethylenediamine)-cobalt(III) hydrate, cis[en$_2$Co(N$_3$)(C$_2$O$_4$)]·H$_2$O, abbreviated as cis-N$_3$(C$_2$O$_4$)

The azido–oxalato complexes are prepared by substitution on the cation *cis*[en$_2$Co(N$_3$)Cl]$^+$. *cis*-[en$_2$Co(N$_3$)Cl]Cl is prepared [26] from *cis*[en$_2$Co(N$_3$)$_2$]NO$_3$, *vide infra*, and the desired cation is isolated with NaClO$_4$ from saturated aqueous solution as the perchlorate salt. In a typical preparation, 1.00 g *cis*[en$_2$Co(N$_3$)Cl]ClO$_4$ and 0.375 g Na$_2$C$_2$O$_4$ are dissolved in 30 ml H$_2$O and warmed to 35 °C in the dark for 2.5 h, during which considerable quantities of the bidentate oxalato cation $[en_2Co(C_2O_4)]^+$ precipitate as the perchlorate salt. The mixture is cooled to room temperature, filtered and the neutral products in the filtrate are separated from cationic species by elution from a Sephadex SP C-25 column with H_2O. The purple *trans* isomer is well separated from the pink *cis*. Each is collected separately and concentrated by flash evaporation to 3 and 5 ml respectively. Ethanol (15 ml) is introduced through a medium porosity fritted glass gas dispersion tube into the 5 ml solution of the *cis* isomer at 5 °C over a period of 2 h. The pink solid is filtered and air dried. Yield: 0.057 g. *Anal.* Calc. for $[(C_2N_2H_8)_2Co(N_3)(C_2O_4)]\cdot H_2O$: C, 22.02; H, 5.50; N, 29.96; Co, 18.01. Found: C, 22.13; H, 5.65; N, 30.18; Co, 17.79%. IR spectrum (KBr): azido, 2035; oxalato, 1575, 1295, 765. UV–Vis spectrum, 516(251), 301(9250), 215(17 250). ^{13}C NMR, CH_2: 47.40(7200), 46.85(3500), 46.15(3500). ^1H NMR, CH_2: broad multiplet, 2.73.

(d) trans-(Azido)(oxalato)bis(ethylenediamine)cobalt(III) dihydrate, trans[$en_2Co(N_3)(C_2O_4)$]·$2H_2O$, abbreviated as trans-$N_3(C_2O_4)$

The preparation and purification of the *trans* isomer are as described above for the *cis* isomer. Ethanol (3.5 ml) is added to the 3 ml solution of the *trans* isomer through a medium porosity fritted glass gas dispersion tube at 5 °C over a period of 1 h. The dark purple solid is collected and air dried. A second crop is obtained by further infusions of ethanol to the filtrate. Yield: 0.15 g. Crystals suitable for X-ray structural determination are obtained by recrystallization from a saturated aqueous solution into which a four-fold volume excess of ethanol is allowed to diffuse at 5 °C over a period of two days. *Anal.* Calc. for $[(C_2N_2H_8)_2Co(N_3)(C_2O_4)]\cdot 2H_2O$: C, 20.87; H, 5.80; N, 28.41; Co, 17.10. Found: C, 20.73; H, 5.85; N, 27.98; Co, 17.07%. IR spectrum (KBr): azido, 2030; oxalato, 1580, 1300, 758. UV–Vis spectrum, 547(246), 313(10 400), 209(17 230). ^{13}C NMR, CH_2: 47.18. ^1H NMR, CH_2: broad singlet, 2.83.

(e) Ammonium cis-bis(ethylenediamine)(sulfito-S)(thiosulfato-S)cobaltate(III)·trihydrate, (NH_4)-cis[$(en)_2Co(SO_3)(S_2O_3)$]·$3H_2O$, abbreviated as cis-$S_2O_3(SO_3)$

Preparation and characterization of the anion and its isolation as the ammonium salt have been previously reported [6]. Crystals of crystallographic quality were obtained by slow diffusion of a five-fold excess of ethanol into a concentrated aqueous solution of the salt at −5 °C over a period of days. Two crystalline modifications were obtained, red–orange needles and dark orange blocks. The needles were separated from the blocks by repeatedly swirling the product in 95% ethanol and decanting the suspended needles. The blocks were rinsed with 95% ethanol and air-dried. *Anal.* Calc. for $NH_4[(C_2N_2H_8)_2Co(SO_3)(S_2O_3)]\cdot 3H_2O$: C, 10.83; H, 5.91; N, 15.86; S, 21.69; Co, 13.29. Found: C, 10.93; H, 5.66; N, 15.72; S, 21.91; Co, 12.93%.

(f) cis-(Azido)(sulfito)bis(ethylenediamine)cobalt(III), cis[$en_2Co(N_3)SO_3$]·$1.5H_2O$, abbreviated cis-$N_3(SO_3)$

The sulfitoazido complex is prepared, following the method of Hughes and McWhinnie [27], by sulfite substitution on the cation, *cis*$[en_2Co(N_3)_2]^+$, *vide infra*. In a typical preparation, 1.0 g *cis*$[en_2Co(N_3)_2]NO_3$ and 0.37 g Na_2SO_3 are dissolved in 45 ml H_2O and warmed to 40 °C for 0.5 h. The mixture is cooled to 0 °C and the dark red product is filtered. Crystals suitable for X-ray structural determination were obtained by recrystallization from aqueous solution. *Anal.* Calc. for $[(C_2N_2H_8)_2Co(N_3)SO_3)]\cdot 1.5H_2O$: C, 14.65; H, 5.84; N, 29.89; S, 9.77; Co, 17.47. Found: C, 14.51; H, 5.84; N, 29.44; S, 9.77; Co, 17.47%. IR spectrum (KBr): azido, 2041; sulfito, 633, 970, 1056, 1072. UV–Vis spectrum, 495(378), 279(15 700), 211(11 700).

(g) cis-(Nitro)(sulfito)bis(ethylenediamine)cobalt(III), cis[$en_2Co(NO_2)SO_3$]·H_2O, abbreviated as cis-$NO_2(SO_3)$

The sulfitonitrito-N complex is prepared, following the method of Klement [28] by sulfite substitution on the cation, *cis*$[en_2Co(NO_2)_2]^+$. In our hands, the reported synthesis [29] of *cis*$[en_2Co(NO_2)_2]NO_3$ results in an irresoluble mixture of isomers. To obtain authentic *cis*$[en_2Co(NO_2)_2]^+$, two mmol $NaNO_2$ and one mmol *cis*$[en_2Co(NO_2)Cl]Cl$ [7] are dissolved in the minimum amount of water at 90 °C and the solution allowed to cool overnight in the dark. Large orange crystals of the *cis*$[en_2Co(NO_2)_2]NO_2$ are filtered and air dried. The isomeric purity of the product was confirmed spectroscopically [30]. To prepare the sulfitonitrito-N complex, 0.30 g *cis*$[en_2Co(NO_2)_2]NO_2$ and 0.18 g Na_2SO_3 are dissolved in 5 ml H_2O and warmed to 50 °C for 1 h with stirring. The mixture is cooled to room temperature and the yellow product is filtered. Crystals suitable for X-ray structural determination were obtained by recrystallization from aqueous solution. *Anal.* Calc. for $[(C_2N_2H_8)_2Co(NO_2)SO_3]\cdot H_2O$: C, 14.87; H, 5.61; N, 21.67; S, 9.93; Co, 17.47. Found: C, 14.87; H, 5.64; N, 21.38; S, 10.14; Co, 17.16%. IR spectrum (KBr): nitrito-N, 1377, 1327, 828; sulfito, 627, 971, 1101, 1120. UV–Vis spectrum, 430(222), 281(17 500), 232(15 900).

