Conclusion

Le sulfate double CdK$_2$(SO$_4$)$_2$.2H$_2$O possède une macle mécanique; par compression perpendiculairement au plan (001) du cristal, on suit en lumière polarisée la propagation de bandes fines, correspondant aux émergences des plans de macle. Ces cristaux se maclent par simple contact. Les deux sulfates doubles tricliniques dihydratés stables à température ordinaire ne sont pas isomorphes. Cependant, en chauffant une lame de MnK$_2$(SO$_4$)$_2$.2H$_2$O vers 70°C, on voit le cristal se macler, avec formation de bandes semblables à celles que l'on rencontre toujours avec CdK$_2$(SO$_4$)$_2$.2H$_2$O. La transformation est très brutale; si le cristal n'est pas mince, il se divise parallèlement aux bandes en un nombre de lamelles. Cette nouvelle phase est stable jusqu'à 120°C, et possède la macle observée pour le sulfate de cadmium dihydraté, il existe donc un isomorphisme entre ces deux corps.

Nous avons essayé de rattacher les deux structures déterminées à celle du sulfate triclinique de cadmium, mais aucun rapport simple n'a pu être mis en évidence, les mailles n'ayant pas des dimensions comparables. Dans le cas de CdK$_2$(SO$_4$)$_2$.2H$_2$O, il n'y a qu'un atome de cadmium par maille, il se trouve donc soit sur l'une des séries de entre de symétrie dans l'hypothèse d'une structure centrosymétrique, ou en un point quelconque

dans l'autre cas; dans les deux alternatives, les distances Cd–Cd sont totalement différentes de celles du sulfate double monoclinique.

Il semble probable que la liaison Cd(1)–O(2)–Cd(2) du sel monoclinique se coupe au niveau de la molécule d'eau O(2), pour permettre l'adjonction de la demi-molécule d'eau supplémentaire.

Les données actuelles n'étant pas suffisantes, l'interprétation structurale de la formation de la macle mécanique ne pourra être trouvée que par la résolution de la structure.

La liste des facteurs de structure peut été obtenue au Centre de Documentation du C.N.R.S., 15 quai Anatole France, Paris 7e, sous le numéro A.O. 489.

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The Crystal Structure of (+)D-Tris(ethylenediamine)cobalt(III) Nitrate*

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The crystal structure of D-[Co(en)$_3$] (NO$_3$)$_3$ has been determined by three-dimensional single-crystal X-ray analysis. The compound crystallizes in the orthorhombic space group $P2_12_12_1$. The lattice constants are $a = 14.570 \pm 0.017$, $b = 12.607 \pm 0.016$, and $c = 8.756 \pm 0.003$ Å with four formula units in the unit cell. Atoms of Co, N, C, and O were refined anisotropically. The derived structure was refined by least-squares methods to an unweighted R index of 8.4%. The coordination about the central cobalt atom is essentially octahedral with an average Co–N distance of 1.964 ± 0.008 Å.

Introduction

The crystal structures and absolute configurations of (+)$_D$-2[Co(en)$_3$]Cl$_3$.3H$_2$O (Nakatsu, Saito & Kuroya, 1956), (+)$_D$-2[Co(en)$_3$]Cl$_3$.NaCl.6H$_2$O (Nakatsu, Shiro Saito & Kuroya, 1957), (+)$_D$-[Co(en)$_3$]Br$_3$.H$_2$O (Nakatsu, 1962) and (+)$_D$-[Co(en)$_3$]Cl$_3$.H$_2$O (Iwata, Nakatsu & Saito, 1969), where en = ethylenediamine, have been determined. The space group of the chloride and bro-

mide complexes is tetragonal, with space group $P4_12_12$ or $P4_32_12$. The present work was undertaken to aid in explaining the anomalous ΔH^* of this salt observed in the study of solid state racemization, performed in this laboratory.

Experimental

A sample of the compound was first prepared by Werner (1912) and yellow crystals were obtained by recrystallization from a water solution. Microscopic examination revealed that the crystals were either triangular prisms or needles with sharply defined faces.

