

Table 4. *Equations of mean planes with atomic displacements*

The equation of the plane is $lX + mY + nZ - P = 0$ where X , Y and Z are fractional coordinates and P is the origin-to-plane distance in Å.

Plane	Atoms (displacements in Å)			Equation
1	Co	S	C(2)	$-0.1047X - 0.4184Y + 0.9022Z + 2.2770 = 0$
2	S(-0.002)	C(2)(0.007)		$0.3102X + 0.6096Y + 0.7294Z - 7.3196 = 0$
	N(1)(-0.002)	N(3)(-0.002)		
3	S(-0.008)	C(2)(0.012)		$0.3173X + 0.6113Y + 0.7250Z - 7.3725 = 0$
	N(1)(0.014)	C(4)(-0.011)		
	C(5)(0.001)	N(3)(0.001)		
	C(1)(-0.009)			
	Displacement of Co atom from plane 3 = 2.062			Dihedral angles (°) with e.s.d.'s in parentheses
				$P1$ and $P2$ 68.3 (1.5)
				$P1$ and $P3$ 68.6 (1.5)
				$P2$ and $P3$ 0.5 (1.0)

Within the unit cell the four cations are grouped in pairs around symmetry centres (Fig. 2). Two types of H-bond involving N(3)—H(3)···O(1) contacts (2.872 Å) occur. One type involves both O(1) atoms from the same perchlorate group and N—H groups from different ligands but in the same cation; in the other case, O(1) atoms link N—H groups from neighbouring cations into extended chains of H-bonds along **b**.

All calculations were performed on the NUMAC IBM 370/167 computer at the University of Newcastle upon Tyne, England. *SHELX* (Sheldrick, 1976) and related programs were used in the analysis.

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The Crystal Structure of Δ, Δ - μ -Hydroxo-bis[bis(ethylenediamine)hydroxochromium(III)] Triperchlorate Monohydrate

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Abstract

$[(\text{OH})(\text{en})_2\text{Cr}(\text{OH})\text{Cr}(\text{en})_2(\text{OH})](\text{ClO}_4)_3 \cdot \text{H}_2\text{O}$, $[\text{Cr}_2(\text{C}_2\text{H}_8\text{N}_2)_4(\text{OH})_3](\text{ClO}_4)_3 \cdot \text{H}_2\text{O}$, $\text{C}_8\text{H}_{35}\text{Cr}_2\text{N}_8\text{O}_3^+$, $3\text{ClO}_4^- \cdot \text{H}_2\text{O}$, crystallizes in space group $P2_1/c$, with

$a = 12.426$ (6), $b = 12.027$ (4), $c = 18.343$ (7) Å, $\beta = 104.13$ (4)°, $Z = 4$. The structure was refined to $R = 0.072$ for 3604 diffractometer intensities. The conformation of the complex ion is ${}^s\Delta\Delta_1^s$ and the Cr···Cr separation is 3.677 (2) Å. The complex ion has an intra-

molecular hydrogen bond [2.729 (6) Å] between the two terminal OH groups. The Cr—O—Cr angle of $135.4(2)^\circ$ is considerably smaller than the 166° found in the acid *rhodo* cation $[(\text{NH}_3)_5\text{Cr}(\text{OH})\text{Cr}(\text{NH}_3)_5]^{3+}$. The crystal structure is extensively hydrogen bonded.

Introduction

Binuclear Cr^{III} compounds with OH as a bridging ligand have been the subject of studies at this laboratory (Springborg & Toftlund, 1975, 1976*a,b*, 1979; Springborg, 1978; Springborg & Schäffer, 1976*a,b*, 1978; Kaas, 1976, 1979). The present structure analysis was initiated to establish the structure of the monohydroxo-bridged product formed in the reversible ring opening of the Δ, Δ -di- μ -hydroxo-bis[bis(ethylenediamine)chromium(III)] cation (Springborg & Toftlund, 1975, 1976*b*). The crystal structures of two salts of the latter have been reported (Kaas, 1976; Cline, Scaringe, Hatfield & Hodgson, 1977).

Experimental

The red prismatic crystal used for data collection was provided by J. Springborg (Springborg & Toftlund, 1976*a,b*). Photographs showed that $h0l$ were absent for $l \neq 2n$ and $0k0$ for $k \neq 2n$, so that the space group is $P2_1/c$. The cell dimensions obtained by least-squares refinement of 16 diffractometer-measured 2θ angles (Mo $K\alpha$, $\lambda = 0.71069$ Å) are $a = 12.426(6)$, $b = 12.027(4)$, $c = 18.343(7)$ Å, $\beta = 104.13(4)^\circ$, $V = 2658$ Å³.

