

References

- BLOW, D. M. (1960). *Acta Cryst.* **13**, 168.
 BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1964). *ORFFE*. Report ORNL-TM-306. Oak Ridge National Laboratory, Tennessee.
 CANTY, A. J., FYFE, M. & GATEHOUSE, B. M. (1978). *Inorg. Chem.* **17**, 1467–1471.
 CROMER, D. T. & LIBERMAN, D. (1970). *J. Chem. Phys.* **53**, 1891–1898.
 CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* **A24**, 321–324.
 GATEHOUSE, B. M. & MISKIN, B. K. (1974). *Acta Cryst.* **B30**, 1311–1317.
 GRDENIĆ, D. (1965). *Q. Rev. Chem. Soc.* **19**, 303–328.
 HORNSTRA, J. & STUBBE, B. (1972). *PW 1100 Data Processing Program*. Philips Research Laboratories, Eindhoven, The Netherlands.
 JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.
 PAULING, L. (1960). *The Nature of the Chemical Bond*, 3rd ed., p. 260. Ithaca: Cornell Univ. Press.
 SHELDRIK, G. (1976). Program for crystal structure determination. Univ. of Cambridge, England.

Acta Cryst. (1979). **B35**, 596–599

The Crystal Structure of Δ, Δ - μ -Hydroxo- μ -sulfato-bis[bis(ethylenediamine)chromium(III)] Dithionate Hydrate

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Abstract

$[(\text{en})_2\text{Cr}(\text{OH})(\text{SO}_4)\text{Cr}(\text{en})_2]_2(\text{S}_2\text{O}_6)_3 \cdot 2\text{H}_2\text{O}$, $[\text{Cr}_2(\text{C}_2\text{H}_8\text{N}_4)_4(\text{OH})(\text{SO}_4)_2(\text{S}_2\text{O}_6)_3 \cdot 2\text{H}_2\text{O}$, $2(\text{C}_8\text{H}_{33}\text{Cr}_2\text{N}_8\text{O}_5\text{S})^3+3(\text{S}_2\text{O}_6)^{2-} \cdot 2\text{H}_2\text{O}$, crystallizes in space group $P2_1/c$, with $a = 9.206(2)$, $b = 26.931(8)$, $c = 12.012(3)$ Å, $\beta = 110.40(2)^\circ$, $Z = 2$. The structure was refined to $R = 0.069$ for 4227 diffractometric intensities. The complex ion contains a non-crystallographic mirror plane and the conformation of the chelate rings is ${}^{\lambda}_8\Delta A_1^{\delta}$. The bridging six-membered ring has a distorted chair conformation. The Cr–Cr separation is $3.706(2)$ Å. The crystal structure is intensively hydrogen-bonded.

Introduction

The present investigation was undertaken in order to establish the configuration of the compound formed by the novel reaction between the *meso* diol Δ, Δ - $[(\text{en})_2\text{Cr}(\text{OH})_2\text{Cr}(\text{en})_2]^{4+}$ and sulfuric acid. The resulting sulfato-bridged cation Δ, Δ - $[(\text{en})_2\text{Cr}(\text{OH})(\text{SO}_4)\text{Cr}(\text{en})_2]^{4+}$ is the first sulfato-bridged binuclear Cr^{III} complex isolated as a salt. It is very robust in acid solution. In basic solution the hydroxo bridge is first deprotonated ($\text{pK} \approx 12$) and then the sulfato bridge is cleaved giving the mono-ol Δ, Δ - $[(\text{OH})(\text{en})_2\text{Cr}(\text{OH})\text{Cr}(\text{en})_2(\text{OH})]^{3+}$ (Springborg, 1978). The present compound may serve as a model for the poorly characterized

sulfato-bridged species involved in the chemistry of Cr tanning processes.