(h) cis-Bis(azido)bis(ethylenediamine)cobalt(III) nitrate, cis-[en$_2$Co(N$_3$)$_2$]NO$_3$, abbreviated as cis-(N$_3$)$_2$

The anhydrous salt is prepared by the method of Staples and Tobe [31] and recrystallized from *ca.* 70 °C aqueous solution. **Caution**: this compound flares and burns when heated on a hot-plate. *Anal.* Calc. for $[(C_2N_2H_8)_2Co(N_3)_2]NO_3$: C, 14.77; H, 5.00; N, 47.39; Co, 18.12. Found: C, 14.78; H, 4.96; N, 46.88; Co, 17.17%. IR spectrum (KBr): azido, 2092, 2017; nitrate, 1385, 798. UV–Vis spectrum, 519(316), 303(11 700), 213(25 700).

X-ray Characterizations

Space group determinations

Small single crystals were mounted on glass fibers and precession photographs taken on an Enraf-Nonius Precession Camera. Systematic absences were observed for the $0k0$, k = odd and $h0l$, $h + l$ = odd reflections, indicating a space group, $P2_1/n$, for a monoclinic cell for (NH_4)*cis*$[(en)_2Co(SO_3)(S_2O_3)]\cdot3H_2O$, *cis*$[en_2Co(N_3)SO_3)]\cdot1.5H_2O$ and *trans*-$[en_2Co(NO_2)(C_2O_4)]\cdot2H_2O$. Systematic absences were observed for the $0k0$, k = odd and $h0l$, l = odd reflections, indicating a space group, $P2_1/c$, for a monoclinic cell for *cis*$[en_2Co(NO_2)(SO_3)]\cdot H_2O$ and *cis*-$[en_2Co(N_3)(C_2O_4)]\cdot H_2O$. No systematic absences were observed and a triclinic cell, space group $P\bar{1}$, was assigned for *cis*$[en_2Co(NO_2)(C_2O_4)]\cdot2H_2O$. Systematic absences were observed for the reflections $h + k + l$ = odd, $00l$, $l \neq 4n$ and $hk0$, h = odd, indicating an $I4_1/a$ space group, for a tetragonal cell for *trans*$[en_2Co(N_3)(C_2O_4)]\cdot2H_2O$. Systematic absences are observed for the reflections $0kl$, $k + l$ = odd and $hk0$, h = odd, indicating either a *Pnma* or $Pn2_1a$ space group for an orthorhombic cell for *cis*$[en_2Co(N_3)_2]NO_3$. From the cell volume and the density the number of ion pairs in the unit cell is calculated to be eight. The space group was assumed to be *Pnma*, and successful refinement of the structure confirmed this assumption. Data were collected in the non-standard space group *Pbnm* and transformed to the standard space group *Pnma* by a matrix transformation:

$$\begin{vmatrix} 0 & 0 & 1 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{vmatrix}$$

General

Crystallographic data are given in Table 1. Densities were measured by neutral bouyancy in CHCl$_3$/

TABLE 1. Crystallographic Data for $[(en)_2CoXX']$ Complexes[a]

	cis-NO$_2$(C$_2$O$_4$)· 2H$_2$O	*trans*-NO$_2$(C$_2$O$_4$)· 2H$_2$O	*cis*-N$_3$(C$_2$O$_4$)· H$_2$O	*trans*-N$_3$(C$_2$O$_4$)· 2H$_2$O
Formula	$CoO_8N_5C_6H_{20}$	$CoO_8N_5C_6H_{20}$	$CoO_5N_7C_6H_{18}$	$CoO_6N_7C_6H_{20}$
Formula weight (g/mol)	349	349	327	345
Crystal class	triclinic	monoclinic	monoclinic	tetragonal
Space group	$P\bar{1}$	$P2_1/n$	$P2_1/c$	$I4_1/a$
Color	orange	yellow–orange	red–orange	purple–black
a (Å)	6.925(3)	8.218(2)	8.379(1)	26.684(2)
b (Å)	8.055(3)	15.613(1)	15.548(4)	
c (Å)	12.158(4)	10.694(1)	9.736(3)	7.625(2)
α (°)	80.16(2)			
β (°)	77.87(2)	101.49(1)	97.44(2)	
γ (°)	87.90(2)			
V (Å^3)	653	1344	1258	5429
Z	2	4	4	16
ρ_{calc} (g/cm^3)	1.78	1.73	1.73	1.69
ρ_{exp} (g/cm^3)	1.76	1.74	1.69	1.69
Diffractometer	CAD4[b]	CAD4[c]	CAD4[b]	CAD4[c]
Radiation	Mo Kα	Mo Kα	Mo Kα	Mo Kα
μ (cm^{-1})	13.6	13.2	13.9	13.0
Scan	ω–2h	θ–2θ	ω–2θ	θ–2θ
Scan speed (°/min)	0.78–5.5	1.03–4.12	0.75–5.5	1.03–4.12
Scan range (°)	1.0 + 0.35 tan θ	0.85 + 0.35 tan θ	1.0 + 0.35 tan θ	0.8 + 0.35 tan θ
2θ limit (°)	4–50	4–62	4–50	4–54.9
hkl measured	$+h, \pm k, \pm l$	$+h, +k, \pm l$	$+h, +k, \pm l$	$+h, +k, +l$
No. standard reflections	3	4	3	4
No. independent data	2504	4294	2472	3088
No. data with $\lvert F_o\rvert > 3\sigma(F)$	1942	3717	1330	1704

(continued)

TABLE 1. *(continued)*

	cis-$NO_2(C_2O_4)\cdot$ $2H_2O$	*trans*-$NO_2(C_2O_4)\cdot$ $2H_2O$	*cis*-$N_3(C_2O_4)\cdot$ H_2O	*trans*-$N_3(C_2O_4)\cdot$ $2H_2O$
No. parameters	181	181	173	199
Data/parameter	10.7	20.5	7.7	8.6
Residual *ED*	0.7	0.7	0.6	1.0
R_1 (%)[d]	5.5	3.5	4.3	6.6
R_2 (%)[e]	9.4	5.6	4.8	7.9
	$[cis\text{-}S_2O_3(SO_3)]^-$ $NH_4^+\cdot 3H_2O$	*cis*-$N_3(SO_3)\cdot$ $1.5H_2O$	*cis*-$NO_2(SO_3)\cdot$ $1H_2O$	$[cis\text{-}(N_3)_2]^+$ NO_3^-
Formula	$CoS_3O_9N_5C_4H_{26}$	$CoSO_{4.5}N_7C_4H_{19}$	$CoS_1O_6N_5C_4H_{18}$	$CoO_3N_{11}C_4H_{16}$
Formula weight (g/mol)	443	328	323	325
Crystal class	monoclinic	monoclinic	monoclinic	orthorhombic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/c$	*Pnma*
Color	orange	red	orange	purple
a (Å)	10.094(9)	7.749(1)	6.629(2)	11.903(3)
b (Å)	12.205(12)	10.701(2)	11.429(4)	23.566(6)
c (Å)	13.358(3)	15.101(4)	15.156(4)	8.877(2)
β (°)	90.19(4)	102.80(2)	93.27(2)	
V ($Å^3$)	1645.7	1221.1	1146.4	2490.1
Z	4	4	4	8
ρ_{calc} (g/cm^3)	1.79	1.78	1.87	1.73
ρ_{exp} (g/cm^3)	1.78	1.78	1.86	1.73
Diffractometer	CAD4[b]	CAD4[b]	CAD4[b]	CAD4[b]
Radiation	Mo Kα	Mo Kα	Mo Kα	Mo Kα
μ (cm^{-1})	14.5	15.9	16.9	14.0
Scan	$\omega-2\theta$	$\omega-2\theta$	$\omega-2\theta$	$\omega-2\theta$
Scan speed (°/min)	0.92–3.3	0.92–5.5	1.1–3.3	1.0–3.3
Scan range (°)	1.2 + 0.35 tan θ	0.6 + 0.35 tan θ	1.2 + 0.35 tan θ	0.7 + 0.35 tan θ
2θ limit (°)	4–50	4–50	4–50	4–50
hkl measured	$+h, +k, \pm l$	$+h, +k, \pm l$	$+h, +k, \pm l$	$+h, +k, +l$
No. standard reflections	3	3	3	3
No. independent data	3192	2450	2318	3101
No. data with $\|F_o\| > 3\sigma(F)$	2478	1885	1713	2224
No. parameters	197	171	154	175
Data/parameter	12.6	11.0	11.2	12.7
Residual *ED*	2.2	0.7	0.8	1.5
R_1 (%)	7.6	3.2	3.5	4.8
R_2 (%)	9.2	4.0	4.4	5.9

[a] The number in parentheses is the e.s.d. in the last significant figure. [b] Data were collected by Masood Parvez, Pennsylvania State University. [c] Data were collected by Charles Eigenbrot, University of Notre Dame. [d] $R_1 = [\Sigma(\|F_o\| - \|F_c\|)/\Sigma|F_o|]$. [e] $R_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]$ weights are $1/\sigma$.