A needle crystal was selected for diffraction work. Preliminary precession photographs exhibited *mmm* symmetry, as did the triangular prism, indicating an orthorhombic space group. The conditions limiting the possible reflections were $h00$, extinct if $h=2n+1$; $0k0$, extinct if $k=2n+1$; and $00l$, extinct if $l=2n+1$. These conditions uniquely determine space group $P2_12_12_1$. A pseudo extinction of the type hkl, $h+l=2n+1$ occurs and is indicative of pseudo B centering. This was interpreted to mean that the cobalt atom was midway between the screw axes along X and at $Y=\frac{1}{4}$, $Z=\frac{3}{4}$. The unit cell parameters at $22\pm3\,°C$ are: $a=14\cdot570\pm0\cdot017$, $b=12\cdot607\pm0\cdot016$, and $c=8\cdot756\pm0\cdot003$ Å. These parameters and their standard deviations were obtained by centering the diffractometer on independent reflections whose maxima were determined by left–right, top–bottom beam splitting on a previously aligned Hilger–Watts four-circle diffractometer (Mo $K\alpha$ radiation, $\lambda=0\cdot7107$ Å). A calculated density of $1\cdot756$ g.cm^{-3} for four molecules per unit cell agrees reasonably well with the observed density of $1\cdot773$ g.cm^{-3} obtained by flotation techniques. For data collection, a crystal having approximate dimensions $0\cdot07\times0\cdot07\times0\cdot08$ mm along the a, b and c crystal axes respectively, was mounted such that the $0\cdot08$ mm axis was along the spindle axis. The orientation of the crystal was then modified by rotation through a few degrees before commencing to collect data, to minimize the occurrence of multiple reflections. A right-handed coordinate system was used.

Data were collected at room temperature ($22\pm3\,°C$) using a Hilger–Watts four-circle diffractometer equipped with scintillation counter and using Zr-filtered Mo $K\alpha$ ($\lambda=0\cdot7107$ Å) radiation. Within a 2θ sphere of $60°$ all data in one octant was recorded using the stationary-crystal stationary-counter technique with a take-off angle of $6°$. Peak height data were converted to integrated intensities by the method of Alexander & Smith (1962). Stationary-crystal stationary-counter background counts of 5 sec were taken at $\theta=\theta_{hkl}\pm(0\cdot25+0\cdot01\theta_{hkl})$ and peak heights were measured for 10 sec. In all, 2647 reflections were measured in this way.

As a general check on electronic and crystal stability the intensities of three standard reflections ($10,0,0$, 060, 006) were remeasured periodically during the data collection period. These reflections did not change significantly and therefore no corrections were made.

The intensity data were corrected for Lorentz–polarization effects. The absorption coefficient, μ, is $10\cdot4$ cm^{-1}. The maximum and minimum transmission factors are $92\cdot9$ and $92\cdot3\%$ respectively. These were calculated by using the minimum and maximum path lengths. Since the transmission factors are large, no absorption corrections were made. Of the 2647 measured intensities, 1943 were found to be above background (*i.e.* greater than three times the standard error based on counting statistics) and were therefore considered as observed. The standard errors in the intensities and the observed structure functions were cal-

Table 1. *Final positional parameters and anisotropic thermal parameters for* D-[Co(en)₃](NO₃)₃

Numbers in parentheses are standard deviations in the last digit of the parameter.

The form of the anisotropic temperature factor expression is

$$\exp\left[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)\times10^5\right].$$

