Crystal Structure and Absolute Configuration of (+)-Tris[(−)-1,2-diphenylethylenediamine]cobalt(III) Nitrate Monohydrate

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The crystal structure and absolute configuration of the title compound has been determined from single-crystal *X*-ray data and refined by full-matrix least squares to *R* 0.085. The orange trigonal crystal has the unit-cell dimensions: $a = 16.623(4)$, $c = 14.834(9)$ Å, space group $P3_221$, with $Z = 3$. The complex ion has strict C_2 symmetry but, excluding the phenyl substituents, approximates to D_3 symmetry. The average Co–N distance is 1.98 Å and the mean N–Co–N angle within a chelate ring is 83.4°. The $[CoN_6]$ chromophore is compressed along the trigonal axis and azimuthally contracted. The complex ion is a *lel* isomer with the absolute configuration $\Lambda\ \delta\delta\delta$, while the ligand (−)dpen [(−)-1,2-diphenylethylenediamine] has the *S,S* configuration.

THE tris(diamine) complexes of cobalt(III) are of primary significance for studies of the relation between stereochemistry and optical activity in chiral metal co-ordination compounds. The crystal and molecular structure of tris(diamine)cobalt(III) complexes, including determinations of absolute configuration by the Bijvoet method, have been investigated in detail,[1] as have the circular dichroism (c.d.) spectra of these complexes.[2] The two series of studies provide the basis for a recent quantitative interpretation of the *d*-electron optical activity of cobalt(III) complexes in terms of a ligand-polarisation model.[3]

The metal complexes of (—)-1,2-diphenylethylenediamine [(—)dpen], a 1,2-diamine which contains phenyl substituents having a large and anisotropic polarisability, provide test cases for the ligand-polarisation model. Cobalt(III) complexes of the ligand give c.d. spectra which differ significantly in magnitude from those of the analogous complexes containing alkyl-substituted 1,2-diamines,[2] although the c.d. spectra are anomalous only if (—)dpen is assigned [4,5] the *R,R* configuration.

Initially the laevorotatory isomer of dpen was assigned the *S,S* configuration from the similarities observed between the optical rotatory dispersion (o.r.d.) curves of the complexes, $[Co(diamine)_3]^{3+}$ [diamine = (—)dpen, (*S*)(+)-propylenediamine, or other alkyl-substituted 1,2-diamines with the *S* or *S,S* configuration].[6] The

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[1] Y. Saito, *Co-ordination Chem. Rev.*, 1974, **13**, 305.

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[3] S. F. Mason and R. H. Seal, *J.C.S. Chem. Comm.*, 1975, 331; *Mol. Phys.*, 1976, **31**, 755.

[4] B. Bosnich and J. MacB. Harrowfield, *J. Amer. Chem. Soc.*, 1972, **94**, 3425.

[5] P. L. Fereday and S. F. Mason, *Chem. Comm.*, 1971, 1314.

[6] R. D. Gillard, *Tetrahedron*, 1965, **21**, 503.

isolation of both (−)- and (+)-$[\mathrm{Co}\{(-)\mathrm{dpen}\}_3]^{3+}$, with the (−) isomer predominating at equilibrium, suggested that the chelate ring formed by (−)dpen is restricted to the λ conformation,[4] giving the thermodynamically more stable *lel* isomer,[7] $\Delta(-)[\mathrm{Co}\{(-)\mathrm{dpen}\}_3\lambda\lambda\lambda]^{3+}$, and the less stable *ob* isomer, $\Lambda(+)[\mathrm{Co}\{-)\mathrm{dpen}\}_3\lambda\lambda\lambda]^{3+}$.

The formation of a chelate ring with a preferred λ conformation requires that (−)dpen has the *R*,*R* configuration,[4] as does the attribution,[5] from an exciton analysis of the c.d. spectrum, of the *R*,*R* configuration to (−)-2,4,5-triphenyl-2-imidazoline from which (−)dpen is obtained by hydrolysis. However, a similar analysis [8] of the simpler c.d. spectrum of the $[\mathrm{Zn}\{(-)\mathrm{dpen}\}_n]^{2+}$ complexes (n = 1 or 2) indicates that the ligand has the *S*,*S* configuration, as does a chemical conversion [9] of (−)dpen into (−)-1,2-diphenylethylamine, which has a known configuration.[10]

In the present work the structure and the absolute configuration of the complex ion and of the ligand in (+)-$[\mathrm{Co}\{(-)\mathrm{dpen}\}_3][\mathrm{NO}_3]_3\cdot\mathrm{H}_2\mathrm{O}$ have been determined by *X*-ray diffraction methods, in order to resolve the vicissitudes in the attributions of configuration to (−)dpen and to obtain the structural basis required for a ligand-polarisation analysis of the *d*-electron optical activity of the complex ion.