$CHBr_3$. The general position of the cobalt atom was determined from a Patterson vector map [32] or by direct methods [33]. The remaining atoms were located from electron density difference maps [32]. Ethylenediamine hydrogen atomic positions were calculated using C–H bond lengths of 0.98 Å, N–H bond lengths of 0.90 Å and bond angles of 109.5° with their thermal parameters assigned as 1.0 $Å^2$ greater than the isotropic equivalent thermal parameter of the atom to which they were attached. Scattering factor curves for Co, O, N and C were taken from Cromer and Mann [34]. Hydrogen scattering facters were taken from Stewart *et al.* [35]. No corrections for anomalous dispersion were made. Non-hydrogen atoms, except as noted below, are described with anisotropic thermal parameters. Hydrogen positions and thermal parameters were not refined. Refinement to convergence using full-matrix least-squares [36] methods on models as described below was followed by calculation of estimated standard deviations [37]. The F_c and F_o values are available, see 'Supplementary Material'.

Specific

(a) cis[$en_2Co(NO_2)(C_2O_4)]\cdot 2H_2O$. No special features.

(b) trans[$en_2Co(NO_2)(C_2O_4)]\cdot 2H_2O$. No special features.

(c) cis[en$_2$Co(N$_3$)(C$_2$O$_4$)]·H$_2$O. Both the occupancy factor and the anisotropic thermal parameters of the oxygen of the water of hydration, OW1, were refined. Even with a refined occupancy of 89%, the isotropic equivalent for the thermal parameters is 9.4 Å^2. The possibility of only partial occupancy of the water molecule is also suggested by the low experimental density, Table 1.

(d) trans[en$_2$Co(N$_3$)(C$_2$O$_4$)]·2H$_2$O. One of the ethylenediamine ligand rings is disordered. Carbons C3 and C4 were assigned an occupancy of 60%, with C3′ and C4′ at 40%. Only the eight hydrogens on ethylenediamine N1–C1–C2–N2 were calculated and included in the calculations.

(e) (NH$_4$)cis[en$_2$Co(S$_2$O$_3$)(SO$_3$)]·3H$_2$O. The ethylenediamine N3–C3–C4–N4 was determined to be disordered in the twist of the carbon atoms C3 and C4. The delta configuration for N3–C3–C4–N4 is assigned 70% occupancy with the lambda configuration N3–C3′–C4′–N4 being assigned 30% occupancy. The final model holds C3, C4, C3′ and C4′ isotropic. The nitrogen of the ammonium cation was distinguished from the three waters of hydration on hydrogen bonding networks and final convergence factors.

(f) cis-[en$_2$Co(N$_3$)(SO$_3$)]·1.5H$_2$O. One and a half waters of hydration were located in the unit cell and determined to be disordered. The $\frac{1}{2}$ water of hydration is located near the center of inversion $0, \frac{1}{2}, 0$. This molecule of water is disordered and the two positions, OW2 and OW2′, are assigned occupancies of $\frac{1}{4}$. The other water of hydration is located at a general position and is also disordered with the two positions, OW1 and OW1′, assigned occupancies of $\frac{1}{2}$ each. The final model held the oxygen atoms OW2 and OW2′ isotropic.

(g) cis-[en$_2$Co(NO$_2$)(SO$_3$)]·H$_2$O. No unusual features.

(h) cis[en$_2$Co(N$_3$)$_2$]NO$_3$. The nitrate anion is located at a special position and is disordered. Two half nitrates, at special positions across the mirror at $y = \frac{1}{4}$, are in the asymmetric unit. Each is disordered. The $\frac{1}{4}$ nitrate consisting of N11 O1 O2 and that consisting of N11 O1′ O2′ form a dihedral angle of 27.5°. The other pair, N12 O3 O4 and N12 O3 O4′ form a dihedral angle of 19.7°. The final model used for refinement held the disordered oxygens O1, O1′, O2, O2′, O4, and O4′ isotropic.

Results and Discussion

Structural Results

Crystal coordinates are given in Table 2. See also 'Supplementary Material'. Bond distances are given

TABLE 2. Crystal Coordinates[a]

Atom	$10^4 \times x$	$10^4 \times y$	$10^4 \times z$
(a) *cis*-[(en)$_2$Co(NO$_2$)(C$_2$O$_4$)]·2H$_2$O			
Co	8771(1)	1879(1)	2132(1)
O1	9897(6)	−320(5)	2365(4)
O2	13031(6)	85(5)	2466(4)
O3	10347(6)	−3602(5)	2695(5)
O4	13442(7)	−3375(5)	2795(5)
O5	11274(8)	1739(7)	60(4)
O6	11483(7)	4032(5)	662(4)
OW1	6574(6)	−2565(6)	3558(4)
OW2	3833(7)	3546(6)	4097(4)
N1	7208(7)	1008(6)	1203(4)
N2	7343(7)	3978(6)	1852(4)
N3	10193(7)	2807(6)	3094(4)
N4	6835(7)	1072(6)	3540(4)
N5	10766(7)	2627(6)	803(4)
C1	6341(8)	2446(7)	526(5)
C2	5651(8)	3686(7)	1315(5)
C3	8986(8)	2721(8)	4263(5)
C4	7761(9)	1140(8)	4518(5)
C5	11621(8)	−805(7)	2470(5)
C6	11847(9)	−2777(7)	2663(5)
(b) *trans*-[(en)$_2$Co(NO$_2$)(C$_2$O$_4$)]·2H$_2$O			
Co	1691(1)	1266(1)	−2338(1)
O1	3779(1)	1053(1)	−1165(1)
O2	5428(2)	2092(1)	−1667(1)
O3	6552(2)	1284(1)	1108(2)
O4	7478(2)	554(1)	−392(1)
O5	−621(2)	1924(1)	−4302(2)
O6	−1623(2)	971(1)	−3258(2)
OW1	6117(2)	3837(1)	−1706(2)
OW2	3794(2)	696(1)	2172(2)
N1	2828(2)	1502(1)	−3742(1)
N2	1743(2)	66(1)	−2820(2)
N3	698(2)	1011(1)	−879(1)
N4	1660(2)	2468(1)	−1814(1)
N5	−452(2)	1404(1)	−3421(2)
C1	3597(2)	689(1)	−4074(2)
C2	2347(2)	−12(1)	−4035(2)
C3	799(2)	1786(1)	−49(2)
C4	511(2)	2552(1)	−918(2)
C5	5143(2)	1458(1)	−1043(2)
C6	6515(2)	1072(1)	−13(2)
(c) *cis*-[(en)$_2$Co(N$_3$)(C$_2$O$_4$)]·H$_2$O			
Co	1576(1)	729(1)	−1873(1)
OW1	4218(9)	−3549(6)	834(9)
O1	−37(5)	−138(2)	−2323(4)
O2	709(9)	−831(5)	−4086(7)
O3	−1687(5)	−1711(3)	−2061(4)
O4	−2392(5)	−1515(3)	−4315(4)
N1	2980(5)	414(3)	−3244(4)
N2	3190(5)	1596(3)	−1278(5)
N3	176(5)	1106(3)	−545(4)
N4	347(5)	1519(3)	−3155(4)
N5	2695(6)	−43(3)	−475(5)
N6	3265(6)	−699(4)	−822(5)
N7	3846(7)	−1335(4)	−1090(6)