The formula weight is 711.8 ($\text{C}_8\text{H}_{37}\text{Cl}_3\text{Cr}_2\text{N}_8\text{O}_{16}$); $D_o = 1.78$ measured by flotation at 295 K, $D_c = 1.79$ Mg m⁻³ for $Z = 4$, corresponding to one formula unit (*i.e.* one complex ion, three perchlorate ions and one water molecule) per asymmetric unit. $\mu(\text{Mo } K\alpha) = 1.24$ mm⁻¹. All X-ray data were obtained on a Nonius three-circle automatic diffractometer with graphite-monochromated Mo $K\alpha$ radiation.

A crystal of average diameter 0.3 mm was sealed in a glass capillary and oriented with a along the ϕ axis of the goniometer. The ω scanning mode was used with scan speed $1.2^\circ \text{ min}^{-1}$. Each reflexion was scanned over a range of 1.2° , and the background was measured at each of the scan-range limits for half the scanning time. A standard reflexion was remeasured after every 25 reflexions. The intensities of all 4760 independent reflexions in a quarter of a sphere in reciprocal space in the range $2.5 \leq \theta \leq 25.0^\circ$ were measured. In the range $2.5 \leq \theta \leq 20.0^\circ$ all reflexions in a hemisphere were measured and in this range an average of the intensities of two symmetry-related reflexions was used. 3604 reflexions having structure factors greater than 3.0 times their e.s.d.'s obtained

from counting statistics were considered observed and used in the subsequent refinement. No absorption corrections were applied.

Determination and refinement of the structure

The two Cr atoms and two of the Cl atoms were located by a combination of Patterson and direct methods (*MULTAN*; Main, Woolfson, Declercq & Germain, 1974). The remaining non-hydrogen atoms were found by heavy-atom methods. The input tapes for the diffractometer were produced by the program *INDIFF* (Sørensen, unpublished), and the preliminary data reduction by *NRC2* (Ahmed, 1966) (revised by Alcock & Sørensen). The XRAY system (Stewart, Kruger, Ammon, Dickinson & Hall, 1972) was used for the remaining calculations. All atoms were assumed to be uncharged and the scattering factors of the XRAY system were used. Correction for anomalous dispersion was included for Cr atoms (*International Tables for X-ray Crystallography*, 1962).

Isotropic full-matrix least-squares refinement led to an R of 0.14. Introduction of anisotropic temperature factors for all atoms except C and N led to an R of 0.10. A difference map at this stage showed all H atoms except those of the water molecule and one of the terminal OH groups. The positions of the peaks ($0.4\text{--}0.9 \text{ e } \text{Å}^{-3}$) were in accordance with the calculated positions (C—H = 1.00, N—H = 0.90, and O—H = 0.85 Å). The H atoms were inserted at calculated positions. The H atoms of the water molecule and the terminal OH groups were inserted on the lines representing the respective hydrogen bonds (Table 5).

In the following cycles of full-matrix least-squares refinement, anisotropic temperature factors were used for all non-hydrogen atoms. The H atom parameters were not refined, but were calculated from the positions of the atoms to which they are bonded (U was set to 0.06 Å²). The parameters had to be divided into three blocks owing to capacity restrictions of the least-squares program. The final R was 0.072 for 3604 reflexions. The quantity minimized was $\sum w(|F_o| - |F_c|)^2$. At this stage the shifts of all parameters were < 0.4 times their e.s.d.'s (average shift/error 0.04). During the later stages of refinement the weighting scheme was $1/w = 0.00004|F|^3 + 0.0018|F|^2 - 0.0014|F| + 0.32\sigma^2(F) + 3.10$; the coefficients were fitted by the program *WTRFA* (Nielsen, 1977). The drawings were prepared by *ORTEP II* (Johnson, 1971). The final atomic positions of the non-hydrogen atoms are listed in Table 1.*

* Lists of structure factors, thermal parameters and H atom positional parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34358 (20 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Final atomic positions (and *e.s.d.*'s) of non-hydrogen atoms ($\times 10^4$)

