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The Crystal and Molecular Structure of an Isomer of Ammine(diethylenetriamine)oxalatocobalt(III) Nitrate

M. CLAIRE COULDWELL, D. A. HOUSE and B. R. PENFOLD
Department of Chemistry, University of Canterbury, Christchurch, New Zealand
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The crystal and molecular structure of one of the four possible isomers of ammine(diethylenetriamine) oxalatocobalt(III) nitrate has been determined from three-dimensional X-ray diffraction data collected on a four-circle diffractometer, using Mo-K_α radiation. The compound crystallises in space group Cc with $a = 7.72$, $b = 12.21$, $c = 14.88$ Å, $\beta = 121.3°$, and $Z = 4$. The structure was solved by conventional Patterson and Fourier techniques and full matrix least squares refinement of 878 observed reflections $[(F_o^2 > 3\sigma(F_o^2)]$ gave a final discrepancy factor of 0.074. The complex has a distorted octahedral configuration with the nitrogen atoms of the dien ligand in the same coordination plane as the Co, and the proton on the secondary nitrogen atom being directed toward the coordinated ammonia ligand.

Introduction

Two of the four possible isomers of the Co(ox)(NH_3)(dien)$^+$ ion have been isolated.[1,2,3] As the geometry of these were of interest to us in order to interpret the stereochemistry of the acid bydrolysis of *trans*-$CoCl_2$(NH_3)(dien)$^+$,[1,2] X-ray crystallographic studies have been undertaken. Unfortunately, the poor crystal quality of one of the isomers has thwarted a complete investigation of this form, but we report here the results of our preliminary investigations, and the full structure analysis of the second form.

Experimental

The preparation of the isomers is outlined in the following reaction schemes:[2]

$$\text{(A) } CoCl_3(dien) \xrightarrow{ox} CoCl(ox)(dien) \xrightarrow{NH_3} Co(ox)(NH_3)(dien)^+$$

$$\text{(B) } Co(NO_2)_3(dien) \xrightarrow{HCl} Co(Cl)(NO_2)_2(dien) \xrightarrow{NH_3} Co(NO_2)_2(NH_3)(dien)^+ \xrightarrow{HCl} trans\text{-}CoCl_2(NH_3)(dien)^+ \xrightarrow{ox} Co(ox)(NH_3)(dien)^+$$

For ir. comparisons, the complexes were isolated as the ClO_4^- or I^- salts, but for both isomers, the crystals were of poor quality. Suitable crystals for X-ray analysis were obtained as the nitrate salt of the isomer from method A and preliminary investigations using the PF_6 salt of the other isomer were carried out.

[Co(ox)(NH_3)(dien)]NO_3 and [Co(ox)(NH_3)(dien)] PF_6 both form red crystals which are stable to X-rays. Precession photographs, using Mo-*Kα* and Cu-*Kα* radiation were used to determine the crystal symmetry. Unit cell dimensions were obtained at 23° C by a least squares procedure using the setting angles of 12 reflections on the four-circle diffractometer.[4] Densities were obtained by flotation in diiodomethane–carbon tetrachloride solution.

Crystal Data

[Co(ox)(NH_3)(dien)]NO_3, $CoN_5C_6H_{16}O_7$; formula weight 329.2; monoclinic with $a = 7.717(6)$, $b = 12.206(8)$, $c = 14.875(8)$ Å, $\beta = 121.25(4)°$, $V = 1197.9$ Å^3: $D_{obs} = 1.83(5)$g cm^{-3}: $Z = 4$; $D_{calc} = 1.92$ g cm^{-3}; μ(Mo-K_α) = 15.35 cm^{-1}. Throughout this section, numbers in parenthesis are estimated standard deviations in the least significant digit, usually derived from the inverse matrix in non-linear least squares calculations. Unit cell parameters assume λ(Mo-K_α) = 0.7107Å.

Two space groups, *Cc* (non-centrosymmetric) and *C*2/*c* (centrosymmetric) were consistent with the observed conditions limiting possible reflections ($h\ k\ l$, $h + k = 2n$; $h\ 0\ l$, $l = 2n$). The centrosymmetric space group would impose exact symmetry 2 or $\bar{1}$ on the cation. As no such molecular symmetry appeared possible the non-centrosymmetric space group was chosen.