	x/a	y/b	z/c	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Co	0·1607 (1)	0·2439 (1)	0·7575 (1)	322 (4)	428 (5)	1064 (12)	10 (4)	−12 (7)	41 (10)
N(1)	0·0787 (5)	0·1229 (5)	0·7300 (11)	408 (33)	557 (45)	1514 (136)	−40 (33)	20 (58)	183 (67)
N(2)	0·2672 (5)	0·1546 (5)	0·7082 (9)	368 (30)	489 (39)	1476 (126)	−22 (30)	−32 (51)	74 (56)
N(3)	0·2503 (5)	0·3607 (5)	0·7673 (9)	395 (33)	576 (42)	1300 (113)	39 (30)	100 (59)	−153 (66)
N(4)	0·0586 (6)	0·3363 (6)	0·8209 (9)	405 (35)	547 (48)	1531 (117)	28 (36)	11 (58)	187 (62)
N(5)	0·1743 (5)	0·2131 (6)	0·9765 (9)	446 (37)	510 (41)	1400 (103)	59 (34)	−169 (53)	118 (57)
N(6)	0·1363 (5)	0·2745 (5)	0·5394 (8)	431 (35)	488 (44)	1102 (95)	−53 (30)	−143 (46)	147 (53)
N(7)	0·1492 (5)	0·6019 (6)	0·6455 (9)	345 (35)	677 (47)	1675 (133)	−48 (37)	−21 (61)	54 (67)
N(8)	0·2059 (6)	0·8853 (7)	0·8021 (10)	629 (50)	707 (60)	1725 (133)	123 (46)	−236 (68)	27 (77)
N(9)	0·5059 (6)	0·5172 (6)	0·9032 (11)	690 (54)	479 (48)	1750 (136)	−39 (43)	80 (73)	211 (68)
C(1)	0·3531 (5)	0·2122 (7)	0·7408 (13)	292 (35)	727 (53)	1813 (151)	54 (33)	−19 (75)	−145 (91)
C(2)	0·3361 (6)	0·3268 (7)	0·6927 (13)	380 (41)	554 (52)	2151 (175)	−94 (42)	47 (79)	−192 (78)
C(3)	0·0716 (7)	0·3620 (8)	0·9824 (11)	474 (50)	735 (66)	1315 (134)	62 (48)	24 (72)	19 (76)
C(4)	0·1020 (7)	0·2647 (8)	1·0657 (11)	665 (57)	652 (66)	1377 (121)	74 (53)	186 (73)	214 (85)
C(5)	0·0553 (7)	0·2089 (8)	0·4936 (13)	542 (51)	759 (68)	1568 (153)	−65 (51)	−227 (74)	46 (86)
C(6)	0·0620 (7)	0·1049 (8)	0·5654 (11)	608 (55)	724 (64)	1442 (142)	−174 (54)	−7 (79)	−73 (86)
O(1)	0·1221 (5)	0·5627 (5)	0·7664 (8)	531 (35)	776 (43)	2011 (123)	−42 (31)	143 (58)	296 (70)
O(2)	0·1040 (5)	0·6739 (5)	0·5827 (9)	632 (39)	677 (45)	2059 (117)	66 (37)	−144 (61)	276 (64)
O(3)	0·2210 (5)	0·5686 (7)	0·5883 (10)	511 (37)	1512 (83)	1914 (120)	262 (47)	277 (62)	433 (90)
O(4)	0·2343 (5)	0·9556 (5)	0·8915 (8)	610 (41)	798 (50)	1636 (110)	−23 (40)	−130 (59)	206 (64)
O(5)	0·2140 (7)	0·7914 (6)	0·8405 (10)	1480 (83)	542 (43)	2880 (167)	130 (50)	−1078 (101)	20 (74)
O(6)	0·1705 (7)	0·9103 (6)	0·6789 (9)	1076 (63)	785 (51)	1528 (98)	225 (53)	−312 (81)	103 (64)
O(7)	0·4365 (7)	0·5511 (7)	0·8368 (11)	1029 (61)	847 (60)	2923 (176)	109 (56)	−651 (95)	−162 (87)
O(8)	0·5645 (8)	0·4661 (7)	0·8343 (13)	1084 (70)	950 (65)	3824 (230)	86 (62)	727 (113)	−383 (110)
O(9)	0·5169 (6)	0·5423 (7)	1·0399 (10)	844 (53)	1054 (63)	1873 (135)	57 (52)	−121 (74)	80 (89)

culated by the method of Williams & Rundle (1964) and are given by

$$\sigma_I = [TC + BG + (0.05TC)^2 + (0.05BG)^2]^{1/2}$$

$$\sigma_F = (Lp)^{-1/2}[(I + \sigma_I)^{1/2} - I^{1/2}].$$

The function for σ_F is based on the finite difference method. The unobserved reflections were not used in the solution and refinement of the derived structure.