	<i>x</i>	<i>y</i>	<i>z</i>
Cr(1)	8018 (1)	3566 (1)	4085 (1)
Cr(2)	7657 (1)	6602 (1)	4009 (1)
O(1)	8592 (4)	4173 (4)	5059 (2)
O(2)	7507 (3)	5041 (3)	3644 (2)
O(3)	8990 (3)	6335 (4)	4755 (3)
N(11)	8466 (4)	2013 (4)	4579 (3)
N(12)	6516 (4)	3124 (5)	4350 (3)
N(13)	9498 (4)	3732 (4)	3758 (3)
N(14)	7533 (5)	2825 (5)	3003 (3)
N(21)	6727 (4)	6245 (4)	4792 (3)
N(22)	7672 (4)	8196 (4)	4487 (3)
N(23)	8470 (4)	7114 (5)	3191 (3)
N(24)	6253 (4)	7068 (4)	3161 (3)
C(11)	7515 (8)	1425 (9)	4717 (7)
C(12)	6702 (8)	2148 (7)	4836 (7)
C(13)	9486 (6)	3075 (6)	3076 (4)
C(14)	8341 (7)	3150 (6)	2565 (4)
C(21)	6430 (7)	7278 (7)	5133 (5)
C(22)	7355 (7)	8083 (6)	5219 (4)
C(23)	7665 (6)	7240 (6)	2462 (4)
C(24)	6624 (6)	7763 (6)	2592 (4)
Cl(1)	9987 (2)	4937 (1)	1319 (1)
O(11)	9594 (5)	5627 (5)	678 (3)
O(12)	9774 (7)	3798 (5)	1138 (4)
O(13)	9461 (10)	5279 (7)	1885 (5)
O(14)	11145 (7)	5104 (7)	1558 (6)
Cl(2)	6156 (1)	455 (2)	1419 (1)
O(21)	7126 (6)	-205 (7)	1447 (5)
O(22)	5917 (13)	990 (19)	768 (12)
O(23)	6240 (11)	1128 (18)	1960 (14)
O(24)	5244 (5)	-224 (7)	1388 (6)
Cl(3)	5414 (2)	4872 (2)	1494 (1)
O(31)	5883 (7)	4596 (8)	2226 (4)
O(32)	4462 (7)	4331 (8)	1200 (5)
O(33)	6166 (15)	4837 (14)	1058 (8)
O(34)	5137 (11)	6034 (8)	1534 (7)
O(4)	9405 (4)	935 (5)	1535 (3)

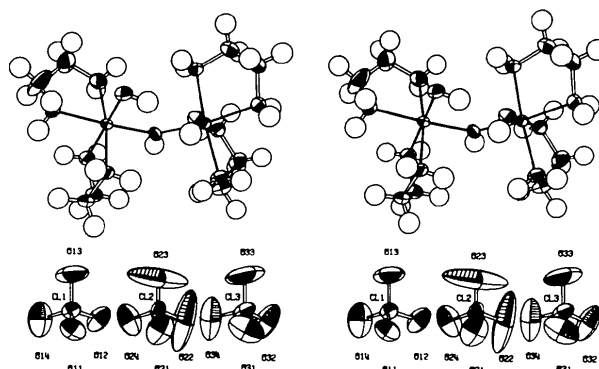
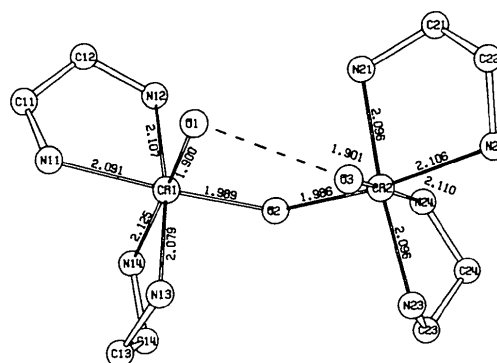
Fig. 1. Stereoscopic ORTEP drawing of the complex cation (the labelling is shown in Fig. 2) and the perchlorate anions (arbitrarily placed). The thermal ellipsoids enclose 50% probability. The conformation of the cation is δA_1^2 .

Fig. 2. Bond distances (Å) in the coordination octahedra. The angles are Cr(1)—O(2)—Cr(2) 135.4, O(1)—Cr(1)—O(2) 92.8, and O(2)—Cr(2)—O(3) 94.4°.

Description and discussion of the structure

The structure consists of binuclear Δ, Δ -[(OH)(en)₂-Cr(OH)Cr(en)₂(OH)]³⁺ cations, ClO₄⁻ anions, and water molecules held together by hydrogen bonds and electrostatic forces.

Conformation of the complex ion

The cation is shown in Fig. 1, and the atomic labelling and the bond distances of the inner coordination sphere in Fig. 2. All bond distances and angles in the cation are given in Table 2.