[Co(ox)(NH_3)(dien)]PF_6, $CoN_4C_6H_{16}O_4PF_6$; formula weight 412.1; orthorhombic with $a = 17.33(2)$, $b = 7.737(7)$, $c = 10.986(9)$, $V = 1473.3$ Å^3: $D_{obs} = 1.89(1)$ g cm^{-3}; $Z = 4$, $D_{calc} = 1.90$ g cm^{-3}; μ(Mo-K_α) = 14.47. Unit cell parameters assume λ(Mo-K_α) = 0.7107 Å.

The conditions limiting possible reflections ($h00$, $h = 2n$, $0k0$, $k = 2n$, $00l$, $l = 2n$) uniquely indicate space group $P2_12_12_1$. The crystal showed bad mosaicity, and streaking along reciprocal lattice rows indicate disordering.

X-ray Data Collection and Reduction for [Co(ox)(NH$_3$)(dien)]NO$_3$

Diffraction data were collected from a well-formed crystal of irregular habit and average diameter 0.5 mm; the ten boundary faces were ($\bar{1}10$), ($\bar{1}\bar{1}0$), (110), ($1\bar{1}0$), ($0\bar{2}\bar{1}$), (021), ($02\bar{1}$), ($0\bar{2}1$), ($\bar{1}12$) and ($1\bar{1}\bar{2}$) and the necessary measurements were made to enable accurate absorption corrections to be applied.

The crystal was mounted in a random orientation on a Hilger and Watts computer controlled four-circle diffractometer. Its orientation was precisely specified in the same least squares procedure used for determining unit cell parameters.[4] The mosaicity of the crystal was examined by means of open-counter ω-scans at a take-off angle of 3°. The width at half-height for a typical strong, low-angle reflection was 0.18°.

The intensity data were collected with Zr filtered Mo-K_α radiation. The circular receiving aperture, positioned 23 cm from the crystal, was of diameter 5 mm. Data were collected by the Θ–2Θ scan technique to a 2Θ limit of 40°. A symmetric scan range of 1.80° in 2Θ, centred on the calculated peak position, was composed of 90 steps each of 0.65 second duration. Stationary-crystal, stationary-counter background counts of 15 sec were measured at each end of the scan range. For several of the most intense reflections it was necessary to reduce the count rate below 8000 counts per sec. by insertion of copper foil attenuators of known absorbing power.

The intensities of three reflections which were monitored at regular intervals showed only the deviations from the mean predicted by counting statistics. Crystal transmission factors were calculated and applied[5] using Gaussian integration (4^3 grid points) and ranged from 0.57 to 0.65.

Solution and Refinement of the Crystal Structure

The structure has been successfully solved and refined in space group *Cc*. The unit cell origin was initially fixed by assigning the value zero to both the x and z coordinates of the cobalt atom. Its y coordinate was then determined from a three-dimensional Patterson synthesis.

In the ensuing least squares refinement all data for which $F_o^2 \geq 3\sigma(F_o^2)$ were used. Refinement was based on F and the function $\Sigma w(|F_o|-|F_c|)^2$ was minimised. The weights, w, were taken as $4F_o^2/\sigma^2(F_o^2)$. $|F_o|$ and $|F_c|$ are the observed and calculated structure factor amplitudes. The atomic scattering factors for hydrogen were taken from Stewart, Davidson and Simpson[6] and those for all other atoms and ions from the usual tabulation.[7] The effects of anomalous dispersion from the cobalt atom only were included in F_c;[8] values of $\Delta f'$ and $\Delta f''$ for Co^{3+} were taken from the International Tables.[7] Preliminary least squares adjustment of the y coordinate, in which the cobalt atom was assigned an isotropic vibrational parameter, gave agreement factors $R_1 = 0.388$ and $R_2 = 0.444$ where $R_1 = \Sigma|\,|F_o|-|F_c|\,|/\Sigma|F_o|$ and R_2 (the weighted R-factor) $= [\Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2]^{1/2}$.