Experimental

The red prismatic crystal used for data collection was prepared as described by Springborg (1978). Photographs showed that $h0l$ were absent for $l \neq 2n$ and $0k0$ for $k \neq 2n$, so the space group is $P2_1/c$. The cell dimensions are $a = 9.206(2)$, $b = 26.931(8)$, $c = 12.012(3)$ Å, $\beta = 110.40(2)^\circ$, $V = 2791$ Å³. They were obtained by least-squares refinement of 98 θ angles (Mo $K\alpha$, $\lambda = 0.71069$ Å) measured on a Nonius three-circle automatic diffractometer with a graphite monochromator. The formula weight is 1431.4 ($\text{C}_{16}\text{H}_{70}\text{Cr}_4\text{N}_{16}\text{O}_{30}\text{S}_8$); D_o measured by flotation at 295 K = 1.71, $D_c = 1.71$ Mg m⁻³ for $Z = 2$, corresponding to half a formula unit (*i.e.* one complex ion, one and a half dithionate ions and one water molecule) per asymmetric unit. $\mu(\text{Mo } K\alpha) = 1.18$ mm⁻¹.

A crystal with average diameter 0.2 mm was mounted along a and intensities were measured out to $\theta = 28.6^\circ$ with a computer-controlled Supper diffractometer (Kryger, 1975). Monochromatic Mo $K\alpha$ radiation was used with a scintillation counter and pulse-height analyzer. About 14 000 reflections within a hemisphere were measured by the background-peak-background method. 4227 independent reflections with structure factors greater than 2.5 times their e.s.d.'s

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obtained from counting statistics were considered observed and used in the subsequent analysis. No absorption correction was applied.

Determination and refinement of the structure

The two Cr atoms and three of the S atoms were located by a combination of Patterson and direct methods (*MULTAN*, Main, Woolfson, Lessinger, Germain & Declercq, 1974). The rest of the structure was solved by heavy-atom methods. The XRAY system (Stewart, Kruger, Ammon, Dickinson & Hall, 1972) was used for nearly all the calculations. All atoms were assumed to be uncharged and the scattering factors of the XRAY system were used. A correction for anomalous dispersion was included for Cr (*International Tables for X-ray Crystallography*, 1962). Isotropic full-matrix least-squares refinement led to $R = \sum (|F_o| - |F_c|) / \sum |F_o| = 0.14$. A difference map at this stage showed all H atoms, except those of the water molecule, in their expected positions (C-H = 1.00, N-H = 0.90, O-H = 0.85 Å). In the following anisotropic full-matrix least-squares refinement the H atom parameters were not refined but calculated from the positions and the isotropic temperature factors of the atoms to which they were bonded. In the final difference map two peaks which could be interpreted as the two H atoms of the water molecule were found near the hydrogen bonds connecting the water molecule O(2) and two dithionate ions, but they were not included in the analysis. Scale factors for each of the thirteen layer lines ($h \rightarrow 0-12$) were varied separately as the scaling made at the data collection did not seem adequate. The parameters had to be divided into four blocks due to capacity restrictions of the least-squares program. The final R was 0.069 for 4227 reflections. At this stage the shifts of all parameters were < 0.6 times their e.s.d.'s (average shift/error 0.09). The weighting scheme was $1/w = 0.000163|F|^3 - 0.0145|F|^2 + 0.0490|F| + 2.20\sigma^2(F) + 16.6$. The coefficients were fitted by *WTRFA* (Nielsen, 1977). The drawings were prepared by *ORTEP* (Johnson, 1965). The final positions of the non-hydrogen atoms are listed in Table 1.*

Description and discussion of the structure

The structure consists of binuclear $[(en)_2Cr(OH)(SO_4)Cr(en)_2]^{3+}$ cations, $S_2O_6^{2-}$ anions, and water molecules held together by hydrogen bonds and electrostatic forces.

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34080 (26 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Conformation of the complex ion

The cation is shown in Fig. 1. The atomic labeling, and the bond distances of the inner coordination sphere