(continued)

TABLE 2. *(continued)*

Atom	$10^4 \times x$	$10^4 \times y$	$10^4 \times z$
(c) *cis*-$[(en)_2Co(N_3)(C_2O_4)]\cdot H_2O$			
C1	4620(7)	747(4)	−2777(6)
C2	4411(7)	1641(4)	−2261(7)
C3	−766(7)	1866(4)	−1074(6)
C4	−1158(7)	1742(4)	−2609(6)
C5	−200(7)	−710(4)	−3223(6)
C6	−1567(8)	−1352(3)	−3182(6)
(d) *trans*-$[(en)_2Co(N_3)(C_2O_4)]\cdot 2H_2O$			
Co	8311(1)	617(1)	2363(1)
O1	8399(2)	880(2)	38(6)
O2	8952(2)	1483(2)	361(7)
O3	9028(2)	1262(2)	−3368(7)
O4	8205(2)	1373(2)	−3130(7)
OW1	587(2)	2591(2)	2302(8)
OW2	1974(3)	2544(3)	1456(9)
N1	8574(3)	−8(3)	1456(9)
N2	8993(2)	762(2)	3130(7)
N3	8065(3)	1264(2)	3194(8)
N4	7630(2)	479(3)	1583(9)
N5	8133(1)	293(3)	4543(3)
N6	8416(3)	181(3)	5713(9)
N7	8658(3)	52(3)	6886(10)
C1	9121(4)	35(4)	1340(12)
C2	9301(3)	306(3)	2949(11)
C5	8672(3)	1222(3)	−489(9)
C6	8636(3)	1291(3)	−2552(10)
C3	7482(9)	1261(11)	3340(24)
C3′	7549(13)	1304(13)	2518(48)
C4	7338(9)	970(8)	1690(24)
C4′	7267(13)	815(13)	2368(52)
(e) NH_4-*cis*$[(cn)_2Co(S_2O_3)(SO_3)]\cdot 3H_2O$			
Co	1324(1)	2180.2(9)	−1679.7(8)
S1	2376(2)	3727(2)	−1335(2)
S2	−371(2)	2899(2)	−767(2)
S3	−1443(2)	1694(2)	−82(2)
N1	2060(8)	1405(6)	−522(5)
N2	2935(8)	1650(6)	−2388(5)
N3	640(8)	2878(6)	−2891(5)
N4	336(8)	849(6)	−2142(6)
C1	3166(11)	697(9)	−841(8)
C2	3900(11)	1258(9)	−1658(8)
C3	−469(17)	2209(13)	−3330(11)
C4	−9(15)	1054(13)	−3236(11)
C3′	83(34)	1965(28)	−3531(24)
C4′	−728(33)	1159(27)	−2875(24)
O1	3084(8)	3641(6)	−356(5)
O2	3361(7)	3907(6)	−2137(5)
O3	1454(7)	4670(5)	−1314(5)
O4	−579(8)	1104(7)	591(6)
O5	−1991(9)	973(7)	−838(6)
O6	−2477(8)	2296(6)	442(5)
OW1	6115(9)	2846(7)	−3032(6)
OW2	−1776(8)	4477(7)	−2995(6)
OW3	6032(9)	3565(8)	−1039(6)
NH4	−1171(10)	5605(8)	−1158(7)

(continued)

TABLE 2. *(continued)*

Atom	$10^4 \times x$	$10^4 \times y$	$10^4 \times z$
(f) *cis*-$[(en)_2Co(SO_3)(N_3)\cdot 1.5$			
Co	135.6(6)	−141.7(5)	−1972.1(3)
S1	7.0(13)	1912.4(9)	−2127.5(7)
N1	−1732(4)	−449(3)	−3046(2)
N2	1764(4)	−228(3)	−2796(2)
N3	2084(4)	44(3)	−905(2)
N4	392(5)	−1991(3)	−1718(2)
N5	−1572(4)	−103(3)	−1179(2)
N6	−3031(4)	283(3)	−1476(2)
N7	−4453(5)	654(4)	−1721(3)
C1	−932(6)	−908(4)	−3797(3)
C2	730(6)	−180(4)	−3747(3)
C3	2946(6)	−1184(5)	−675(3)
C4	1515(7)	−2142(4)	−795(3)
O1	−1552(4)	2269(3)	−2842(2)
O2	−96(5)	2510(3)	−1263(2)
O3	1648(4)	2323(3)	−2392(2)
OW1	3299(10)	2540(8)	176(6)
OW1′	2317(14)	3265(11)	246(7)
OW2	434(24)	4698(19)	−116(14)
OW2′	485(28)	4973(22)	−615(15)
(g) *cis*-$[(en)_2Co(SO_3)(NO_2)]\cdot H_2O$			
Co	2816.1(6)	3463.0(3)	2612.3(3)
S1	2239(1)	1767.2(7)	1932.1(6)
N1	1178(4)	2949(2)	3569(2)
N2	3224(4)	4930(2)	3341(2)
N3	4349(4)	4051(2)	1645(2)
N4	480(4)	4187(2)	1976(2)
N5	5227(4)	2803(3)	3188(2)
O1	2686(4)	813(2)	2578(2)
O2	59(4)	1711(2)	1646(2)
O3	3497(4)	1656(2)	1171(2)
O4	6865(4)	2879(3)	2843(2)
O5	5180(4)	2326(3)	3918(2)
OW1	−2171(5)	3103(3)	417(2)
C1	860(6)	3914(3)	4203(2)
C2	2732(6)	4660(3)	4256(2)
C3	2958(6)	4441(3)	899(2)
C4	1178(6)	5011(3)	1302(2)
(h) *cis*-$[(en)_2Co(N_3)_2]NO_3$			
Co	2546.9(2)	877.9(2)	424.7(4)
N1	3561(2)	654(1)	2061(3)
N2	2342(2)	1580(1)	1566(3)
N3	1572(2)	1130(1)	−1214(3)
N4	3779(2)	1209(1)	−771(3)
N5	1249(2)	594(1)	1523(3)
N6	903(2)	119(1)	1479(3)
N7	517(2)	−328(1)	1524(3)
N8	2710(2)	148(1)	−620(3)
N9	3453(2)	−169(1)	−248(3)
N10	4145(3)	−491(1)	60(4)
C1	3772(3)	1145(1)	3078(3)
C2	2707(3)	1488(1)	3144(4)
C3	2266(3)	1276(2)	−2556(4)
C4	3294(3)	1570(1)	−1989(4)

(continued)

TABLE 2. *(continued)*

Atom	$10^4 \times x$	$10^4 \times y$	$10^4 \times z$
(h) *cis*-$[(en)_2Co(N_3)_2]NO_3$			
N11	4970(3)	2500	787(6)
02	5449(5)	2045(3)	1095(7)
02′	5463(6)	2969(3)	482(7)
01	3948(6)	2500	522(8)
01′	3901(8)	2500	959(11)
N12	415(3)	2500	−247(4)
03	6(3)	2037(1)	56(4)
04	1260(9)	2500	−1127(12)
04′	1443(7)	2500	−529(10)

[a] The number in parentheses is e.s.d. in the last significant figure.

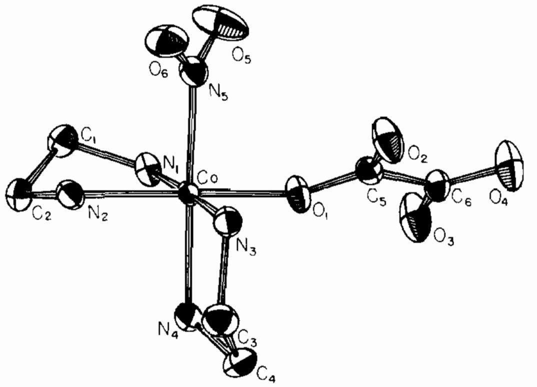

Fig. 1. Structure of the Δδλ-*cis*$[en_2Co(NO_2)(C_2O_4)]$ molecule.

in Table 3 and bond angles are given in Table 4. Computer-drawn models [38] of the complexes with the atoms labeled are given in Figures 1–8, in which the thermal ellipsoids represent 50% probability and hydrogen atoms have been omitted for clarity. The cobalt center of each complex is essentially octahedral. The average ethylenediamine bite angle is 85.7(7)°. In the *cis* complexes, N(1) and N(3) are the nitrogens on the ethylenediamine ligands that are *trans* to each other. In the *trans* complexes, two pairs of nitrogens are *trans* to each other. The average Co–N(en) distance *trans* to another ethylenediamine is 1.950(8) Å.