Structure determination

A three-dimensional Patterson synthesis was computed from the data and careful analysis revealed the position of the cobalt atom. This atom's location at the peculiar position $(x, y/4, 3z/4)$ caused a pseudo-twofold axis in the z direction in the electron density map. This pseudo-axis disappeared after careful placement of the other atoms. These positions were then refined by full-matrix least-squares techniques with isotropic thermal parameters to a conventional discrepancy index of $R = \sum ||F_o| - |F_c|| / \sum |F_o| = 0.108$ and a weighted R index of

$\omega R = [\sum \omega(|F_o| - |F_c|)^2 / \sum \omega |F_o|^2]^{1/2} = 0.134$. The scattering factors were those of Doyle & Turner (1968).

A difference electron-density map at this stage showed that all the non-hydrogen atoms had been accounted for, but that some anisotropic motion was evident. The anisotropic refinement was carried out in two steps. First, the complex was varied and then the nitrates, with the cobalt atom held common in both refinements. This was done because of the large number of variables in the total molecule. After a few cycles the values of R and ωR, of 0.085 and 0.101 respectively, were obtained. Modifications for the real and imaginary parts of the anomalous dispersion, taken from Cromer & Liberman (1970), were now added. The final values of R and ωR, of 0.084 and 0.100 respectively, were obtained. A final electron density difference map shows no peaks higher than 0.5 e.Å^{-3}. A final statistical analysis of the F_o and F_c values as a function of the indices, the scattering angle and the magnitude of F_o showed no unusual trends and suggests that the relative weighting scheme used is a reasonable one.
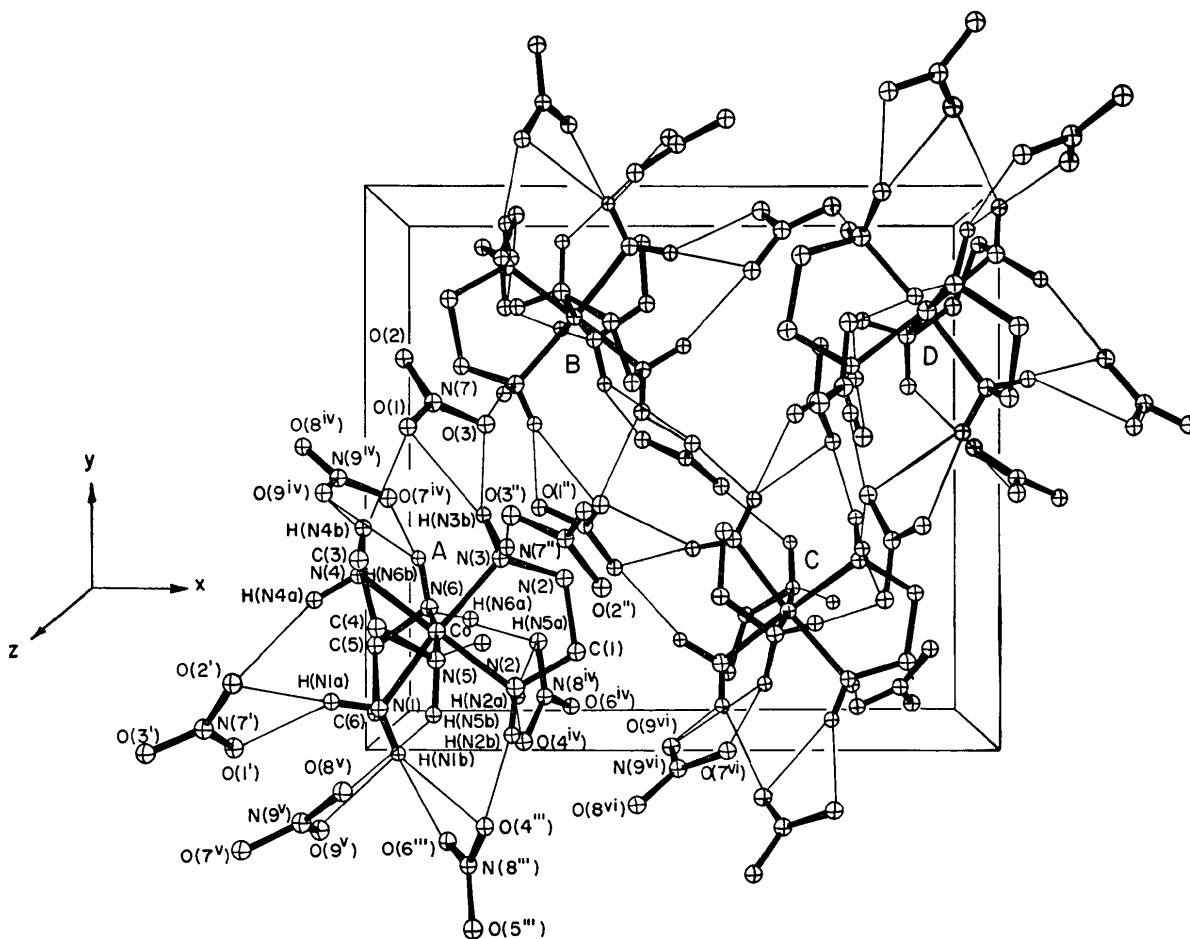