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

	x	y	z
Cr(1)	511 (1)	3864 (-3)	1650 (1)
Cr(2)	415 (1)	3872 (-3)	-1459 (1)
O(1)	1200 (4)	3740 (1)	279 (3)
S(1)	-2006 (2)	4399 (1)	-507 (1)
O(11)	-941 (4)	4383 (1)	765 (3)
O(12)	-1024 (4)	4385 (1)	-1284 (3)
O(13)	-2842 (4)	4865 (1)	-708 (4)
O(14)	-3011 (4)	3964 (1)	-754 (4)
N(11)	2180 (6)	4405 (2)	2344 (4)
N(12)	2255 (6)	3408 (2)	2747 (4)
N(13)	-425 (6)	3945 (2)	2989 (4)
N(14)	-1136 (5)	3302 (2)	1147 (4)
N(21)	2025 (5)	4425 (2)	-1359 (4)
N(22)	2132 (5)	3423 (2)	-1687 (4)
N(23)	-585 (6)	3953 (2)	-3283 (4)
N(24)	-1215 (5)	3306 (2)	-1787 (4)
C(11)	3715 (8)	4169 (3)	2881 (8)
C(12)	3551 (8)	3714 (3)	3514 (7)
C(13)	-1983 (8)	3703 (3)	2622 (7)
C(14)	-1885 (8)	3214 (3)	2048 (6)
C(21)	3574 (7)	4196 (3)	-1116 (7)
C(22)	3374 (7)	3738 (3)	-1858 (7)
C(23)	-2092 (8)	3685 (3)	-3719 (6)
C(24)	-1917 (7)	3202 (3)	-3082 (6)
O(2)	6876 (7)	2522 (3)	4204 (5)
S(2)	1430 (2)	2236 (1)	330 (1)
O(21)	878 (5)	2437 (2)	1228 (5)
O(22)	1416 (6)	1700 (2)	311 (4)
O(23)	802 (5)	2457 (2)	-831 (4)
S(3)	3787 (2)	2474 (1)	915 (1)
O(31)	4494 (6)	2271 (2)	2073 (5)
O(32)	4401 (7)	2290 (2)	53 (6)
O(33)	3649 (5)	3013 (2)	905 (5)
S(4)	1217 (2)	70 (1)	248 (2)
O(41)	1408 (7)	586 (2)	474 (6)
O(42)	1505 (10)	-38 (3)	-833 (7)
O(43)	1906 (9)	-236 (4)	1201 (10)

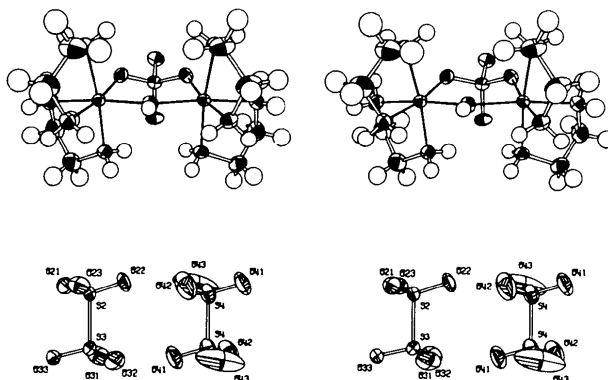


Fig. 1. Stereoscopic *ORTEP* drawing of the complex cation (the labeling is shown in Fig. 2) and the dithionate anions. The thermal ellipsoid encloses 50% probability. The cation has a non-crystallographic mirror plane through O(1), S(1), O(11) and O(12). The conformation is $\frac{1}{2}AA_1^2$.

and the bridging ring are shown in Fig. 2. All bond distances and angles are given in Table 2.

The ion contains a non-crystallographic mirror plane through the O atom of the OH bridge and the S and the two non-ligating O atoms of the sulfate bridge. This plane is approximately perpendicular to the *bc* plane.