TABLE 3. Bond Distances (A) for $[(en)_2CoXX']$ Complexes[a]

Bond type	*cis*-$NO_2(C_2O_4)\cdot 2H_2O$	*trans*-$NO_2(C_2O_4)\cdot 2H_2O$	*cis*-$N_3(C_2O_4)\cdot H_2O$	*trans*-$N_3(C_2O_4)\cdot 2H_2O$
Co–N1	1.944(5)	1.956(2)	1.952(5)	1.939(7)
Co–N2	1.943(5)	1.946(2)	1.945(5)	1.951(6)
Co–N3	1.933(5)	1.939(2)	1.945(5)	1.952(6)
Co–N4	1.967(5)	1.961(2)	1.949(5)	1.947(7)
Co–N5	1.916(5)	1.917(2)	1.959(5)	1.933(6)
Co–O1	1.910(4)	1.941(2)	1.919(4)	1.921(5)
N1–C1	1.487(7)	1.488(3)	1.484(7)	1.467(11)
N2–C2	1.499(7)	1.484(3)	1.490(8)	1.475(10)
N3–C3	1.482(7)	1.489(3)	1.476(7)	1.561(25)
N4–C4	1.475(8)	1.480(3)	1.472(8)	1.527(22)
C1–C2	1.499(8)	1.508(4)	1.496(9)	1.504(12)
C3–C4	1.508(9)	1.508(4)	1.501(8)	1.515(42)
C5–O1	1.268(7)	1.273(3)	1.243(7)	1.234(9)
C5–O2	1.230(7)	1.233(3)	1.219(7)	1.213(9)
C5–C6	1.573(7)	1.537(3)	1.524(8)	1.588(10)
C6–O3	1.244(7)	1.245(3)	1.242(7)	1.220(9)
C6–O4	1.219(7)	1.254(3)	1.250(7)	1.250(9)
N5–O5	1.233(7)	1.226(3)		
N5–O6	1.222(6)	1.224(3)		
N5–N6			1.194(7)	1.207(9)
N6–N7			1.147(7)	1.155(9)
N3–C3′				1.476(38)
N4–C4′				1.449(34)
C3′–C4′				1.511(51)
	$[$*cis*-$S_2O_3(SO_3)]^-NH_4^+\cdot 3H_2O$	*cis*-$N_3(SO_3)\cdot 1.5H_2O$	*cis*-$NO_2(SO_3)\cdot 1H_2O$	$[$*cis*-$(N_3)_2]^+NO_3^-$
Co–S1	2.213(3)	2.211(1)	2.218(1)	
Co–S2	2.280(3)			
Co–N1	1.958(8)	1.948(4)	1.951(3)	1.962(2)
Co–N2	1.992(7)	1.960(3)	2.019(3)	1.957(3)

(continued)

TABLE 3. *(continued)*

	$[cis\text{-}S_2O_3(SO_3)]^- NH_4^+ \cdot 3H_2O$	$cis\text{-}N_3(SO_3) \cdot 1.5H_2O$	$cis\text{-}NO_2(SO_3) \cdot 1H_2O$	$[cis\text{-}(N_3)_2]^+ NO_3^-$
Co–N3	1.952(7)	1.960(4)	1.950(3)	1.955(3)
Co–N4	2.003(8)	2.017(3)	1.960(3)	1.973(3)
Co–N5		1.972(3)	1.931(3)	1.945(3)
Co–N8				1.964(3)
N1–C1	1.48(1)	1.492(6)	1.487(5)	1.489(4)
N2–C2	1.46(1)	1.483(5)	1.475(4)	1.484(4)
N3–C3	1.50(2)	1.479(6)	1.486(5)	1.490(4)
N3–C3′	1.51(3)			
N4–C4	1.52(2)	1.479(6)	1.483(5)	1.493(4)
N4–C4′	1.50(3)			
N5–N6		1.194(5)		1.193(3)
N6–N7		1.152(5)		1.153(4)
N8–N9				1.204(4)
N9–N10				1.154(4)
C1–C2	1.49(1)	1.493(6)	1.504(5)	1.503(4)
C3–C4	1.49(2)	1.491(7)	1.507(5)	1.493(5)
C3′–C4′	1.55(5)			
S1–O1	1.493(7)	1.480(3)	1.484(3)	
S1–O2	1.480(6)	1.471(3)	1.486(3)	
S1–O3	1.482(7)	1.481(3)	1.466(3)	
S2–S3	2.044(3)			
S3–O4	1.443(8)			
S3–O5	1.449(8)			
S3–O6	1.457(7)			
N5–O4			1.235(4)	
N5–O5			1.234(4)	
N11–O1				1.238(9)
N11–O1′				1.281(10)
N11–O2				1.244(6)
N11–O2′				1.281(7)
N12–O3				1.223(3)
N12–O4				1.273(10)
N12–O4′				1.249(9)

[a]The number in parentheses is the e.s.d. in the last significant figure.

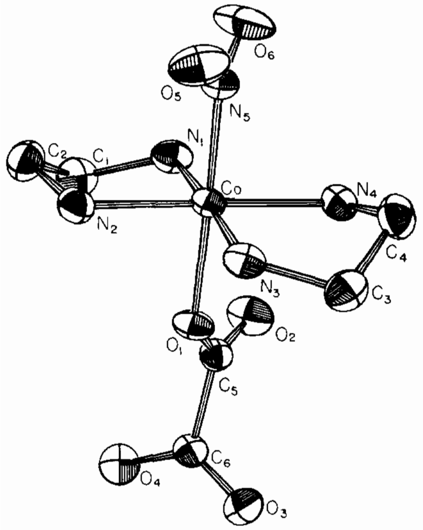

Fig. 2. Structure of the λλ-*trans*[$en_2Co(NO_2)(C_2O_4)$] molecule.

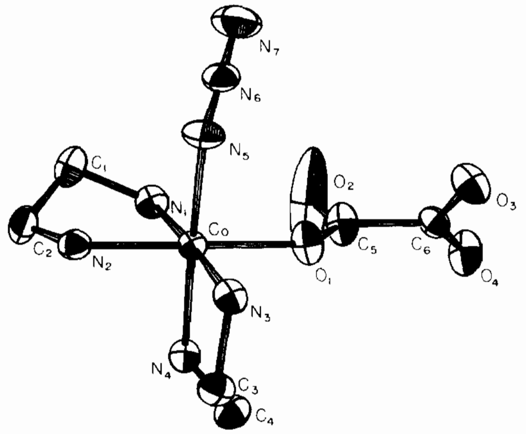

Fig. 3. Structure of the Δδλ-*cis*[$en_2Co(N_3)(C_2O_4)$] molecule.