EXPERIMENTAL

Materials.—The chloride and perchlorate salts of (+)-$[\mathrm{Co}\{(-)\mathrm{dpen}\}_3]^{3+}$ were kindly supplied by Dr. R. H. Seal.[11] Samples of the chloride salt were converted into the corresponding bromide and iodide salts which were crystallised from methanol and from dimethylformamide, respectively. Although sealed in capillary tubes, the monoclinic halide crystals exhibited up to 25% decomposition during attempted data collection, and they were not investigated further. The orange orthorhombic crystals of $(+)[\mathrm{Co}\{(-)\mathrm{dpen}\}_3][\mathrm{ClO}_4]_3\cdot4\mathrm{H}_2\mathrm{O}$ were more stable and decomposed by less than 5% during data collection. However, in this crystal there are two independent complex ions in an asymmetric unit (Z = 8 for the space group $P2_12_12_1$) and the relative positions of the two cobalt atoms produced pseudo-mirror symmetry. Because of the pseudo-symmetry and the weak intensity of many of the reflections, the lighter atoms in the structure could not be located.

On changing the anion to nitrate, two types of orange needle-like crystals were obtained from ethanol–water solution, one a trigonal hydrate and the other an orthorhombic ethanolate. Preliminary crystal data were determined from Weissenberg photographs and the unit-cell dimensions of the trigonal hydrate were refined by the use of a diffractometer.

Crystal Data.—(*i*) $(+)[\mathrm{Co}\{(-)\mathrm{dpen}\}_3][\mathrm{NO}_3]_3\cdot x\mathrm{EtOH}$, Orthorhombic, a = 16.40, b = 22.57, c = 28.42 Å, space group $P2_12_12_1$. (*ii*) $(+)[\mathrm{Co}\{(-)\mathrm{dpen}\}_3][\mathrm{NO}_3]_3\cdot\mathrm{H}_2\mathrm{O}$, $\mathrm{C}_{42}\mathrm{H}_{50}\mathrm{CoN}_9\mathrm{O}_{10}$, M = 899.8, $F(000)$ = 1 416, Trigonal, a = 16.623(4), c = 14.834(9) Å, U = 3 549.8 Å^3, D_c = 1.263, D_m = 1.27 g cm^{-3} (by flotation), Z = 3, space group $P3_221$, μ = 3.81 cm^{-1} for Mo-K_α radiation (λ 0.710 7 Å).

A crystal of the trigonal hydrate with dimensions 0.17 × 0.15 × 0.45 mm was employed for the structure determination, the crystal being sealed in a glass capillary tube to minimise loss of water of hydration. Intensities were measured with Mo-K_α radiation using a Nonius CAD-4 automatic diffractometer operated in the θ–2θ scan mode, up to 2θ 40°. Of the 1 540 observed reflections, 1 076 with $|F_0| \geqslant 4\sigma$ were used for the refinement. These reflections were independent under the Laue group. No corrections for absorption were made.

Structure Determination.—The cobalt atom, and the nitrogen and oxygen atoms of one of the nitrate ions, are necessarily located on sets of three-fold special positions by the requirements of the space group. The co-ordinates of the cobalt atom were obtained from the three-dimensional Patterson map. Fourier synthesis and least-squares refinement, with the aid of the known geometry of the nitrate ion, subsequently indicated the positions of all the non-hydrogen atoms. Using anisotropic temperature factors for atoms other than those of the phenyl substituents in the chelate rings of the complex ion, R was reduced to 0.094. The positional parameters obtained were used to calculate the idealised bonded positions of the hydrogen atoms, except for those of the water molecule, and a difference-Fourier synthesis at this stage supported the positions calculated.