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

Cr...Cr	3.706 (2)		
Cr(1)—O(1)	1.988 (4)	Cr(2)—O(2)	1.990 (4)
Cr(1)—O(11)	1.970 (4)	Cr(2)—O(12)	1.976 (4)
Cr(1)—N(11)	2.070 (5)	Cr(2)—N(21)	2.075 (5)
Cr(1)—N(12)	2.085 (5)	Cr(2)—N(22)	2.083 (5)
Cr(1)—N(13)	2.085 (6)	Cr(2)—N(23)	2.072 (5)
Cr(1)—N(14)	2.079 (5)	Cr(2)—N(24)	2.077 (5)
S(1)—O(11)	1.502 (4)	S(1)—O(12)	1.509 (5)
S(1)—O(13)	1.448 (4)	S(1)—O(14)	1.457 (4)
N(11)—C(11)	1.476 (9)	N(21)—C(21)	1.487 (8)
N(12)—C(12)	1.479 (8)	N(22)—C(22)	1.493 (9)
N(13)—C(13)	1.496 (9)	N(23)—C(23)	1.488 (8)
N(14)—C(14)	1.491 (10)	N(24)—C(24)	1.488 (8)
C(11)—C(12)	1.478 (12)	C(21)—C(22)	1.495 (10)
C(13)—C(14)	1.505 (11)	C(23)—C(24)	1.488 (10)
O(1)—Cr(1)—O(11)	91.4 (2)	O(1)—Cr(2)—O(12)	91.4 (2)
O(1)—Cr(1)—N(11)	92.6 (2)	O(1)—Cr(2)—N(21)	94.4 (2)
O(1)—Cr(1)—N(12)	91.6 (2)	O(1)—Cr(2)—N(22)	91.2 (2)
O(1)—Cr(1)—N(14)	92.8 (2)	O(1)—Cr(2)—N(24)	92.5 (2)
O(11)—Cr(1)—N(11)	89.3 (2)	O(12)—Cr(2)—N(21)	89.1 (2)
O(11)—Cr(1)—N(13)	87.5 (2)	O(12)—Cr(2)—N(23)	88.3 (2)
O(11)—Cr(1)—N(14)	94.1 (2)	O(12)—Cr(2)—N(24)	93.7 (2)
N(11)—Cr(1)—N(12)	82.0 (2)	N(21)—Cr(2)—N(22)	82.2 (2)
N(11)—Cr(1)—N(13)	93.7 (2)	N(21)—Cr(2)—N(23)	91.7 (2)
N(12)—Cr(1)—N(13)	90.5 (2)	N(22)—Cr(2)—N(23)	90.1 (2)
N(12)—Cr(1)—N(14)	94.5 (2)	N(22)—Cr(2)—N(24)	94.7 (2)
N(13)—Cr(1)—N(14)	81.1 (2)	N(23)—Cr(2)—N(24)	81.4 (2)
O(11)—S(1)—O(12)	108.0 (2)	O(13)—S(1)—O(14)	113.6 (2)
O(11)—S(1)—O(13)	108.4 (2)	O(12)—S(1)—O(13)	108.5 (3)
O(11)—S(1)—O(14)	109.1 (2)	O(12)—S(1)—O(14)	109.1 (2)
Cr(1)—N(11)—C(11)	109.7 (4)	Cr(2)—N(21)—C(21)	109.3 (4)
Cr(1)—N(12)—C(12)	110.0 (4)	Cr(2)—N(22)—C(22)	110.0 (4)
Cr(1)—N(13)—C(13)	109.8 (4)	Cr(2)—N(23)—C(23)	109.7 (4)
Cr(1)—N(14)—C(14)	112.3 (4)	Cr(2)—N(24)—C(24)	111.0 (4)
N(11)—C(11)—C(12)	109.1 (6)	N(21)—C(21)—C(22)	108.4 (5)
C(11)—C(12)—N(12)	110.3 (6)	C(21)—C(22)—N(22)	109.1 (6)
N(13)—C(13)—C(14)	108.2 (6)	N(23)—C(23)—C(24)	108.8 (5)
C(13)—C(14)—N(14)	108.1 (6)	C(23)—C(24)—N(24)	107.6 (5)
Cr(1)—O(1)—Cr(2)	137.4 (2)		

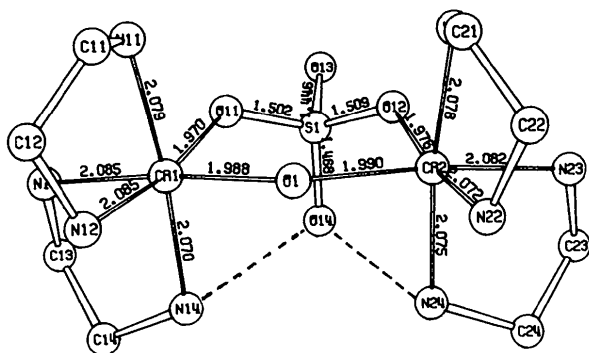


Fig. 2. Bond distances (Å) in the coordination octahedra and the bridging system. The angles of the ring are: Cr(1) 91.4, O(1) 137.4, Cr(2) 91.4, O(12) 130.7, S(1) 108.0, O(11) 130.5°.

