Structure of the Active Racemic Complex [(±)Co(en)₃](C₂O₄)I.1·5H₂O: a hydrogen-Bond-Induced Case of Asymmetry

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Abstract. Tris(ethylenediamine)cobalt(III) iodide oxalate sesquihydrate, [(±)Co(C₂H₈N₂)₃](C₂O₄)I.1·5H₂O, $M_r = 481 \cdot 2$, orthorhombic, $P2_12_12_1$, $a = 12 \cdot 482$ (3), $b = 14 \cdot 369$ (2), $c = 18 \cdot 458$ (1) Å, $V = 3311$ (1) Å³, $Z = 8$, D_m(by flotation) $= 1 \cdot 92$, $D_x = 1 \cdot 93$ Mg m⁻³, Mo $K\alpha$, $\lambda = 0 \cdot 71069$ Å, $\mu = 2 \cdot 798$ mm⁻¹, $F(000) = 1928$, room temperature, $R = 0 \cdot 025$ for 2817 observed reflections $[I > 2 \cdot 5\sigma(I)]$. Two 'nearly enantiomeric' crystallographically independent octahedral [Co-(en)₃]³⁺ groups are distinguished. The configurations around the metals are $\Delta\delta\delta\delta$ and $\Delta\lambda\lambda\lambda$. The structure can be described as a distorted body-centred cubic packing of 'complex-cation spheres', with iodide and oxalate anions occupying pseudo-tetrahedral and octahedral holes, respectively. A complex network of hydrogen bonds ensures intermolecular packing and lies behind the striking inequivalence of the metal atoms.

Introduction. The obtaining of single crystals of di-μ-oxo dinuclear Moᵛᴵ compounds is an old challenge for us (Beltrán-Porter & Martínez-Tamayo, 1984). In the course of the preparation of the corresponding oxalate derivative, using [Co(en)₃]³⁺ as counter-ion (Beltrán-Porter, Martínez-Tamayo & Caturla, 1984), orange, well formed, isostructural rectangular and triangular prismatic crystals resulted. Structure determination of the rectangular crystals showed that they were actually the double salt [Co(en)₃]-(C₂O₄)I.1·5H₂O. It was striking to find the non-centrosymmetric space group $P2_12_12_1$ because the synthesis was carried out from the racemic [(±)-Co(en)₃]I₃ without the participation of any resolving agent. As far as we know, no other case of an active-racemic salt [(+)M(en)₃(−)M'(en)₃]L_m.xH₂O (M, M' = Coᴵᴵᴵ, Crᴵᴵᴵ, Rhᴵᴵᴵ; L = Cl⁻, Br⁻, I⁻, SCN⁻, NO₃⁻, *etc.*) containing only [Co(en)₃]³⁺ as active species has previously been reported (Spinat, Brouty & Whuler, 1980). In this paper we report the crystal-structure determination of the title compound in order

to understand its specificity and its relationship with the nice structural correlation established for complexes of this kind (Spinat, Brouty & Whuler, 1980).

Experimental. Suitable rectangular prismatic crystals were prepared in the following way: diffusion of a $0 \cdot 033 M$ solution of [(±)Co(en)₃]I₃.H₂O (Angelici, 1977) into another solution containing $0 \cdot 025 M$ Na₂MoO₄.2H₂O and $0 \cdot 050 M$ NaHC₂O₄.H₂O was allowed in a thermostatted [315 (1)K] U-shaped tube with a sintered glass plate separating its two branches. After separation of the orange microcrystals formed on the plate, the mother liquor was allowed to cool slowly to produce well formed crystals after several days. Crystals $0 \cdot 2 \times 0 \cdot 2 \times 0 \cdot 5$ mm. Enraf–Nonius CAD-4 diffractometer with graphite-monochromated Mo $K\alpha$ radiation. Cell constants from least-squares refinement of 25 reflections ($6 \leq 2\theta \leq 30°$). 3274 unique reflections ($2 \leq 2\theta \leq 50°$, $0 \leq h \leq 14$, $0 \leq k \leq 17$, $0 \leq l \leq 21$) measured with the variable-speed ω–2θ scan technique, but only 2817 with $I > 2 \cdot 5\sigma(I)$ (from counting statistics) were used in the refinement. Variation of standard reflections 123, 666, 555 and 143, $\pm 1 \cdot 6\%$. Data corrected for Lorentz–polarization but not for absorption. Structure solved by multi-solution direct methods (*MULTAN*11/84; Main, Germain & Woolfson, 1984), using the 356 highest E values; 12 non-H atoms found in first E map; remaining non-H atoms were located by subsequent Fourier syntheses. Full-matrix least-squares refinement with anisotropic temperature factors (*SHELX*76; Sheldrick, 1976). All H atoms were located from difference maps. Additional refinement with all non-H atoms treated anisotropically and fixed H atoms ($U = 0 \cdot 05$ Å²) converged at $R = 0 \cdot 025$, $wR = 0 \cdot 026$, $S = 1 \cdot 2$ for the 2817 observed reflections and 388 parameters. $\sum w(|F_o| - |F_c|)^2$ minimized with $w = 1/[\sigma^2(F_o) + 0 \cdot 00015 F_o^2]$, $\sigma^2(F_o)$ from counting statistics. $(\Delta/\sigma)_{max}$ in last least-squares cycle $< 0 \cdot 9$. Max. value in final difference density map