Subsequent difference Fourier syntheses and least squares refinements revealed the positions of all O, N and C atoms of the cation as well as the N and O atoms of the anion. In the final least squares cycles, the Co atom was assumed to be vibrating anisotropically and was assigned six vibrational parameters while the remaining eighteen atoms were each assigned a single isotropic parameter. This refinement, using 878 data which had $F^2 \geq 3\sigma(F^2)$, converged to $R_1 = 0.078$ and $R_2 = 0.109$.

The sixteen hydrogen atoms of the cation were then included in their calculated positions (d(N–H) = 0.99 Å, d(C–H) = 1.00 Å, B = 5.0 Å^2); and further least squares cycles in which the hydrogen parameters were not varied converged with $R_1 = 0.074$ and $R_2 = 0.104$. No further significant decrease in R_1 or R_2 resulted from the application of corrections for crystal absorption followed by further refinement.

Apart from six low angle reflections, average values of the minimised function obtained after the last cycle of refinement show little systematic dependence on $|F_o|$ or on $\lambda^{-1}\sin\Theta$ which indicated that the weighting scheme is reasonable. A final difference Fourier synthesis contained residual peaks of height up to 1.3 e Å^{-3} around the oxygen and nitrogen atoms of the anion although the electron density does not rise elsewhere above 0.6 e Å^{-3} or one fifth the height of the last carbon atom located by this technique. The residual peaks suggested some anisotropic motion of the light atoms but no anisotropic refinement was attempted for them since such expensive calculations were not expected to reveal any further points of chemical interest.[9]

Structure factor calculations for the 62 reflections having $F_o^2 < 3\sigma(F_o^2)$ revealed no anomalies.

The positional and vibrational parameters and their e.s.d.'s obtained from the final cycle of least squares refinement are listed in Table I. Table II contains the final values of $|F_o|$ and $|F_c|$ for the 878 reflections which were used in the refinement. There is no evidence for secondary extinction and no corrections were made.

Description of the Crystal Structure

The structure consists of monomeric Co(ox)(NH$_3$)(dien)$^+$ units packed with well separated nitrate anions, the shortest interionic distance being the N(1)–O(7) separation of 3.00 Å.

Description of the Cation

Figure 1 shows a perspective view of the Co(ox)(NH$_3$)(dien)$^+$ cation and indicates the atom number-

TABLE I. Positional and Thermal Parameters for [Co(ox)(NH$_3$)(dien)]NO$_3$.

Atom	x	y	z	B Å^2
Co	0.0000	0.0189(1)	0.0000	
O(1)	–0.197(2)	–0.074(1)	0.0034(9)	2.5(2)
O(2)	–0.164(2)	0.137(1)	0.0012(9)	1.9(2)
O(3)	–0.469(3)	–0.061(1)	0.016(1)	4.9(3)
O(4)	–0.449(2)	0.163(1)	–0.001(1)	3.6(3)
O(5)	0.271(4)	0.222(2)	0.263(2)	7.7(5)
O(6)	0.517(4)	0.168(2)	0.266(2)	7.6(5)
O(7)	0.483(4)	0.331(2)	0.228(2)	8.9(6)
N(1)	–0.141(2)	0.031(1)	–0.155(1)	1.6(3)
N(2)	0.156(2)	–0.108(1)	0.002(1)	2.2(2)
N(3)	0.190(2)	0.123(1)	0.003(1)	1.8(3)
N(4)	0.168(3)	0.028(1)	0.153(2)	2.7(4)
N(5)	0.427(2)	0.248(1)	0.252(1)	2.3(2)
C(1)	–0.026(3)	0.101(2)	–0.183(1)	3.0(3)
C(2)	0.081(2)	0.184(1)	–0.101(1)	2.0(3)
C(3)	0.277(2)	0.186(1)	0.097(1)	2.3(3)
C(4)	0.342(2)	0.102(1)	0.183(1)	2.6(3)
C(5)	–0.340(3)	–0.023(1)	0.002(1)	2.9(3)
C(6)	–0.314(2)	0.105(1)	–0.001(1)	1.8(2)