The eight independent Cr—N distances are in the range 2.070 (5) to 2.085 (6), mean 2.078 (6) Å. The pseudo-threefold axes of the two coordination octahedra are tilted 48° towards each other. The C—C bonds of the upper ethylenediamine rings (Figs. 1 and 2) are nearly parallel to these axes (the angles are 9°), whereas the C—C bonds of the lower rings make angles of 61°. The dimensions of the chelate diamine rings are very similar to those in the diol Δ, Δ - $[(en)_2Cr(OH)_2Cr(en)_2]Cl_2 \cdot (ClO_4)_2 \cdot 2H_2O$ and other previously reported values for Cr^{III} ethylenediamine complexes (Kaas, 1976), though the conformation is $\lambda_3^1 \Delta \lambda_1^6$ and not $\lambda_1^1 \Delta \lambda_3^6$ as in the diol. (For a description of the nomenclature see Thewalt, Jensen & Schäffer, 1972.)

The six-membered bridging ring has a distorted chair conformation with torsion angles as given in Table 3. The sulfate group is a slightly distorted tetrahedron; the S—O bonds to the ligating O atoms are 0.05 Å longer than a normal sulfate S—O bond, and the O—S—O angle between non-ligating O atoms is 113.6 (2)°. The dimensions of the sulfate bridge are similar to those in the cation Δ, Δ - and Λ, Λ - μ -amido- μ -sulfato-bis[bis(ethylenediamine)cobalt(III)] (Thewalt, 1971). The latter, however, has a puckered bridging ring with a twofold axis, as a consequence of the different chirality of the Co atoms. The angle in the hydroxo bridge is 137.4 (2)° and the Cr—Cr distance is 3.706 (2) Å. These values are close to the corresponding values 135.4 (2)° and 3.678 (2) Å in the mono-ol Δ, Δ - $[(OH)(en)_2Cr(OH)Cr(en)_2(OH)](ClO_4)_3 \cdot H_2O$ (Kaas, 1978), showing that the bridging ring is not strained.

The non-ligating O atoms [O(14) and O(13)] of the sulfate group are both involved in two hydrogen bonds (Table 4). O(14) forms two intramolecular hydrogen bonds to the nearest N—H groups of the two adjacent ethylenediamine rings, in which the Cr—N—C angles are larger than usual [112.3 (4) and 111.0 (4)°]. O(13) forms two intermolecular hydrogen bonds to N—H groups of the neighboring cation. The two hydrogen-bonded cations are crystallographically related by an inversion center. The remaining NH groups and the OH group all act as hydrogen donors in hydrogen bonds to dithionate ions.

Dithionate ion

There are one and a half dithionate ions in the asymmetric unit, as one of the ions is placed at an inversion center. The dithionate ions are shown in Fig. 1. The

Table 3. *Torsion angles (°) of the bridging ring*

Cr(1)	O(1)	Cr(2)	O(12)	+18.3 (3)
O(1)	Cr(2)	O(12)	S(1)	−39.6 (3)
Cr(2)	O(12)	S(1)	O(11)	+62.1 (3)
O(12)	S(1)	O(11)	Cr(1)	−63.3 (4)
S(1)	O(11)	Cr(1)	O(1)	+41.4 (4)
O(11)	Cr(1)	O(1)	Cr(2)	−18.9 (3)

dimensions [except those involving O(43), which did not refine well] are very close to previously reported values (e.g. Robertson & Whimp, 1975; Cline, Scaringe, Hatfield & Hodgson, 1977). The S—S distances are 2.133 (3) and 2.142 (3) Å. The S—O distances are in the range 1.414 (6) to 1.458 (5), average 1.438 (14) Å, except that S—O(43) appears to be very short, probably due to lack of correction for thermal motion. The average O—S—O and S—S—O angles are 114 (2) and 105 (2)°, respectively. The conformation is staggered with torsion angles ± 60 and 180° within experimental error. All O atoms except

O(41) are involved in hydrogen-bonding to NH or OH groups of the complex ions or the water molecule (Table 4).

Water molecule

The water molecule O(2) is hydrogen-bonded to two dithionate ions (Table 4). The H atoms were not located until the calculations were finished, and the positions were too uncertain to justify further calculations.

Packing

The structure is intensively hydrogen-bonded. Nearly all possible hydrogen donors and acceptors are involved in hydrogen bonds (Table 4 and Fig. 3). The complex ions are arranged in hydrogen-bonded pairs at inversion centers in the *bc* plane and surrounded by dithionate ions. The water molecules are placed between the layers formed. All hydrogen bonds except those of the water molecule are within the layers.