A final full-matrix least-squares refinement was carried out with the hydrogen atoms located at their idealised bonded positions and each phenyl substituent constrained to a regular hexagonal geometry with a C–C bond length of 1.395 Å. Anisotropic and isotropic temperature factors were applied for non-hydrogen and for hydrogen atoms, respectively. A common temperature factor was adopted for each of the carbon atoms of a given phenyl ring in order to optimise the ratio of the number of observed reflections to the number of parameters. A correction for the anomalous scattering due to the cobalt atom was made and equal weight was assigned to all the reflections. The final R value was 0.085. The atomic scattering factors and the correction for anomalous scattering were taken from ref. 12; scattering factors for the hydrogen atoms were those given by Stewart *et al*.[13] Calculations were made on the University of London CDC 7600 computer, using the program SHELX, written by Dr. G. Sheldrick, and '*X*-Ray ' 72'. The final set of atomic parameters is listed in Table 1. The observed and calculated structure amplitudes and the thermal parameters of the atoms are listed in Supplementary Publication No. SUP 22016 (8 pp.).*

Determination of the Absolute Configuration of the Complex Ion.—Equi-inclination Weissenberg photographs were taken of the zeroth to second layer lines around the crystal c axis with Cu-K_α radiation. The relations between $F_c^2(hkil)$ and $F_c^2(\bar{h}\bar{i}\bar{k}l)$, calculated for the Λ configuration of the complex ion, are compared with those observed in Table 2. The agreement found indicates that $(+)[\mathrm{Co}\{(-)\mathrm{dpen}\}_3]^{3+}$ has a *lel* form [7] with the Λ configuration and a δ conformation of each chelate ring (Figure 1). Accordingly the laevorotatory

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1976, Index issue. (Items less than 10 pp. are supplied as full-size copies.)

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TABLE 1

Fractional atomic co-ordinates ($\times 10^4$) with estimated standard deviations

	x	y	z
Co	5 760(2)	5 760(2)	5 000
N(1)	5 050(10)	4 681(10)	5 829(9)
N(2)	5 210(10)	6 481(10)	5 548(9)
N(3)	6 704(10)	6 387(11)	5 924(10)
C(1)	4 321(13)	3 893(11)	5 289(14)
C(2)	5 873(12)	7 201(14)	6 147(12)
C(3)	6 330(13)	6 734(11)	6 657(11)
C(11)	3 630(11)	3 190(9)	6 002(9)
C(12)	2 733(11)	3 043(9)	6 112(9)
C(13)	2 180(11)	2 493(9)	6 821(9)
C(14)	2 524(11)	2 091(9)	7 420(9)
C(15)	3 421(11)	2 238(9)	7 310(9)
C(16)	3 974(11)	2 788(9)	6 601(9)
C(21)	5 350(11)	7 515(11)	6 786(9)
C(22)	5 328(11)	8 303(11)	6 502(9)
C(23)	4 812(11)	8 611(11)	6 984(9)
C(24)	4 319(11)	8 131(11)	7 749(9)
C(25)	4 341(11)	7 342(11)	8 034(9)
C(26)	4 857(11)	7 034(11)	7 552(9)
C(31)	7 110(12)	7 331(12)	7 316(9)
C(32)	7 772(12)	8 249(12)	7 122(9)
C(33)	8 513(12)	8 747(12)	7 710(9)
C(34)	8 593(12)	8 326(12)	8 492(9)
C(35)	7 931(12)	7 408(12)	8 686(9)
C(36)	7 189(12)	6 910(12)	8 098(9)
N(4)	1 506(20)	0	1 667
N(5)	2 605(14)	5 226(12)	6 703(14)
O(1)	788(15)	0	1 667
O(2)	2 265(13)	745(13)	1 707(12)
O(3)	1 937(13)	5 310(13)	6 542(11)
O(4)	3 229(13)	5 415(13)	6 137(12)
O(5)	2 634(13)	4 916(13)	7 463(13)
O(6)	9 532(13)	5 211(11)	5 703(13)

TABLE 2

Determination of the absolute configuration. Relations between $F_c^2(hkil)$ and $F_c^2(\bar{h}i\bar{k}l)$ observed and calculated for the Λ configuration *

h	k	l	$F_c^2(hkil)$	Relation	$F_c^2(\bar{h}i\bar{k}l)$
3	0	0	2 052	>	882
2	2	1	9 584	>	7 073
3	4	1	497	<	1 136
−6	4	1	299	<	751
−8	5	1	2 411	<	3 672
1	7	2	713	<	1 608
2	4	2	930	>	182
−10	9	2	66	<	296