$[(\pm)Co(en)_3](C_2O_4)I.1\cdot 5H_2O$

Table 1. *Fractional coordinates* $(\times 10^4$, Co *and* I $\times 10^5)$ *and equivalent isotropic temperature factors* (Å^2) *for non-hydrogen atoms (e.s.d.'s in parentheses)*

$$B_{eq} = \tfrac{8}{3}\pi^2 \Sigma_i \Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$B_{eq}(\text{Å}^2)$
I(1)	33658 (5)	17300 (5)	27101 (4)	3·66
I(2)	24618 (5)	33875 (5)	49474 (3)	3·26
Co(1)	72536 (7)	48715 (6)	48980 (5)	1·70
Co(2)	22285 (7)	48991 (7)	24176 (5)	1·69
O(25)	991 (5)	4300 (5)	−754 (4)	3·29
O(26)	895 (5)	4298 (5)	453 (4)	3·56
O(29)	3024 (5)	4047 (5)	537 (3)	3·17
O(30)	3172 (5)	4181 (5)	−660 (3)	3·28
O(31)	3882 (5)	59 (5)	6957 (3)	2·97
O(32)	3960 (5)	8 (5)	8165 (3)	2·93
O(35)	2078 (5)	1083 (4)	7029 (3)	3·17
O(36)	2185 (5)	1077 (4)	8238 (3)	3·33
O(W1)	1094 (5)	2819 (4)	7107 (4)	4·15
O(W2)	5214 (5)	3520 (5)	9757 (5)	6·00
O(W3)	636 (7)	2319 (5)	8910 (4)	5·47
N(1)	6475 (5)	5842 (4)	5432 (3)	1·95
N(4)	7691 (6)	5862 (5)	4236 (4)	2·59
N(5)	8511 (5)	5007 (5)	5528 (3)	2·56
N(8)	8125 (5)	3953 (5)	4366 (3)	2·20
N(9)	6666 (6)	3940 (4)	5556 (4)	2·23
N(12)	6035 (5)	4603 (4)	4274 (3)	2·10
N(13)	1982 (5)	3720 (5)	1905 (3)	2·36
N(16)	1124 (5)	4486 (5)	3101 (4)	2·38
N(17)	3382 (6)	5191 (5)	1742 (4)	2·51
N(20)	3346 (6)	4376 (5)	3059 (4)	2·44
N(21)	1183 (5)	5518 (5)	1781 (4)	2·32
N(24)	2329 (6)	6094 (4)	2923 (3)	2·46
C(2)	6819 (7)	6767 (6)	5164 (5)	3·18
C(3)	7001 (8)	6696 (7)	4355 (5)	3·54
C(6)	9281 (7)	4231 (7)	5402 (5)	3·04
C(7)	9267 (7)	4054 (7)	4588 (5)	2·51
C(10)	5568 (7)	3696 (6)	5318 (5)	2·98
C(11)	5547 (7)	3696 (6)	4492 (5)	2·70
C(14)	947 (7)	3308 (7)	2163 (5)	2·81
C(15)	895 (7)	3484 (6)	2981 (5)	3·06
C(18)	4370 (7)	4655 (7)	1951 (5)	3·13
C(19)	4421 (7)	4633 (7)	2758 (5)	3·06
C(22)	1197 (8)	6530 (6)	1918 (5)	3·41
C(23)	1367 (7)	6653 (6)	2731 (5)	3·22
C(27)	1377 (7)	4263 (5)	−137 (5)	2·43
C(28)	2652 (7)	4160 (5)	−78 (5)	2·58
C(33)	3539 (6)	238 (6)	7577 (4)	2·40
C(34)	2490 (7)	834 (5)	7621 (4)	2·41

Table 2. *Bond lengths* (Å) *and bond angles* $(°)$ *with e.s.d.'s in parentheses*