TABLE 4. Bond Angles (°) for [(en)$_2$CoXX′] Complexes[a]

Angle type	*cis*-$NO_2(C_2O_4)\cdot 2H_2O$	*trans*-$NO_2(C_2O_4)\cdot 2H_2O$	*cis*-$N_3(C_2O_4)\cdot H_2O$	*trans*-$N_3(C_2O_4)\cdot 2H_2O$
O1–Co–N1	87.1(2)	91.9(1)	97.9(2)	86.6(3)
O1–Co–N2	172.7(2)	86.8(1)	175.9(2)	95.1(2)
O1–Co–N3	95.2(2)	84.5(1)	84.1(2)	91.0(3)
O1–Co–N4	85.2(2)	92.1(1)	90.0(2)	84.4(2)
O1–Co–N5	92.9(2)	175.4(1)	89.4(2)	170.7(3)
N1–Co–N2	86.2(2)	86.4(1)	85.4(2)	86.5(3)
N1–Co–N3	176.8(2)	176.4(1)	176.8(2)	177.2(3)
N1–Co–N4	91.7(2)	94.4(1)	92.0(2)	93.7(3)
N1–Co–N5	90.5(2)	92.0(1)	92.6(2)	90.6(3)
N2–Co–N3	91.4(2)	92.9(1)	92.8(2)	92.3(3)
N2–Co–N4	92.1(2)	178.7(1)	92.5(2)	179.4(3)
N2–Co–N5	90.9(2)	90.8(1)	88.1(2)	93.5(3)
N3–Co–N4	86.2(2)	86.3(1)	85.5(2)	87.4(3)
N3–Co–N5	91.6(2)	91.6(1)	89.9(2)	92.0(3)
N4–Co–N5	177.0(2)	90.2(1)	175.4(2)	87.0(3)
C1–N1–Co	109.0(4)	108.4(1)	108.6(3)	108.3(5)
C2–N2–Co	109.3(3)	109.9(1)	110.5(3)	109.1(5)
C3–N3–Co	110.9(3)	109.4(1)	110.5(3)	110.6(11)
C4–N4–Co	108.1(3)	108.4(1)	108.9(3)	107.3(8)
N1–C1–C2	106.3(5)	106.7(2)	106.4(5)	107.8(7)
N2–C2–C1	107.1(4)	108.4(2)	107.0(5)	107.2(7)
N3–C3–C4	107.1(5)	107.2(2)	106.4(5)	101.3(14)
N4–C4–C3	108.4(5)	106.6(2)	107.6(5)	110.6(15)
C5–O1–Co	131.5(4)	128.9(2)	132.3(4)	130.0(5)
O1–C5–Co	127.2(5)	126.9(2)	125.0(6)	128.1(7)
O1–C5–C6	113.0(5)	112.5(2)	117.7(5)	111.9(7)
O2–C5–C6	119.8(5)	120.6(2)	117.1(6)	120.0(7)
C5–C6–O3	116.4(5)	117.3(2)	117.6(6)	116.4(7)
C5–C6–O4	118.2(5)	116.2(2)	116.2(5)	115.1(7)
O3–C6–O4	125.4(5)	126.2(2)	125.9(6)	128.5(7)
O5–N5–Co	120.8(4)	119.4(2)		
O6–N5–Co	119.8(4)	120.3(2)		
O5–N5–O6	119.4(5)	120.2(2)		
N6–N5–Co			120.0(4)	126.3(6)
N7–N6–N5			176.7(6)	174.8(9)
C3′–N3–Co				105.3(14)
C4′–N4–Co				112.3(17)
N3–C3′–C4				115.4(26)
N4–C4′–C3′				103.5(22)
	[*cis*-$S_2O_3(SO_3)]^-NH_4^+\cdot 3H_2O$	*cis*-$N_3(SO_3)\cdot 1.5H_2O$	*cis*-$NO_2(SO_3)\cdot H_2O$	[*cis*-$(N_3)_2]^+NO_3^-$
S2–Co–S1	85.5(1)			
S2–Co–N1	92.7(2)			
S2–Co–N2	173.9(2)			
S2–Co–N3	90.6(2)			
S2–Co–N4	95.9(2)			
S1–Co–N1	93.9(3)	94.1(1)	89.7(1)	
S1–Co–N2	89.1(2)	90.0(1)	174.1(1)	
S1–Co–N3	88.2(2)	89.7(1)	92.0(1)	
S1–Co–N4	173.7(2)	174.8(1)	91.7(1)	
S1–Co–N5		91.3(1)	89.2(1)	
N1–Co–N2	84.8(3)	85.9(1)	84.6(1)	85.3(1)
N1–Co–N3	176.2(3)	175.7(1)	176.7(1)	177.5(1)
N1–Co–N4	92.2(3)	90.9(1)	92.0(1)	92.7(1)
N1–Co–N5		92.0(1)	91.6(1)	91.4(1)
N1–Co–N8				93.1(1)
N2–Co–N3	92.0(3)	92.3(1)	93.8(1–	93.1(1)
N2–Co–N4	89.8(3)	91.4(1)	89.8(1)	92.1(1)

(continued)

TABLE 4. *(continued)*

	$[cis\text{-}S_2O_3(SO_3)]^-NH_4^+\cdot 3H_2O$	$cis\text{-}N_3(SO_3)\cdot 1.5H_2O$	$cis\text{-}NO_2(SO_3)\cdot H_2O$	$[cis\text{-}(N_3)_2]^+NO_3^-$
N2–Co–N5		177.5(1)	89.7(1)	86.0(1)
N2–Co–N8				176.6(1)
N3–Co–N4	85.6(3)	85.3(1)	85.2(1)	85.3(1)
N3–Co–N5		89.8(1)	91.2(1)	90.4(1)
N3–Co–N8				88.4(1)
N4–Co–N5		87.5(1)	176.3(1)	175.3(1)
N4–Co–N8				91.0(1)
N5–Co–N8				90.9(1)
Co–N1–C1	109.9(6)	109.4(3)	111.3(2)	110.1(2)
Co–N2–C2	109.5(5)	109.1(2)	108.1(2)	109.2(2)
Co–N3–C3	110.3(7)	109.2(3)	110.4(2)	109.7(2)
Co–N4–C4	106.0(7)	107.4(3)	109.8(2)	109.1(2)
Co–N5–N6		119.1(3)		125.4(2)
Co–N8–N9				119.1(2)
N5–N6–N7		176.7(4)		174.9(3)
N8–N9–N10				176.8(3)
N1–C1–C2	108.7(8)	106.8(3)	107.9(3)	107.4(2)
N2–C2–C1	108.0(9)	107.8(3)	107.1(3)	106.7(2)
N3–C3–C4	104.5(12)	107.3(3)	106.7(3)	106.9(3)
N4–C4–C3	107.8(11)	107.8(4)	106.6(3)	107.2(2)
Co–N3–C3′	106.1(13)			
Co–N4–C4′	110.6(13)			
N3–C3′–C4′	110.0(23)			
N4–C4′–C3′	98.7(23)			
Co–S1–O1	110.5(3)	110.4(1)	108.2(1)	
Co–S1–O2	107.4(3)	110.1(1)	108.2(1)	
Co–S1–O3	111.5(3)	107.6(1)	110.5(1)	
O1–S1–O2	108.9(5)	109.8(2)	108.4(2)	
O1–S1–O3	109.7(4)	109.7(2)	110.8(2)	
O2–S1–O3	108.8(4)	109.2(2)	110.8(2)	
O4–S3–O5	111.1(5)			
O4–S3–O6	112.6(4)			
O5–S3–O6	111.7(5)			
Co–S2–S3	111.3(1)			
S2–S3–O4	108.5(3)			
S2–S3–O5	109.1(3)			
S2–S3–O6	103.6(3)			
Co–N5–O4			120.4(2)	
Co–N5–O5			121.0(2)	
O4–N5–O5			118.6(3)	

[a]The number in parentheses is the e.s.d. in the last significant figure.

Hydrogen Bonding Networks

Waters of hydration, ethylenediamine ligands and an ammonium cation can potentially form hydrogen bonds with oxalato, sulfito, thiosulfato and nitro ligands, as well as each other. Intramolecular and intermolecular hydrogen bonds may be the decisive forces controlling the final conformation of these molecules. Potential intermolecular hydrogen bonds are listed in Table 5.

Conformations

Bis-ethylenediamine complexes form chiral complexes with possible conformations $\Delta\delta\delta$, $\Delta\delta\lambda$, $\Delta\lambda\delta$, $\Delta\lambda\lambda$, $\Lambda\delta\delta$, $\Lambda\delta\lambda$, $\Lambda\lambda\delta$, and $\Lambda\lambda\lambda$. Each of the structures reported here crystallized in a centric space group requiring an equal ratio of the enantiomeric pairs in the solid state. The specific enantiomeric forms resulting from the crystal coordinates in Table 2 and pictured in Figs. 1–8 are identified in the figure captions. Disorder of an ethylenediamine ligand makes the assignment of configuration ambiguous in *trans*-$N_3(C_2O_4)$ and *cis*-$S_2O_3(SO_3)$.