Anisotropic Thermal Parameters (Å^2) for the Cobalt Atom

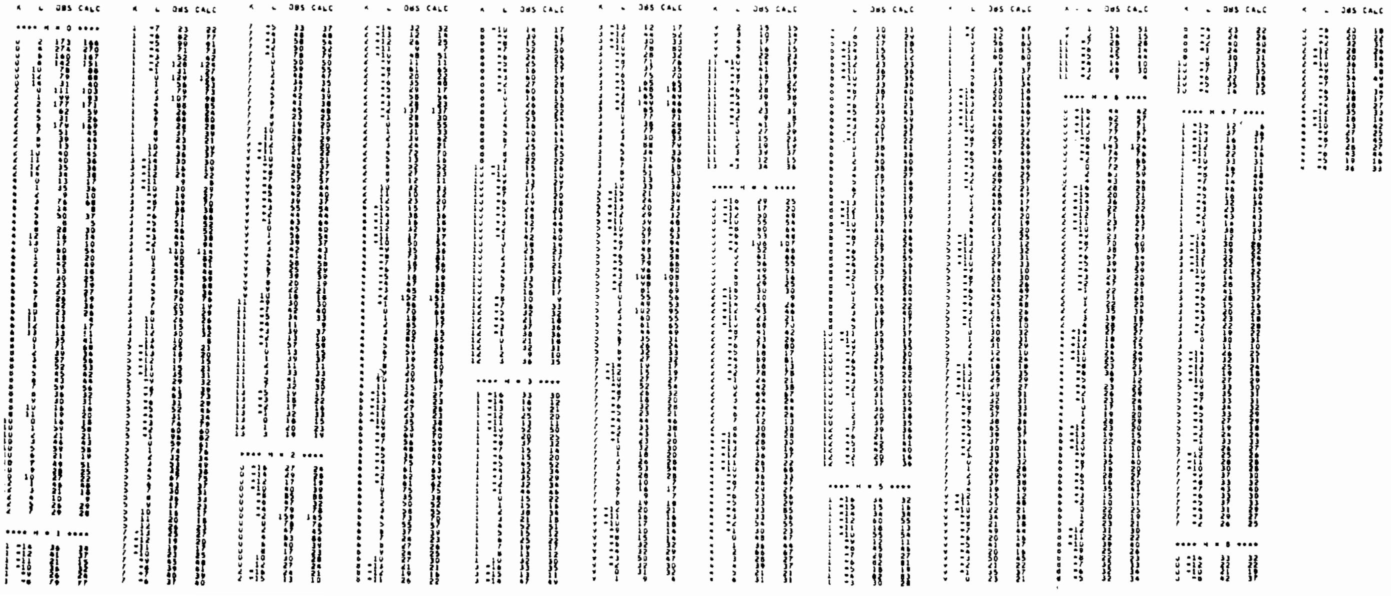
β_{11}[a]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
.0065(4)	.0022(1)	.0033(1)	.0001(3)	.0030(2)	–.0002(2)

Root-mean-square Amplitudes of Vibration (Å) for the Cobalt Atom

Minimum	Intermediate	Maximum
.105(4)	.128(4)	.166(3)

[a] The expression used for the anisotropic temperature factor was, exp $-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)$.

TABLE II. Observed and Calculated Structure Amplitudes for [Co(ox)(NH$_3$)(dien)]NO$_3$.



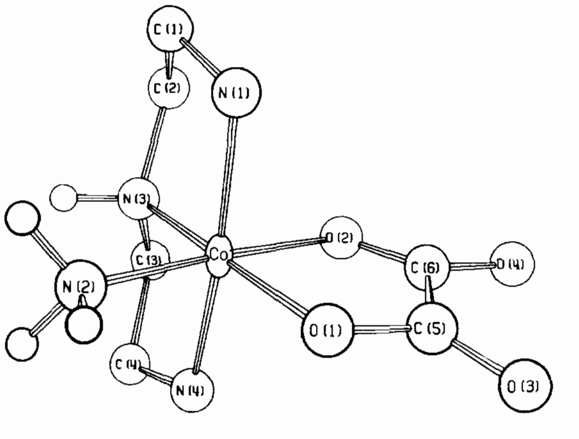


Figure 1. A perspective view of the Co(ox)(NH$_3$)(dien)$^+$ cation.

ing system. As expected, the dien ligand is coordinated tridentate, the oxalate ligand bidentate, and the NH$_3$ ligand completes the octahedral coordination sphere. The geometry of the complex is such that the nitrogen atoms of the dien ligand are in the same coordination plane *(i.e., meridional),* and the proton on the secondary nitrogen atom, N(3), is directed toward the coordinated NH$_3$ ligand.