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References

- CLINE, S. J., SCARINGE, R. P., HATFIELD, W. E. & HODGSON, D. J. (1977). *J. Chem. Soc. Dalton Trans.* pp. 1662–1666.
- International Tables for X-ray Crystallography* (1962). Vol. III, pp. 215. Birmingham: Kynoch Press.
- JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.
- KAAS, K. (1976). *Acta Cryst.* B32, 2021–2025.
- KAAS, K. (1978). In preparation.
- KRYGER, L. (1975). Thesis, Univ. of Aarhus, Denmark.
- MAIN, P., WOOLFSON, M. M., LESSINGER, L., GERMAIN, G. & DECLERCQ, J. P. (1974). *MULTAN. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.
- NIELSEN, K. (1977). *Acta Cryst.* A33, 1009–1010.
- ROBERTSON, G. B. & WHIMP, P. O. (1975). *Aust. J. Chem.* 28, 729–737.
- SPRINGBORG, J. (1978). *Acta Chem. Scand. Ser. A*, 32, 231–233.
- STEWART, J. M., KRUGER, G. J., AMMON, H. L., DICKINSON, C. & HALL, S. R. (1972). The XRAY system, version of June, update of 24 April 1975. Tech. Rep. TR 192. Computer Science Center, Univ. of Maryland, College Park, Maryland.
- THEWALT, U. (1971). *Acta Cryst.* B27, 1744–1752.
- THEWALT, U., JENSEN, K. A. & SCHÄFFER, C. E. (1972). *Inorg. Chem.* 11, 2129–2136.

Table 4. *Hydrogen-bond distances (Å) and angles (°)*

Key to symmetry operations

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

<i>D</i> — <i>H</i> ... <i>A</i>	<i>D</i> ... <i>A</i>	<i>H</i> ... <i>A</i>	\angle <i>D</i> — <i>H</i> ... <i>A</i>
N(11 ⁱ)—H(5 ⁱ)...O(13)	2.988 (7)	2.11	164
N(21 ⁱ)—H(20 ^h)...O(13)	3.016 (6)	2.13	164
N(14 ⁱ)—H(18 ⁱ)...O(14)	2.939 (6)	2.15	146
N(24 ⁱ)—H(35 ⁱ)...O(14)	2.974 (7)	2.17	149
N(14 ⁱ)—H(19 ⁱ)...O(21)	2.958 (7)	2.09	162
N(13 ⁱⁱ)—H(13 ⁱ)...O(22)	3.221 (6)	2.33	167
N(24 ⁱ)—H(34 ⁱ)...O(23)	2.919 (7)	2.05	159
O(2) ⁱ ...O(31)	2.811 (7)		
O(2 ⁱⁱ)...O(32)	2.848 (10)		
O(1)—H(1)...O(33)	2.882 (6)	2.07	160
N(12)—H(11)...O(33)	3.107 (8)	2.26	156
N(22)—H(26)...O(33)	3.138 (7)	2.27	159
N(11 ⁱⁱ)—H(4 ⁱⁱ)...O(42)	3.007 (11)	2.10	176
N(23 ⁱⁱⁱ)—H(29 ⁱⁱⁱ)...O(42)	2.928 (9)	2.03	168
N(13 ^{iv})—H(12 ^{iv})...O(43)	2.929 (2)	2.18	140

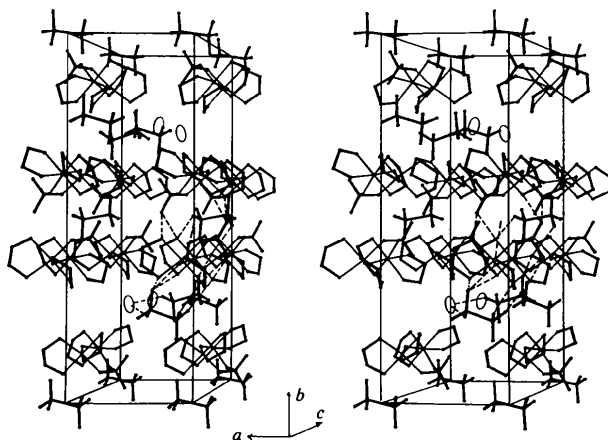


Fig. 3. Stereoscopic illustration of the contents of the unit cell. Thermal ellipsoids enclosing 50% probability are shown for the water molecules. H atoms have been omitted for clarity. Hydrogen bonds from one complex ion are indicated.