* $i = -(h + k)$.

isomer of dpen has the *S,S* configuration. The complex (+)[Co{(−)dpen}$_3$]$^{3+}$ exhibits two c.d. bands of opposite sign in the region of the $^1A_1 \rightarrow {}^1T_1$ octahedral absorption ($\Delta\varepsilon$ +2.4 at 505, $\Delta\varepsilon$ −0.55 at 444 nm),[4,5,11] the major c.d. band being positive and at the lower frequency, as is generally observed for the *lel* isomers with the Λ configuration of the tris(1,2-diamine) complexes formed by Co^{III}.[2]

DISCUSSION

In the trigonal nitrate crystal the complex cation (+)-[Co{(−)dpen}$_3$]$^{3+}$ has rigorous C_2 symmetry but only quasi-D_3 symmetry. The C_2 axis relates the primed to the corresponding unprimed chelate ring or phenyl substituent in Figure 1, which represents a perspective projection of the complex ion on a plane perpendicular to the quasi-three-fold axis. Excluding the phenyl substituents, the complex ion has D_3 symmetry and the C–C bond of each chelate ring is nearly parallel to the C_3 axis, the angle of inclination being 3°. Thus the complex ion is a (*lel*)$_3$ isomer. The five-membered chelate rings are puckered in the δ conformation with each phenyl substituent in the quasi-equatorial position. The interatomic distances and bond angles within the complex and the nitrate ions are given in Table 3. The Co–N distances range from 1.95(2) to 2.00(1) Å, and the N–Co–N angles within a chelate ring are 84.0(8) and 83.2(6)°. These structural features of the chelate rings are similar

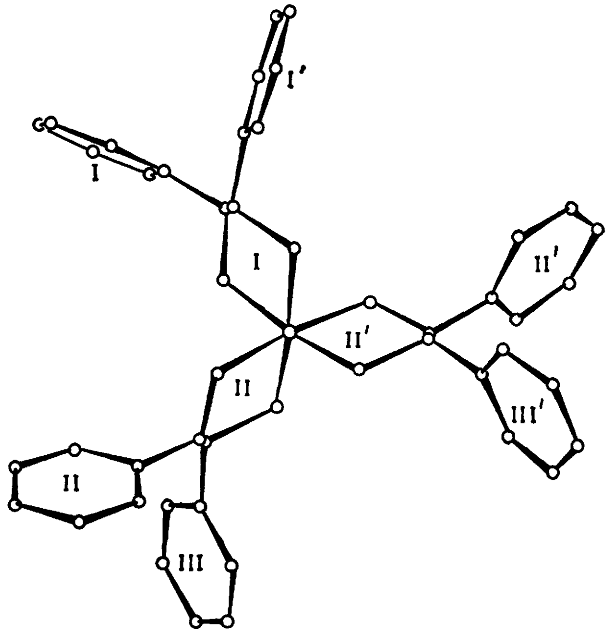

FIGURE 1 Structure of Λ(+)[Co{(−)dpen}$_3$δδδ]$^{3+}$ projected on a plane perpendicular to the quasi-three-fold axis. The primed phenyl substituents and chelate ring are related to the corresponding unprimed structural elements by a two-fold rotation

TABLE 3

Bond lengths (Å) and angles (°) in the complex ion and the nitrate ion

(*i*) Complex ion			
Co–N(1)	2.00(1)	C(2)–C(3)	1.53(2)
N(1)–C(1)	1.50(2)	C(3)–C(31)	1.53(2)
C(1)–C(1′) *	1.50(3)	Co–N(3)	1.95(1)
C(2)–C(21)	1.54(2)	N(3)–C(3)	1.50(2)
Co–N(2)	2.01(1)	C(1)–C(11)	1.57(2)
N(2)–C(2)	1.46(2)		
N(1)–Co–N(1′)	83.9(8)	N(2)–Co–N(3)	83.2(6)
Co–N(1)–C(1)	108(1)	Co–N(2)–C(2)	111(1)
Co–N(3)–C(3)	110(1)	N(1)–C(1)–C(1′)	105(1)
N(2)–C(2)–C(3)	104(1)	N(3)–C(3)–C(2)	104(1)
N(1)–C(1)–C(11)	105(1)	N(2)–C(2)–C(21)	109(1)
N(3)–C(3)–C(31)	110(1)	C(1′)–C(1)–C(11)	114(1)
C(3)–C(2)–C(21)	112(1)	C(2)–C(3)–C(31)	118(1)
(*ii*) Nitrate ions			
N(4)–O(1)	1.19(3)	N(5)–O(5)	1.25(2)
N(5)–O(4)	1.25(2)	N(5)–O(3)	1.21(2)
N(4)–O(2)	1.25(2)		
O(1)–N(4)–O(2)	121(2)	O(2)–N(4)–O(2′)	118(3)
O(3)–N(5)–O(4)	122(2)	O(3)–N(5)–O(5)	117(2)
O(4)–N(5)–O(5)	121(2)		