Fig. 1. Packing in unit cell with fine lines indicating possible hydrogen bonding. O–H distances out to 2·5 Å.

In Table 1 are listed the final values of the positional parameters and anisotropic temperature factors, along with their standard deviations as derived from the in-

Table 2. *Observed and calculated structure factors* ($\times$ 10)

Fig. 2. Stereoscopic view of D-[Co(en)₃]³⁺ moiety.

verse matrix. In Table 2 are listed the values of F_o and F_c in electrons for the 1943 observed reflections. The values of F_c for the unobserved reflections in no case exceeded 3σ (F_o). In Table 3 are listed the calculated hydrogen positions for the carbon and nitrogen atoms. These positions were calculated by means of the following equations:

$$R = -a(\hat{V}_1 + \hat{V}_2) \pm b(\hat{V}_1 \wedge \hat{V}_2) ,$$

$$\frac{b}{a} = \tan \psi , \quad a^2 + b^2 = 1 ,$$

$$\psi = \sin^{-1}\left[\sin^2 \theta - \frac{\cos^2 \theta(1 - \cos \varphi)^2}{\sin^2 \varphi}\right]^{1/2}.$$

$\hat{V}_1$ and $\hat{V}_2$ are unit vectors between the appropriate nitrogen, carbon and cobalt atoms. θ is the Co–N–H or H–C–N bond angle, restricted to the tetrahedral angle. φ is the appropriate Co–N–C or C–C–N bond angle. ψ is half the angle between the hydrogen positions. Distances of 1·036 and 1·080 Å were chosen for the N–H and C–H bond lengths, respectively. These calculated positions were put into the least-squares program and after a few cycles values for R and ωR of 0·074 and 0·086 were obtained. A fixed isotropic temperature factor of 5Å² was used for the hydrogen atoms. Since some of the hydrogen atoms were ill behaved only their calculated positions are reported.

Results and discussion

Fig. 1, an *ORTEP* drawing, illustrates the packing in the unit cell. (The fine lines represent the closest approach of the oxygen atoms to the hydrogen atoms attached to nitrogen atoms of the complex, out to 2·5

Table 3. *Calculated positional parameters for hydrogen atoms*

	x/a	y/b	z/c		x/a	y/b	z/c
H(N1a)	0·0169	0·1381	0·7842	H(C1a)	0·4081	0·1792	0·6732
H(N1b)	0·1086	0·0559	0·7771	H(C1b)	0·3672	0·2093	0·8618
H(N2a)	0·2652	0·1342	0·5936	H(C2a)	0·3920	0·3760	0·7320
H(N2b)	0·2649	0·0859	0·7730	H(C2b)	0·3278	0·3305	0·5702
H(N3a)	0·2635	0·3791	0·8805	H(C3a)	0·0075	0·3895	1·0300
H(N3b)	0·2241	0·4263	0·7107	H(C3b)	0·1235	0·4227	0·9932
H(N4a)	−0·0029	0·2964	0·8070	H(C4a)	0·1290	0·2869	1·1761
H(N4b)	0·0599	0·4055	0·7571	H(C4b)	0·0447	0·2111	1·0778
H(N5a)	0·2379	0·2391	1·0138	H(C5a)	0·0545	0·1998	0·3710
H(N5b)	0·1718	0·1319	0·9939	H(C5b)	−0·0070	0·2475	0·5302
H(N6a)	0·1928	0·2528	0·4746	H(C6a)	−0·0019	0·0628	0·5508
H(N6b)	0·1206	0·3542	0·5266	H(C6b)	0·1192	0·0620	0·5169

Å.) Table 4 lists some of the important interatomic distances outside the complex ion, as calculated by *ORFFE*. Fig. 2 shows the directions of vibration of the atoms refined anisotropically.