Azido Ligands

Five independent azido ligands are reported here. The average terminal N–N bond distance is 1.152(3) Å, which is 0.046 Å shorter than the average interior N–N bond distance of 1.198(7) Å. The average Co–N–N angle is 122(4)° and the average N–N–N angle is 176(1)°. These geometries

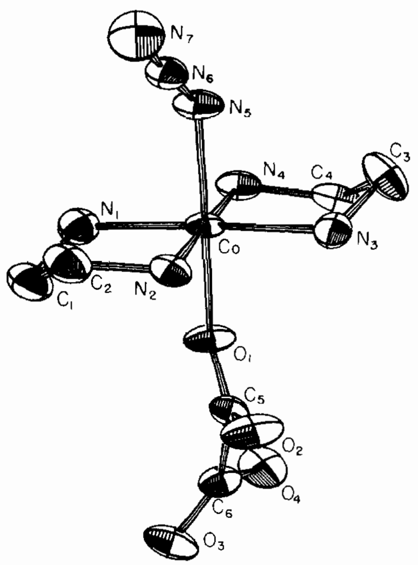

Fig. 4. Structure of the λδ-*trans*[en$_2$Co(N$_3$)(C$_2$O$_4$)] molecule.

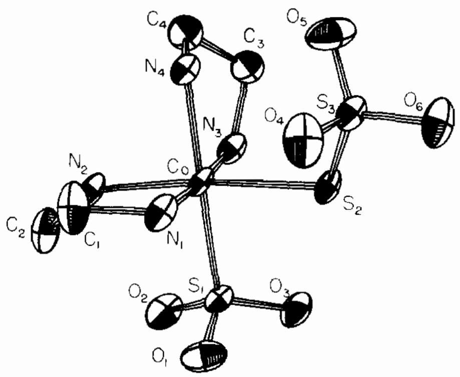

Fig. 5. Structure of the Δλδ-*cis*[en$_2$Co(S$_2$O$_3$)(SO$_3$)]$^-$ anion.

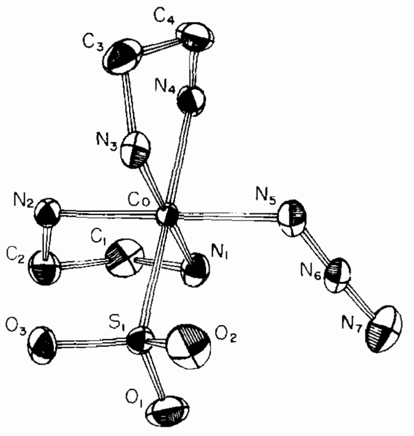

Fig. 6. Structure of the Λδδ-*cis*[en$_2$Co(N$_3$)(SO$_3$)] molecule.

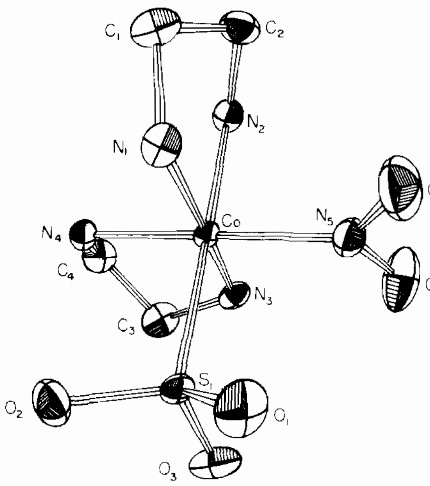

Fig. 7. Structure of the Λδλ-*cis*[en$_2$Co(NO$_2$)(SO$_3$)] molecule.

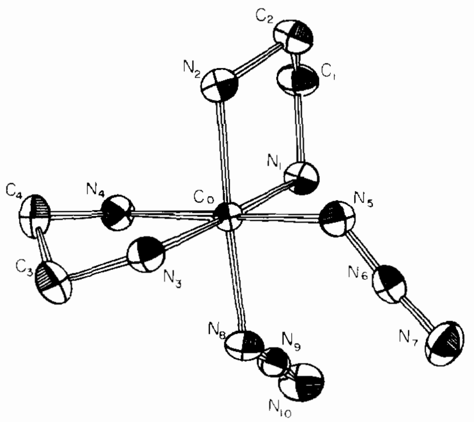

Fig. 8. Structure of the Δλδ-*cis*[en$_2$Co(N$_3$)$_2$]$^+$ cation.

are consistent with those previously observed for monodentate, non-bridging azido ligands [11,20]. The anomalous report [19] of terminal N–N bond lengths longer than interior N–N bond lengths led us to redetermine the structure of *cis*-(N$_3$)$_2$.

Nitro Ligands

Three independent nitro ligands, nitrito-N, are reported here. The average N–O bond distance is 1.229(6) Å. The average O–N–O bond angle is 119.4(8)°. The plane of the nitro group forms a dihedral angle with a plane defined by N1, N3, N5 and the atom *trans* to N5 of 2.9° in *cis*-NO$_2$(SO$_3$), 33.6° in *trans*-NO$_2$(C$_2$O$_4$) and 42.1° in *cis*-NO$_2$-(C$_2$O$_4$).

Sulfito and Thiosulfato Ligands

Three independent sulfito ligands and a thiosulfato ligand are reported here. Each is S-bonded to the cobalt and is tetrahedral about the central

TABLE 5. Possible Hydrogen Bonds in $[(\text{en})_2\text{CoXX}']$ Complexes

H bond	Distance (Å)	Transformed by	Linkage	Angle (°)
(a) *cis*-$[\text{en}_2\text{Co}(\text{NO}_2)(\text{C}_2\text{O}_4)]\cdot 2\text{H}_2\text{O}$				
OW1...O4	2.67	$x-1, y, z$	O4–OW1–O3	122.2
OW1...O3	2.76	x, y, z	O4–OW1–N4	112.5
OW1...N4	2.94	x, y, z	O4–OW1–OW2	112.8
OW1...OW2	2.78	$x+1, y, z+1$	O3–OW1–N4	106.1
OW2...O4	2.74	$x-1, y+1, z$	O3–OW1–OW2	103.4
OW2...N4	2.88	x, y, z	N4–OW1–OW2	96.5
O2...N3	2.98	x, y, z	OW1–OW2–O4	131.6
O2...N1	3.03	$x+1, y, z$	OW1–OW2–N4	94.1
O3...N3	2.85	$x, y-1, z$	O4–OW2–N4	125.8
			OW2–N4–OW1	131.4
(b) *trans*-$[\text{en}_2\text{Co}(\text{NO}_2)(\text{C}_2\text{O}_4)]\cdot 2\text{H}_2\text{O}$				
OW1...O2	2.78	x, y, z	O2–OW1–N2	118.3
OW1...N2	3.00	$\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}+z$	O2–OW1–OW2	116.1
OW1...OW2	2.80	$\frac{1}{2}+x, \frac{1}{2}-y, z-\frac{1}{2}$	N2–OW1–OW2	114.6
OW2...O3	2.88	x, y, z	OW1–OW2–O3	146.3
OW2...O4	2.78	$\frac{1}{2}-x, y-\frac{1}{2}, \frac{1}{2}+z$	OW1–OW2–O4	104.8
			O3–OW2–O4	99.9
(c) *cis*-$[\text{en}_2\text{Co}(\text{N}_3)(\text{C}_2\text{O}_4)]\cdot \text{H}_2\text{O}$				
O2...N4	2.92	$-x, -y, -z-1$	N4–O3–N3	97.1
O3...N4	2.97	$-x, -\frac{1}{2}+y, -\frac{1}{2}-z$	N1–O4–N2	133.9
O3...N3	2.84	$-x, -y, -z$	N1–O4–OW1	87.5
O4...N2	3.10	$-x, -\frac{1}{2}+y, -\frac{1}{2}-z$	N2–O4–OW1	77.5
O4...N1	2.92	$-x, -y, -z-1$	O4–OW1–N7	106.2
O4...OW1	2.86	$x-1, -\frac{1}{2}-y, -\frac{1}{2}+z$		
OW1...N7	3.10	$x, -\frac{1}{2}-y, \frac{1}{2}+z$		
(d) *trans*-$[\text{en}_2\text{Co}(\text{N}_3)(\text{C}_2\text{O}_4)]\cdot \text{H}_2\text{O}$				
OW1...O2	2.76	$1-x, \frac{1}{2}-y, \frac{1}{4}-z$	O2–OW1–O4	109.0
OW1...O4	3.05	$y, -x+1, -z$	O2–OW1–N4	99.9
OW1...N4	3.03	$y, -x+1, -z$	O4–OW1–N4	97.6
OW2...O4	2.86	$y, -x+1, -z$	O4–OW2–OW2	100.7
OW2...OW2	2.76	$\frac{1}{2}-y, x-1, -\frac{1}{4}+z$	O4–OW2–OW2	109.1
OW2...OW2	2.76	$y, \frac{1}{2}-x, \frac{1}{4}+z$	OW2–OW2–OW2	118.5
O3...N2	2.99	$x, y, z-1$		
O3...N1	2.99	$1+y, 1-x, -z$		
O4...N3	2.84	$x, y, z-1$		
(e) (NH_4)*cis*-$[\text{en}_2\text{Co}(\text{S}_2\text{O}_3)(\text{SO}_3)]\cdot 3\text{H}_2\text{O}$				
NH4...OW2	2.88	x, y, z	OW2–NH4–O3	86.6
NH4...O3	2.89	x, y, z	OW2–NH4–OW1	97.8
NH4...OW1	2.94	$\frac{1}{2}-x, \frac{1}{2}+y, -z-\frac{1}{2}$	OW2–NH4–O1	126.7
NH4...O1	2.95	$-x, 1-y, -z$	O3–NH4–OW1	108.7
OW1...OW3	2.80	x, y, z	O3–NH4–O1	140.8