Intramolecular bond distances and angles within the complex cation are presented in Table III. The mean Co^{III}–N distance is 1.95 Å, and there is no significant difference between the Co^{III}–NH$_3$, Co^{III}–N(primary) and Co^{III}–N(secondary) bond distances. Comparable distances for related complexes are 1.97 Å in π-[CoCl(en)(dien)]ZnCl$_4$,[10] 1.96 Å in $\varkappa$-[CoCl(en)(dien)]ZnCl$_4$,[10] 1.99 Å in β-[CoCl(en)(dpt)]ZnCl$_4$,[11] 1.95 Å in α-[CoCl(en)(dpt)I$_2\cdot$H$_2$O,[12] and 1.955 Å in racemic α-[CoCl(NH$_3$)(trien)](NO$_3$)$_2$.[13]

The angles subtended at the cobalt atom by the two dien chelate rings [86.1(7) and 84.0(7)°] are both within the range of values found in other Co^{III}–C$_2$ bridged polyamine complexes. [10–13] These chelate rings combine with the oxalate ring to produce significant distortions from regular octahedral coordination about the central cobalt atom (Table III).

The range of C–N and C–C bond distances is similar to that found in other Co^{III}–dien structures.[10, 14, 15] The C(1)–C(2) and C(3)–C(4) bond distances (1.47(2) and 1.51(2) Å, respectively) are not significantly different. This is expected as the dien chelate ring is coordinated in a near symmetrical orientation with respect to the oxalate chelate ring.

A significant angular distortion occurs at the secondary nitrogen atom in the dien ligand; C(2)–N(3)–C(3), 118(1)°. This angle can be compared with similar angular distortions for planar dien rings, *e.g.,* $\varkappa$-[CoCl(en)(dien)]ZnCl$_4$ (118(1)°)[10] and [Cu(dien)$_2$]Br$_2\cdot$H$_2$O (117.4(26), 111.3(22)°)[15].

TABLE III. Intramolecular Bond Distances and Angles for the Co(ox)(NH$_3$)(dien)$^+$ Cation.

Intramolecular Bond Distances

Atoms	Distance, Å	Atoms	Distance, Å
Co–O(1)	1.91(1)	N(4)–C(4)	1.48(2)
Co–O(2)	1.92(1)	C(1)–C(2)	1.47(2)
Co–N(1)	1.98(2)	C(3)–C(4)	1.51(2)
Co–N(2)	1.95(1)	O(1)–C(5)	1.25(2)
Co–N(3)	1.93(1)	O(2)–C(6)	1.21(2)
Co–N(4)	1.95(2)	C(5)–C(6)	1.58(2)
N(1)–C(1)	1.44(2)	C(5)–O(3)	1.21(2)
N(3)–C(2)	1.51(2)	C(6)–O(4)	1.25(2)
N(3)–C(3)	1.43(2)		