Both the present cation and the sulfato bridged species Δ, Δ -[(en)₂Cr(OH)(SO₄)Cr(en)₂]³⁺ are formed from the diol Δ, Δ -[(en)₂Cr(OH)₂(en)₂]⁴⁺ (Springborg, 1978). In the following discussion, in which their geometries are compared, these three binuclear cations are denoted the monool, the sulfato complex and the diol, respectively.

Only one other crystal structure of a monohydroxo-bridged Cr complex is known, that of the acid *rhodo* chloride monohydrate, *i.e.* [(NH₃)₅Cr(OH)Cr(NH₃)₅].Cl₅.H₂O (Veal, Jeter, Hempel, Eckberg, Hatfield & Hodgson, 1973), although crude data for the acid *erythro* halide monohydrate [(NH₃)₅Cr(OH)-Cr(NH₃)₄(H₂O)].X₅.H₂O (X = Cl or Br) have been reported (Yevitz & Stanko, 1971). Another compound of interest in this context is the basic *rhodo* chloride monohydrate [(NH₃)₅CrOCr(NH₃)₅].Cl₄.H₂O (Yevitz & Stanko, 1971) which, however, has a linear oxo bridge. The main structural parameters for the bridges in these compounds are summarized in Table 3.

The eight independent Cr—N distances in the monool are in the range 2.079 (6) to 2.125 (6) Å, the two longest distances being those *trans* to the terminal OH groups. This is entirely consistent with the values reported for the other compounds mentioned, although in the acid *rhodo* the longest Cr—N distance [2.15 (2) Å] is found for the bond *trans* to the bridging OH group.

The terminal Cr—O distances of 1.900 (4) and 1.901 (4) Å are, as expected, less than the Cr—O distances in the bridge (Table 3). No Cr—O distance in a terminal Cr—OH bond has been reported previously.

Table 3 shows that the geometry of the Cr—OH—Cr system of the monool does not resemble those of the other monobridged systems, *viz* the acid *rhodo* and the acid *erythro*, the bridging Cr—O—Cr angle being considerably smaller in the former. In fact, the parameters for the monool are very close to those for the sulfato complex. This is probably a consequence of the intramolecular hydrogen bonding between the two

terminal OH groups of the monool. A similar but more symmetric hydrogen-bond stabilization was proposed for the aquahydroxo-monool [(H₂O)(en)₂Cr(OH)Cr(en)₂(OH)]⁴⁺ by Springborg & Toftlund (1976*a,b*) to account for the relatively high thermodynamic stability of the latter and thereby for the unexpectedly low p*K*_{a1} of the diaqua-monool.

Torsion angles of the bridging system are given in Table 4.

The pseudo threefold axes of the coordination octahedra in the monool and the sulfato complexes make angles of about 49°, whereas in the structures of the other compounds mentioned above they are parallel.

The dimensions of the chelate diamine rings are all very similar, although the relatively large e.s.d.'s and the temperature factors of C(11) and C(12) of the monool, probably due to disorder of these atoms, do not allow detailed comparison. In the monool C(13)—C(14) and C(21)—C(22) are nearly parallel to the pseudo-threefold axes (the angles are 7 and 9°, respectively) whereas C(11)—C(12) and C(23)—C(24) make angles of 53 and 63°, respectively. The conformation can be described as ^δ_λΔA_λ^δ. The conformation in the diol is ^λ_λΔA_δ^δ and in the sulfato complex ^λ_δΔA_λ^δ. [For a description of the nomenclature see Thewalt, Jensen & Schäffer (1972).]

All three O—H and most of the N—H groups in the monool act as donors in hydrogen bonds. There are two hydrogen bonds to the water molecule, two to a neighboring cation, and the remainder to the perchlorate ions.