(continued)

TABLE 5. *(continued)*

H bond	Distance (Å)	Transformed by	Linkage	Angle (°)
OW1...OW2	2.91	$x+1, y, z$	OW1–NH4–O1	88.6
OW1...O4	2.82	$\frac{1}{2}-x, \frac{1}{2}+y, -\frac{1}{2}-z$	OW2–OW1–OW3	78.2
OW2...O5	2.70	$-\frac{1}{2}-x, \frac{1}{2}+y, -\frac{1}{2}-z$	OW2–OW1–O4	98.2
OW3...O6	2.93	$x+1, y, z$	OW3–OW1–O4	117.2
			OW1–OW2–O5	96.7
			OW1–OW3–O6	117.4
(f) *cis*-[$en_2Co(N_3)(SO_3)$]·$1.5H_2O$				
O2...OW1	3.01	x, y, z	O2–OW1–O1	124.5
O2...OW1′	2.73	x, y, z	O2–OW1′–O1	140.9
O2...OW2	2.89	x, y, z		
O2...OW2′	2.81	x, y, z		
O1...OW1	2.97	$\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$		
O1...OW1′	2.89	$\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$		
(g) *cis*-[$en_2Co(NO_2)(SO_3)$]·H_2O				
OW...O2	2.81	x, y, z	O2–OW–O5	135.5
OW...O5	2.83	$x-1, \frac{1}{2}-y, z-\frac{1}{2}$		
(h) *cis*-[$en_2Co(N_3)_2$]·NO_3				
O1...N1	3.03	x, y, z	N1–O1–N1	91.1
O1...N1	3.03	$x, \frac{1}{2}-y, z$	N1–O1′–N1	96.6
O1′...N1	2.90	x, y, z	N1–O4′–N1	90.5
O1′...N1	2.90	$x, \frac{1}{2}-y, z$		
O2′...N3	3.00	$x, \frac{1}{2}-y, z$		
O3...N4	3.05	x, y, z		
O4′...N1	3.05	x, y, z		
O4′...N1	3.05	$x, \frac{1}{2}-y, z$		

sulfur. The average sulfito S–O bond length is 1.480(8) Å, and the average O–S–O angle is 109.6(8)°. The average S–O bond length in the thiosulfato is 1.450(7) Å and the average S–S–O angle is 107(3)°. These values are consistent with reported values [6, 13, 39] and reflect significant S–O π bonding [40].

Oxalato Ligands

Four monodentate oxalato complexes are reported. The average C–O bond distance is 1.24(2) Å. The dihedral angle between the planes of the two carboxylate groups is 3.5° in *cis*-$NO_2(C_2O_4)$, 50.8° in *cis*-$N_3(C_2O_4)$, 56.1° in *trans*-$N_3(C_2O_4)$ and 83.7° in *cis*-$NO_2(C_2O_4)$. The strong hydrogen bonds formed between the waters of hydration and the oxalato oxygens apparently serve to orient the ligands.

Structural trans Effects

The *STE* calculated for the six *cis* complexes are given in Table 6. The *STE*s for SO_3^{2-} of 0.063(7) Å in *cis*-$(N_3)SO_3$ and 0.068(4) Å in *cis*-$(NO_2)SO_3$ are the largest observed in bis(ethylenediamine)-cobalt(III) complexes, but are smaller than the 0.089(4) Å observed in $(NH_3)_5CoSO_3$ [15]. The *STE* of 0.047(9) Å for the sulfito in *cis*-$S_2O_3(SO_3)$ is similar to that [0.050(8) Å] observed in *cis*-[$(en)_2Co(SO_3)_2^-$] [13]. The *STE* due to $S_2O_3^{2-}$ [0.036(9) Å] in *cis*-$S_2O_3(SO_3)$ is the same as that [0.03(1) Å] observed in [$(en)_2Co(NO_2)(S_2O_3)$] [6].

Nitro ligands exert a moderate *STE* consistent with their known labilizing effect [7, 41]. The *STE* [0.028(7) Å] in *cis*-$NO_2(C_2O_4)$ is similar to those [0.02–0.03 Å] found in other nitro bis(ethylenediamine)cobalt(III) complexes [6, 8, 9, 41, 42]. The *STE* of 0.009(4) Å in *cis*-$NO_2(SO_3)$ is anomalously

TABLE 6. Structural *trans* Effects for *cis*-$(en)_2CoXX'$ Complexes

Ligand	Complex	*STE* (Å)	Average (Å)
SO_3^{2-}	*cis*-$NO_2(SO_3)$	0.068(4)	
	cis-$N_3(SO_3)$	0.063(7)	
	cis-$S_2O_3(SO_3)$	0.047(9)	0.059(7)
S-$S_2O_3^{2-}$	*cis*-$S_2O_3(SO_3)$	0.036(9)	
NO_2^-	*cis*-$NO_2(SO_3)$	0.009(4)	
	cis-$NO_3(C_2O_4)$	0.028(7)	0.019(10)
N_3^-	*cis*-$N_3(C_2O_4)$	0.000(5)	
	cis-$(N_3)_2$	−0.002(5)	
	cis-$(N_3)_2$	0.015(5)	
	cis-$N_3(SO_3)$	0.006(7)	0.005(6)
O-$OC(O)CO_2^{2-}$	*cis*-$NO_2(C_2O_4)$	0.004(7)	
(oxalato)	*cis*-$N_3(C_2O_4)$	−0.004(5)	0.000(6)

low, but is consistent with the apparent thermal stability of this complex [24, 28].

Neither azido nor oxalato ligands appears to exert any significant structural effect on the Co–N(en) bond *trans* to them. This lack of a *STE* for azido ligands is consistent with the absence of a kinetic *trans* effect in the spontaneous aquation of $[Co(en)_2N_3Cl]^+$ [12].

Supplementary Material

Calculated and observed structure factors in Supplemental Tables Ia–h, thermal parameters in Supplemental Tables IIa–h, and calculated positions of hydrogens in Supplemental Tables IIIa–h are available from the authors on request.

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