Intramolecular Bond Angles

Atoms	Angle, deg.	Atoms	Angle, deg.
O(1)–Co–O(2)	84.7(5)	O(2)–Co–N(4)	89.6(6)
O(1)–Co–N(1)	96.2(6)	N(1)–Co–N(2)	92.4(5)
O(1)–Co–N(2)	91.2(6)	N(1)–Co–N(3)	86.1(7)
O(1)–Co–N(3)	174.2(6)	N(1)–Co–N(4)	170.0(7)
O(1)–Co–N(4)	93.5(6)	N(2)–Co–N(3)	94.0(6)
O(2)–Co–N(1)	89.3(5)	N(2)–Co–N(4)	89.5(6)
O(2)–Co–N(2)	175.7(6)	N(3)–Co–N(4)	84.0(7)
O(2)–Co–N(3)	90.0(4)		
Co–N(1)–C(1)	109(1)	C(2)–N(3)–C(3)	118(1)
Co–N(3)–C(2)	107(1)	Co–N(4)–C(4)	110(1)
Co–N(3)–C(3)	110(1)		
N(1)–C(1)–C(2)	109(1)	N(3)–C(3)–C(4)	104(1)
C(1)–C(2)–N(3)	107(1)	C(3)–C(4)–N(4)	108(1)
Co–O(1)–C(5)	114(1)	O(2)–C(6)–C(5)	117(1)
Co–O(2)–C(6)	113(1)	O(4)–C(6)–C(5)	117(1)
O(1)–C(5)–O(3)	127(2)	O(1)–C(5)–C(6)	112(1)
O(2)–C(6)–O(4)	127(1)	O(3)–C(5)–C(6)	120(2)

The oxalate ion coordinates to the cobalt atom through two oxygen atoms as a *cis*-bidentate chelate. One oxygen atom, O(1), bonds to the cobalt atom at 1.91(1) Å and, with the three dien nitrogen atoms, completes a square planar arrangement about the cobalt atom. The second oxygen atom, O(2), bonds to the cobalt atom *trans* to the ammonia ligand at 1.92(1) Å, so that there is no significant difference between these two bond distances.

The oxalate ion is planar which is in accord with observations in [Cu(ox)(dien)]$\cdot$4H$_2$O,[16] hydrated calcium oxalate,[17] and α-oxalatodiamminocopper(II).[18]

The bond angles within the oxalate ion and the O–C–O angles [127(1) and 127(2)°] are similar to those found in the free ion[19] and in oxalic acid.[20] The carbon–carbon length of 1.58(2) Å and the average carbon–oxygen length of 1.23 Å are in accord with previously reported values.[16, 20]

Description of the Anion

In the anion there is a distorted planar arrangement of oxygen atoms about the central nitrogen atom (Table IV) with a mean N–O distance of 1.24 Å. The apparent distortions could well be the result of inadequate allowance for thermal motion or, alternatively, of disorder.

The shortest distances, 3.00, 3.04, 3.07 and 3.17 Å, between the oxygen atoms of the nitrate ion and the nitrogen atoms of the dien and ammonia ligands may be indicative of the presence of hydrogen bonds of the N–H···O type between them (Figure 2).

Chemical Implications

The loss of one chloride ion from *trans*-$CoCl_2(NH_3)$(dien)$^+$ in acidic solution results in the formation of two $CoCl(NH_3)$(dien)$(OH_2)^{2+}$ isomers in a constant ratio.[1] The major component (80%) is believed to be the *a*-ammine-*b*-aqua-*c*-chloro-*d,f,e*-diethylenetriaminecobalt(III) isomer (*i.e. facial* dien with the NH_3 *trans* to the sec-NH group, henceforth designated the *cis* isomer). Attempts to isolate this *cis*-aquachloro (or its *cis*-diaqua daughter) in a crystalline form have been unsuccessful, but one isomeric form of Co(ox)(NH_3)(dien)$^+$ was isolated as the ClO_4^-, I^- and PF_6^- salts from *trans*-$CoCl_2(NH_3)$(dien) according to method B in the experimental section. The i.r. spectra of these salts suggest that the dien ligand is in the *facial* configuration and if it is assumed that the nitrogen atoms in the hydrolysis products do not rearrange on chelate formation with oxalate, then this dien configuration is the one adopted in the major aquachloro product from *trans*-$CoCl_2(NH_3)$(dien)$^+$. Unfortunately, poor crystal quality of the salts has prevented confirmation of this assumption using single crystal X-ray techniques.

TABLE IV. Bond Distances and Angles for the Nitrate Anion.