Table 4. *Intermolecular approaches less than* 3·5Å

Superscript	x	y	z
′	−x	y−0·5	1·5−z
″	0·5−x	1−y	0·5+z
‴	x	y−1	z
iv	0·5−x	1−y	z−0·5
v	x−0·5	0·5−y	2−z
vi	1−x	y−0·5	1·5−z

Atom 1	Atom 2	Distance*	Atom 1	Atom 2	Distance*
C(1)	O(2″)	3·385 (13)	N(1)	N(7′)	3·479 (11)
C(1)	O(8ᵛⁱ)	3·392 (14)	N(2)	O(4‴)	3·022 (10)
C(1)	N(9ᵛⁱ)	3·436 (12)	N(2)	O(4ⁱᵛ)	3·102 (11)
C(2)	O(7)	3·421 (13)†	N(2)	O(5ⁱᵛ)	3·303 (12)
			N(2)	O(6‴)	3·384 (12)
C(3)	O(1)	3·250 (12)	N(2)	O(8ᵛⁱ)	3·424 (13)
C(3)	O(3″)	3·278 (14)	N(3)	O(3″)	2·980 (12)
C(3)	O(7″)	3·287 (14)†	N(3)	O(3)	3·084 (11)
C(4)	O(8ᵛ)	3·087 (14)	N(3)	O(1)	3·152 (10)
C(4)	O(3″)	3·318 (15)			
C(4)	O(7″)	3·366 (14)†	N(4)	O(1)	3·045 (10)
C(4)	O(2′)	3·453 (14)	N(4)	O(9ⁱᵛ)	3·089 (11)
C(5)	O(7ⁱᵛ)	3·326 (14)	N(4)	O(2′)	3·232 (11)
C(5)	O(9ⁱᵛ)	3·332 (15)	N(4)	O(6′)	3·444 (13)†
C(6)	O(6‴)	3·078 (14)	N(5)	O(8ᵛ)	3·214 (14)
C(6)	O(1′)	3·110 (14)	N(5)	O(6″)	3·257 (11)†
C(6)	O(4ⁱᵛ)	3·413 (14)	N(5)	O(3″)	3·296 (12)
N(1)	O(1′)	3·009 (11)	N(5)	O(4‴)	3·450 (12)
N(1)	O(9ᵛ)	3·034 (11)	N(6)	O(5ⁱᵛ)	2·913 (14)
N(1)	O(6‴)	3·025 (11)	N(6)	O(7ⁱᵛ)	3·016 (12)
N(1)	O(2′)	3·173 (11)	N(6)	O(9ⁱᵛ)	3·201 (11)
N(1)	O(4‴)	3·400 (10)			

* Numbers in parentheses refer to standard deviations occurring in the last digit, as calculated from e.s.d. given by variance–covariance matrix.
† Not drawn.

Only one type of hydrogen bond is conceivable, that is the N–H···O bond. This occurs between the amines of the complex and the oxygen of the nitrates. The closest N···O distance is 2·913 Å. This agrees with the 2·91 Å reported by Iwata, Nakatzu & Saito for the N–H···O bond length in the chloride structure. They also report the shortest N–H···Cl bond length as 3·12 Å. Table 5 lists the H···O bond distances and the N–H···O bond angles, as calculated by *ORTEP*. These distances and angles were obtained by using the calculated positions of the hydrogen atoms. The N–H stretching frequency, reported by Powell & Sheppard (1959), is 3195–3060 cm⁻¹ for the chloride complex. The corresponding stretching frequency for the nitrate complex occurs at 3210–3110 cm⁻¹. Molecule *A* is related to molecules *B*, *C*, and *D* by screw axes located at x/4, y/2; y/4, z/2; and x/2, z/4 respectively. Additional screw axes occur at 3x/4, y/2; 3y/4, z/2; and x/2, 3z/4. The hydrogen bonding occurring between the amines of the complex and the nitrate oxygens provides for a helical relationship between the complex molecules in the unit cell.