Perchlorate ion

The three crystallographically independent ClO₄⁻ ions are shown in Fig. 1 with the atomic labelling. Some

Table 2. *Interatomic distances (Å) and angles (°)*

Cr(1)···Cr(2)	3.677 (2)	Cr(2)—O(3)	1.901 (4)
Cr(1)—O(1)	1.900 (4)	Cr(2)—O(2)	1.986 (4)
Cr(1)—O(2)	1.989 (4)	Cr(2)—N(22)	2.106 (5)
Cr(1)—N(11)	2.091 (5)	Cr(2)—N(21)	2.096 (5)
Cr(1)—N(12)	2.107 (6)	Cr(2)—N(23)	2.096 (6)
Cr(1)—N(13)	2.079 (6)	Cr(2)—N(24)	2.111 (5)
Cr(1)—N(14)	2.125 (6)	N(22)—C(22)	1.495 (11)
N(11)—C(11)	1.451 (12)	N(21)—C(21)	1.478 (10)
N(12)—C(12)	1.458 (12)	N(23)—C(23)	1.470 (8)
N(13)—C(13)	1.478 (9)	N(24)—C(24)	1.494 (10)
N(14)—C(14)	1.484 (11)	C(21)—C(22)	1.481 (12)
C(11)—C(12)	1.390 (14)	C(23)—C(24)	1.509 (11)
C(13)—C(14)	1.502 (10)		
O(1)—Cr(1)—O(2)	92.8 (2)	O(3)—Cr(2)—O(2)	94.4 (2)
O(1)—Cr(1)—N(11)	86.4 (2)	O(3)—Cr(2)—N(22)	86.4 (2)
O(1)—Cr(1)—N(12)	91.8 (2)	O(3)—Cr(2)—N(21)	90.1 (2)
O(1)—Cr(1)—N(13)	94.5 (2)	O(3)—Cr(2)—N(23)	94.5 (2)
O(2)—Cr(1)—N(12)	96.1 (2)	O(2)—Cr(2)—N(21)	90.9 (2)
O(2)—Cr(1)—N(13)	90.8 (2)	O(2)—Cr(2)—N(23)	93.3 (2)
O(2)—Cr(1)—N(14)	90.3 (2)	O(2)—Cr(2)—N(24)	90.6 (2)
N(11)—Cr(1)—N(12)	80.3 (2)	N(21)—Cr(2)—N(22)	81.5 (2)
N(11)—Cr(1)—N(13)	92.9 (2)	N(22)—Cr(2)—N(23)	94.2 (2)
N(11)—Cr(1)—N(14)	90.8 (2)	N(22)—Cr(2)—N(24)	89.2 (2)
N(12)—Cr(1)—N(14)	92.5 (2)	N(21)—Cr(2)—N(24)	93.7 (2)
N(13)—Cr(1)—N(14)	80.8 (2)	N(23)—Cr(2)—N(24)	81.4 (2)
Cr(1)—N(11)—C(11)	111.6 (5)	Cr(2)—N(22)—C(22)	108.3 (4)
Cr(1)—N(12)—C(12)	109.1 (5)	Cr(2)—N(21)—C(21)	110.7 (5)
Cr(1)—N(13)—C(13)	111.5 (4)	Cr(2)—N(23)—C(23)	110.0 (4)
Cr(1)—N(14)—C(14)	108.7 (4)	Cr(2)—N(24)—C(24)	108.9 (4)
N(11)—C(11)—C(12)	112.1 (8)	N(22)—C(22)—C(21)	109.3 (6)
C(11)—C(12)—N(12)	114.8 (10)	N(21)—C(21)—C(22)	109.1 (7)
N(13)—C(13)—C(14)	107.9 (6)	N(23)—C(23)—C(24)	108.6 (6)
C(13)—C(14)—N(14)	108.0 (6)	C(23)—C(24)—N(24)	107.4 (6)
Cr(1)—O(2)—Cr(2)	135.4 (2)		

Table 3. *Geometry of the bridging Cr—OH—Cr system*

		Mean bridging Cr—O distance (Å)	Cr—O—Cr angle (°)	Cr···Cr distance (Å)
Diol	[(en) ₂ Cr(OH) ₂ Cr(en) ₂] ⁴⁺	(a) 1.952 (2)	103.42 (8)	3.059 (2)
	[(en) ₂ Cr(OH) ₂ Cr(en) ₂] ⁴⁺	(b) 1.979 (5)	100.0 (2)	3.032 (3)
Monool	[(OH)(en) ₂ Cr(OH)Cr(en) ₂ (OH)] ³⁺	1.988 (6)	135.4 (2)	3.677 (2)
Sulfato	[(en) ₂ Cr(SO ₄)(OH)Cr(en) ₂] ³⁺	(c) 1.989 (4)	137.4 (2)	3.706 (2)
Acid <i>rhodo</i>	[(NH ₃) ₅ Cr(OH)Cr(NH ₃) ₅] ⁵⁺	(d) 1.94 (2)	166 (1)	3.852 (9)
Acid <i>erythro</i>	[(NH ₃) ₅ Cr(OH)Cr(NH ₃) ₄ H ₂ O] ⁵⁺	(e) 1.989 (4)	168 (5)	3.91 (5)
Basic <i>rhodo</i>	[(NH ₃) ₅ CrOCr(NH ₃) ₅] ⁴⁺	(e) 1.821 (3)	180.0	3.642 (1)

References: (a) Kaas (1976). (b) Cline *et al.* (1977). (c) Kaas (1979). (d) Veal *et al.* (1973). (e) Yevitz & Stanko (1971).

of the O atom temperature factors did not refine well, the largest being $U_{33} = 0.52(3) \text{ \AA}^2$ for O(23).