* A primed atom is related to the corresponding unprimed atom by a two-fold rotation.

to those of other (*lel*)$_3$ tris(1,2-diamine)cobalt(III) complexes.[14,15]

The [CoN_6] co-ordination octahedron is compressed along the three-fold axis to a small degree and, at the same time, contracted in the azimuthal plane from regular octahedral geometry. The Co–N bonds are inclined at an angle of *ca.* 56° to the three-fold axis, compared with the corresponding angle of 54.75° for a regular octahedron. The azimuthal projection N–Co–N angle within a chelate ring, which is 60° for a regular octahedron, is contracted to *ca.* 52°, representing an anticlockwise rotation of the upper triangle of three nitrogen atoms relative to the corresponding lower triangle of 8° (Figure 1). This angle of azimuthal distortion is significantly larger than the corresponding distortion angle of 5° observed [14] for $\Lambda(+)[Co(en)_3\delta\delta\delta]^{3+}$ (en = ethylenediamine) or of 5.9° found [15] in the case of $\Delta(-)[Co\{(R)pn\}_3\lambda\lambda\lambda]^{3+}$ (pn = propylenediamine).

The molecular planes of the two phenyl substituents in a given chelate ring have a nearly perpendicular mutual orientation, the angle between the two planes being 85 and 89° for chelate ring (I) and (II) or (II′), respectively (Figure 1). The rotation angles of the phenyl substituents about the exocyclic C–C bond to a chelate ring are not uniform in the complex ion. The molecular plane of phenyl ring (I) is inclined at an angle of 47° to the mean plane of chelate ring (I), whereas the molecular planes of phenyl groups (II) and (III) are oriented at an angle of 73 and 74°, respectively, to the mean plane of chelate ring (II) (Figure 1). The major difference of orientation arises from the proximity of a water molecule to phenyl ring (I) in the unit cell. The close contact between the water molecule and phenyl group (I) precludes rotation of the latter about the exocyclic C–C bond to give the complex ion D_3 symmetry overall.