Table 5. *Distances and angles between calculated hydrogen positions and oxygen atoms in the nitrate groups*

Superscripts are listed in Table 4. Distances out to 2.5 Å.

Atom 1	Atom 2	Distance		Angle
H(N1a)	O(2′)	2·150 Å	N(1)–H(N1a)–O(2′)	174·2°
H(N1a)	O(1′)	2·269	N(1)–H(N1a)–O(1′)	127·0
H(N1b)	O(6‴)	2·216	N(1)–H(N1b)–O(6‴)	133·7
H(N1b)	O(9ᵛ)	2·422	N(1)–H(N1b)–O(9ᵛ)	116·9
H(N1b)	O(4‴)	2·432	N(1)–H(N1b)–O(4‴)	154·3
H(N2a)	O(4ⁱᵛ)	2·101	N(2)–H(N2a)–O(4ⁱᵛ)	161·7
H(N2a)	O(5ⁱᵛ)	2·425	N(2)–H(N2a)–O(5ⁱᵛ)	141·8
H(N2b)	O(4‴)	1·993	N(2)–H(N2b)–O(4‴)	169·0
H(N3a)	O(3″)	1·949	N(3)–H(N3a)–O(3″)	172·2
H(N3b)	O(3)	2·092	N(3)–H(N3b)–O(3)	159·8
H(N3b)	O(1)	2·319	N(3)–H(N3b)–O(1)	136·4
H(N4a)	O(2′)	2·336	N(4)–H(N4a)–O(2′)	144·6
H(N4b)	O(1)	2·179	N(4)–H(N4b)–O(1)	138·8
H(N4b)	O(9ⁱᵛ)	2·299	N(4)–H(N4b)–O(9ⁱᵛ)	132·7
H(N5b)	O(8ᵛ)	2·491	N(5)–H(N5b)–O(8ᵛ)	126·9
H(N6a)	O(5ⁱᵛ)	1·874	N(6)–H(N6a)–O(5ⁱᵛ)	173·7
H(N6b)	O(7ⁱᵛ)	2·208	N(6)–H(N6b)–O(7ⁱᵛ)	133·5
H(N6b)	O(9ⁱᵛ)	2·383	N(6)–H(N6b)–O(9ⁱᵛ)	135·1

As for the geometry of the complex, no significant change was found from the previous results of experiments done on the chloride and bromide structures. Table 6 lists the interatomic distances and Table 7 the bond angles of the complex and nitrate groups. The symmetry of the complex molecule is D_3. The non-crystallographic threefold axis of rotation forms an angle of −79·5° with the x axis and 74·1° with the z axis. The six nitrogen atoms of the ligand molecules form an octahedron around the cobalt atom. The average Co–N distance is 1·964 ± 0·008 Å, in good agreement with the values obtained for other $[Co(en)_3]^{3+}$

Table 6. *Distances* (Å) *between atoms in complex*

Atom 1	Atom 2	Distance*
Co	N(1)	1·947 (7)
Co	N(2)	1·956 (7)
Co	N(3)	1·964 (7)
Co	N(4)	1·967 (8)
Co	N(5)	1·967 (8)
Co	N(6)	1·981 (7)
N(1)	C(6)	1·480 (13)
N(2)	C(1)	1·468 (11)
N(3)	C(2)	1·466 (12)
N(4)	C(3)	1·464 (12)
N(5)	C(4)	1·459 (13)
N(6)	C(5)	1·489 (12)
C(1)	C(2)	1·526 (13)
C(3)	C(4)	1·494 (14)
C(5)	C(6)	1·457 (15)
N(7)	O(1)	1·233 (10)
N(7)	O(2)	1·249 (10)
N(7)	O(3)	1·227 (11)
N(8)	O(4)	1·245 (11)
N(8)	O(5)	1·236 (11)
N(8)	O(6)	1·233 (12)
N(9)	O(7)	1·237 (12)
N(9)	O(8)	1·223 (12)
N(9)	O(9)	1·249 (13)

* Numbers given in parentheses refer to standard deviations occurring in the last digit as calculated from e.s.d. given by variance–covariance matrix.