Bond Distances

Atoms	Distance, Å
N(5)–O(5)	1.33(3)
N(5)–O(6)	1.16(2)
N(5)–O(7)	1.23(3)

Bond Angles

Atoms	Angle, deg.
O(5)–N(5)–O(6)	106(2)
O(6)–N(5)–O(7)	119(2)
O(5)–N(5)–O(7)	135(2)

A second* form of Co(ox)(NH_3)(dien)$^+$, isolated using method A, is shown here to be the *a*-ammine-

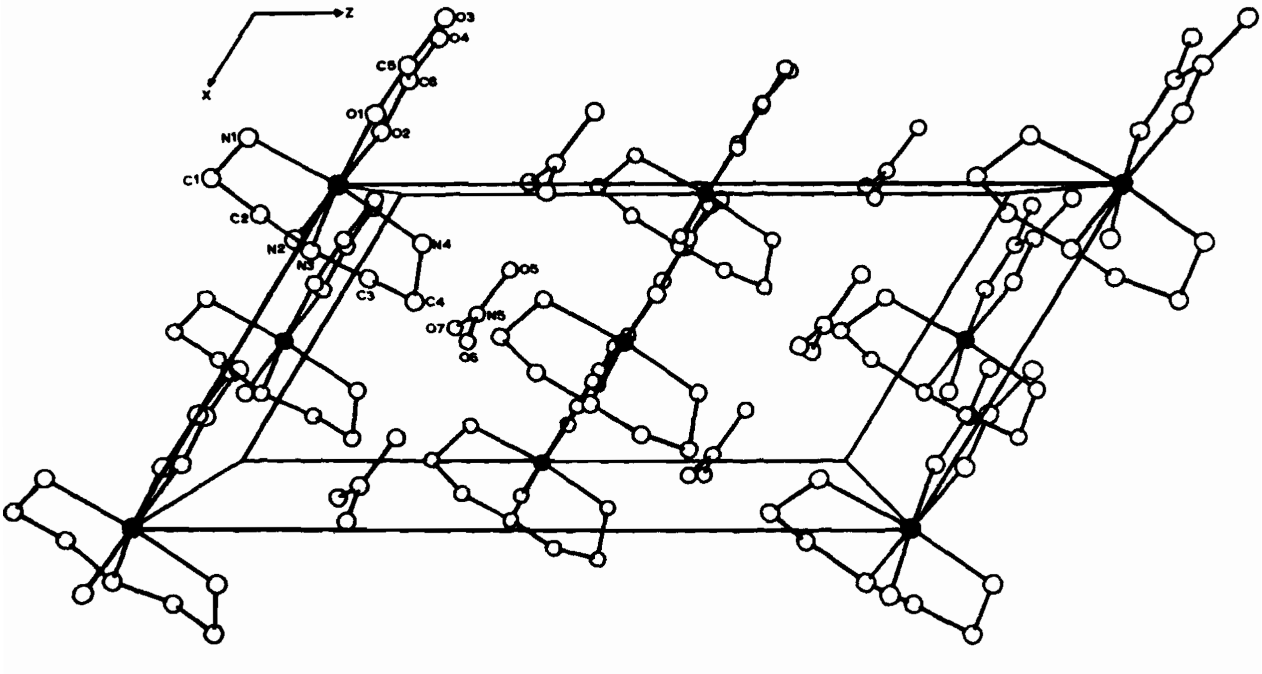


Figure 2. The packing of the ions in [Co(ox)(NH_3)(dien)]NO_3, as viewed down the *b* axis.

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* There are theoretically four Co(ox)(NH_3)(dien)$^+$ isomers, two with *meridional* dien as in Figure 1 with the NH proton of the sec-NH group either adjacent to or remote from the NH_3 group, and two with *facial* dien, the above *cis*-form (*a*-ammine-*b,f,c*-diethylenetriamine-*d,e*-oxalato-) and the *a*-ammine-*b,c,f*-diethylenetriamine-*d,e*-oxalato- isomer.

b,c,d-diethylenetriamine-*e,f*-oxalatocobalt(III) isomer with the NH proton of the sec-NH group of the *meridional* dien ligand adjacent to the NH_3 group.

Thus the *meridional* dien configuration is not adopted in the major hydrolysis products of *trans*-$CoCl_2(NH_3)(dien)^+$.

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