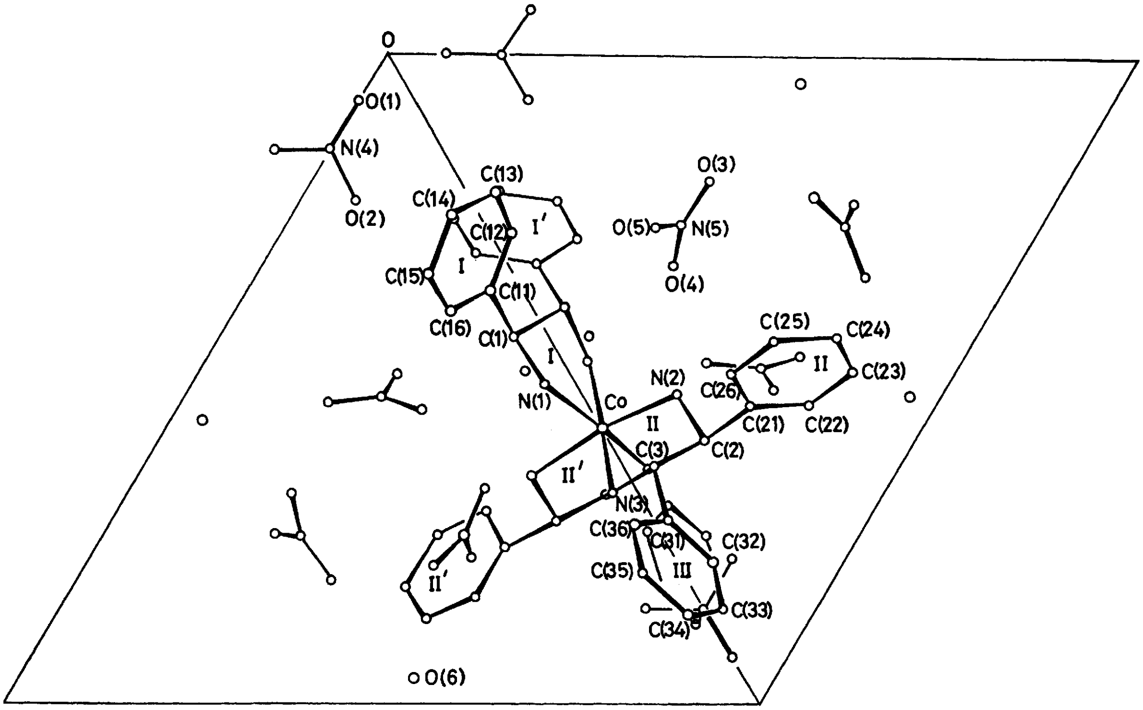

FIGURE 2 Partial projection of the crystal structure of $(+)[Co\{(-)dpen\}_3][NO_3]_3{\cdot}H_2O$ on a plane perpendicular to the crystal *c* axis

TABLE 4

Shorter interatomic distances (Å) external to the complex and the nitrate ions

N(1) ··· O(6^{V})	2.98	N(1) ··· O(3^{VI})	2.98*
N(2) ··· O(4)	2.99 *	N(2) ··· O(5^{II})	3.02
N(3) ··· O(2^{IV})	2.97 *	N(3) ··· O(3^{VI})	3.04
O(5^{VI}) ··· O(5)	2.93 *	N(3) ··· O(2^{III})	3.34
N(3) ··· O(5^{VI})	3.34	C(1) ··· O(4^{I})	3.32
C(2) ··· O(2^{III})	3.26	C(11) ··· O(6^{V})	3.34
C(13) ··· O(2^{I})	3.11	C(14) ··· O(2^{I})	3.37
C(26) ··· O(6^{V})	3.38	C(26) ··· O(4)	3.42
C(32) ··· O(2^{III})	3.24	C(32) ··· N(4^{IV})	3.32
C(33) ··· O(1^{VII})	3.18		

I $y, x, 1 - z$
II $1 - y, 1 + x - y, -\frac{1}{3} + z$
III $1 - x, 1 - x + y, \frac{2}{3} - z$
IV $1 - x + y, 1 - x, \frac{1}{3} + z$
V $x - y, 1 - y, \frac{4}{3} - z$
VI $1 + x - y, 1 - y, \frac{4}{3} - z$
VII $y, 1 + x, 1 - z$

* Substantial hydrogen bonding with a large X–H ··· Y angle. Hydrogen bonding is less certain in the other cases.

A partial projection of the structure along the crystal *c* axis with the numbering scheme is illustrated in Figure 2. The two independent nitrate ions are planar, although only one of these is necessarily planar from the symmetry of the space group. The closer contacts between the complex ion, the nitrate ions, and the water molecules are listed in Table 4. One of the hydrogen atoms of the water molecule was not located, but the O(6) ··· O(5^{VI})

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[14] M. Iwata, K. Nakatsu, and Y. Saito, *Acta Cryst.*, 1969, **B25**, 2562.

[15] R. Kuroda, N. Shimanouchi, and Y. Saito, *Acta Cryst.*, 1975, **B31**, 931.

distance of 2.93 Å indicates the probability of a hydrogen bond between these two oxygen atoms. Each of the three independent amino-nitrogen atoms is hydrogen-bonded to an oxygen atom of the nitrate ion (Table 4).

The uniaxial crystal system of the trigonal hydrate allows a direct determination of the single-crystal axial c.d. spectrum of the complex ion. Estimation of the rotational strengths of the complex from the crystal c.d. measurements, which are in progress, requires a correction [16] for the angle of inclination between the three-fold axis of the complex and the *c* axis of the unit cell, the angle being 58° in the present case. The rotational strengths obtained from the crystal c.d. spectrum are to be compared with the corresponding quantities calculated from the dynamic-coupling ligand-polarisation model.[3]

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