Table 7. *Bond angles in complex*

	Angle (°)*		Angle (°)*
N(1)–Co—N(2)	90·31 (32)	Co—N(4)–C(3)	107·65 (62)
N(1)–Co—N(3)	175·69 (31)	Co—N(5)–C(4)	111·29 (59)
N(1)–Co—N(4)	92·49 (34)	Co—N(6)–C(5)	106·99 (56)
N(1)–Co—N(5)	91·70 (33)	N(1)–C(6)–C(5)	106·87 (86)
N(1)–Co—N(6)	85·85 (30)	N(6)–C(5)–C(6)	109·47 (84)
N(2)–Co—N(3)	85·15 (32)	N(2)–C(1)–C(2)	106·77 (67)
N(2)–Co—N(4)	175·80 (34)	N(3)–C(2)–C(1)	106·64 (81)
N(2)–Co—N(5)	91·15 (33)	N(4)–C(3)–C(4)	108·74 (86)
N(2)–Co—N(6)	92·00 (32)	N(5)–C(4)–C(3)	107·99 (82)
N(3)–Co—N(4)	92·16 (31)	O(1)–N(7)–O(2)	120·62 (92)
N(3)–Co—N(5)	91·83 (32)	O(1)–N(7)–O(3)	118·86 (88)
N(3)–Co—N(6)	90·81 (30)	O(2)–N(7)–O(3)	120·51 (94)
N(4)–Co—N(5)	85·18 (32)	O(4)–N(8)–O(5)	117·95 (97)
N(4)–Co—N(6)	90·74 (31)	O(4)–N(8)–O(6)	120·39 (97)
N(5)–Co—N(6)	175·42 (33)	O(5)–N(8)–O(6)	121·60 (103)
Co—N(1)–C(6)	109·41 (58)	O(7)–N(9)–O(8)	121·26 (126)
Co—N(2)–C(1)	110·06 (53)	O(7)–N(9)–O(9)	117·07 (109)
Co—N(3)–C(2)	108·53 (53)	O(8)–N(9)–O(9)	121·58 (123)

* Numbers given in parentheses refer to standard deviations occurring in the last digit as calculated from e.s.d. given by variance–covariance matrix.

salts listed previously. The average N–Co–N angle is $89·8 \pm 0·3°$. Considering the combination of planes formed by three nitrogen atoms in the complex, the average position of the cobalt atom is fixed at the center of intersection of these planes. The nitrogen atoms in the nitrate groups are also planar with the oxygen atoms within experimental error. The ethylenediamine molecules are of the *gauche* form, and all three C–C bonds approximately align along the non-crystallographic threefold axis of the complex, in the $\delta\delta\delta$ conformation. This conformation is the opposite of that predicted by Raymond, Corfield & Ibers (1968) for a strongly hydrogen-bonded system. This could be caused by bifurcation of some of the proposed hydrogen bonds. The chelate rings are not planar: C(1) and C(2) lie 0·322 Å above and 0·384 Å below the plane of Co, N(2) and N(3) respectively; C(3) and C(4) lie 0·495 Å above and 0·100 Å below the plane of Co, N(4) and N(5) respectively; C(5) and C(6) lie 0·344 Å below and 0·315 Å above the plane of Co, N(1) and N(6) respectively.

The absolute configuration of the complex was determined using the statistical method of Hamilton (1965). The structure was refined anisotropically, with no anomalous correction to, an R value of 0·085 for the structure and its mirror image. When the anomalous correction terms were added, the R value for the structure drawn remained the same, while the R value for the mirror image was raised to 0·089. With convergence, R values of 0·084 and 0·088 were obtained for the structure drawn and its mirror image respectively. A right-handed coordinate system was used in all calculations and in data collection. The circular dichroism of a solution of the complex has a positive peak at 493

mμ ($\Delta_\varepsilon = +1·75$) and a specific rotation at the sodium D-line of $+129°$.

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