Water molecule

The water molecule is involved in four hydrogen bonds. The water H(36) and H(37) atoms were placed on the respective lines connecting the water O(4) and a terminal OH group of the complex ion [O(1)] and the nearest perchlorate ion [O(13)] (Table 4). The water O atom acts as acceptor in hydrogen bonds from two N—H groups of one complex cation.

Table 5. Hydrogen-bond distances (\AA) and angles ($^\circ$)

Key to symmetry operations

(i)	$2-x, 1-y, 1-z$	(iv)	$2-x, y+\frac{1}{2}, \frac{1}{2}-z$
(ii)	$x, \frac{1}{2}-y, z+\frac{1}{2}$	(v)	$x, \frac{1}{2}-y, z-\frac{1}{2}$
(iii)	$2-x, y-\frac{1}{2}, \frac{1}{2}-z$	(vi)	$1-x, y-\frac{1}{2}, \frac{1}{2}-z$

$D-H\cdots A$	$D\cdots A$	$H\cdots A$	$\angle D-H\cdots A$
O(3 ⁱ)-H(3 ⁱ) \cdots O(1)	3.004 (6)	2.10	180
O(4 ⁱⁱ)-H(36 ⁱⁱ) \cdots O(1)	2.652 (6)	1.75	180
O(1)-H(1) \cdots O(3)	2.729 (6)	1.83	180
N(13 ⁱ)-H(12 ⁱ) \cdots O(3)	2.91 (6)	2.10	150
N(13 ⁱⁱⁱ)-H(13 ⁱⁱⁱ) \cdots O(4)	3.086 (8)	2.24	156
N(23 ⁱⁱⁱ)-H(28 ⁱⁱⁱ) \cdots O(4)	2.930 (8)	2.11	152
N(11 ^v)-H(4 ^v) \cdots O(12)	3.082 (8)	2.32	142
N(23 ⁱⁱⁱ)-H(29 ⁱⁱⁱ) \cdots O(12)	3.011 (9)	2.18	154
O(4 ^{iv})-H(37 ^{iv}) \cdots O(13)	3.002 (10)	2.10	180
N(11 ^v)-H(5 ^v) \cdots O(14)	3.216 (12)	2.38	155
N(12 ^v)-H(10 ^v) \cdots O(22)	3.066 (24)	2.34	137
O(2)-H(2) \cdots O(31)	2.925 (8)	2.11	162
N(14)-H(19) \cdots O(31)	3.057 (10)	2.29	144
N(22 ^{vi})-H(27 ^{vi}) \cdots O(32)	2.975 (10)	2.15	151

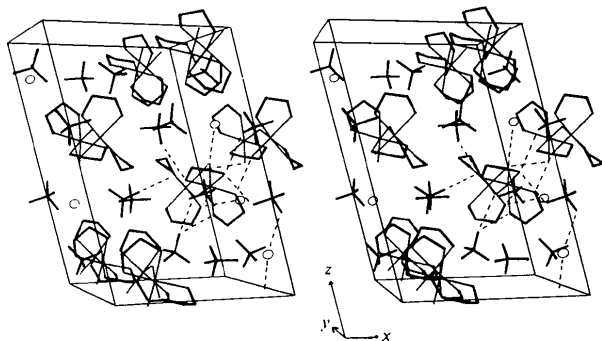


Fig. 3. Stereoscopic illustration of the contents of the unit cell. Thermal ellipsoids enclosing 50% probability are shown for the water molecules. H atoms have been omitted for clarity. Hydrogen bonds from one complex ion and from one water molecule are indicated.

Packing

The structure is extensively hydrogen bonded in all directions, most of the possible donors and acceptors being involved in hydrogen bonds (Table 5 and Fig. 3). Each complex cation is surrounded by one other complex ion (to which it is crystallographically related by an inversion center and hydrogen bonded twice), two water molecules and about ten perchlorate ions.

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