N(1)–Co(1)	1·966 (6)	C(2)–N(1)	1·481 (10)
N(4)–Co(1)	1·954 (7)	C(3)–N(4)	1·492 (11)
N(5)–Co(1)	1·963 (6)	C(7)–N(8)	1·490 (10)
N(8)–Co(1)	1·972 (6)	C(6)–N(5)	1·490 (11)
N(9)–Co(1)	1·951 (6)	C(10)–N(9)	1·482 (11)
N(12)–Co(1)	1·947 (6)	C(11)–N(12)	1·493 (10)
N(13)–Co(2)	1·965 (7)	C(14)–N(13)	1·498 (10)
N(16)–Co(2)	1·961 (7)	C(15)–N(16)	1·485 (11)
N(17)–Co(2)	1·951 (7)	C(18)–N(17)	1·504 (11)
N(20)–Co(2)	1·977 (7)	C(19)–N(20)	1·499 (10)
N(21)–Co(2)	1·969 (7)	C(22)–N(21)	1·476 (11)
N(24)–Co(2)	1·958 (6)	C(23)–N(24)	1·487 (10)
C(27)–O(25)	1·238 (10)	C(3)–C(2)	1·514 (11)
C(27)–O(26)	1·246 (10)	C(7)–C(6)	1·525 (12)
C(28)–O(29)	1·237 (10)	C(11)–C(10)	1·525 (12)
C(28)–O(30)	1·254 (10)	C(15)–C(14)	1·532 (12)
C(33)–O(31)	1·249 (9)	C(19)–C(18)	1·491 (12)
C(33)–O(32)	1·250 (9)	C(23)–C(22)	1·527 (12)
C(34)–O(35)	1·258 (9)	C(28)–C(27)	1·602 (11)
C(34)–O(36)	1·251 (9)	C(34)–C(33)	1·567 (11)
N(4)–Co(1)–N(1)	86·3 (3)	C(6)–N(5)–Co(1)	110·5 (5)
N(5)–Co(1)–N(1)	91·6 (3)	C(10)–N(9)–Co(1)	108·9 (5)
N(5)–Co(1)–N(4)	94·3 (3)	C(11)–N(12)–Co(1)	109·4 (5)
N(8)–Co(1)–N(1)	176·0 (3)	C(14)–N(13)–Co(2)	108·8 (5)
N(8)–Co(1)–N(4)	91·3 (3)	C(15)–N(16)–Co(2)	109·4 (5)
N(8)–Co(1)–N(5)	85·4 (3)	C(18)–N(17)–Co(2)	109·3 (5)
N(9)–Co(1)–N(1)	89·3 (3)	C(19)–N(20)–Co(2)	108·4 (5)
N(9)–Co(1)–N(4)	174·0 (3)	C(22)–N(21)–Co(2)	109·6 (5)
N(9)–Co(1)–N(8)	93·3 (3)	C(23)–N(24)–Co(2)	107·9 (5)
N(9)–Co(1)–N(5)	90·0 (3)	C(3)–C(2)–N(1)	108·2 (7)
N(12)–Co(1)–N(1)	93·0 (3)	C(2)–C(3)–N(4)	106·6 (7)
N(12)–Co(1)–N(4)	89·6 (3)	C(7)–C(6)–N(5)	105·7 (7)
N(12)–Co(1)–N(5)	174·2 (3)	C(6)–C(7)–N(8)	107·3 (7)
N(12)–Co(1)–N(8)	90·2 (3)	C(11)–C(10)–N(9)	108·2 (7)
N(12)–Co(1)–N(9)	86·5 (3)	C(10)–C(11)–N(12)	105·2 (7)
N(16)–Co(2)–N(13)	86·5 (3)	C(15)–C(14)–N(13)	106·5 (7)
N(17)–Co(2)–N(16)	174·6 (3)	C(14)–C(15)–N(16)	107·4 (7)
N(17)–Co(2)–N(13)	89·6 (3)	C(19)–C(18)–N(17)	107·6 (7)
N(20)–Co(2)–N(16)	89·7 (3)	C(18)–C(19)–N(20)	109·7 (7)
N(20)–Co(2)–N(13)	94·0 (3)	C(23)–C(22)–N(21)	106·5 (7)
N(20)–Co(2)–N(17)	86·8 (3)	C(22)–C(23)–N(24)	106·5 (7)
N(21)–Co(2)–N(16)	93·1 (3)	O(26)–C(27)–O(25)	128·0 (8)
N(21)–Co(2)–N(13)	89·9 (3)	C(28)–C(27)–O(25)	117·0 (7)
N(21)–Co(2)–N(17)	90·6 (3)	C(28)–C(27)–O(26)	115·1 (7)
N(21)–Co(2)–N(20)	175·2 (3)	O(30)–C(28)–O(29)	126·4 (8)
N(24)–Co(2)–N(16)	90·2 (3)	C(27)–C(28)–O(29)	116·6 (7)
N(24)–Co(2)–N(13)	174·6 (3)	C(27)–C(28)–O(30)	117·0 (7)
N(24)–Co(2)–N(17)	93·9 (3)	O(32)–C(33)–O(31)	126·6 (8)
N(24)–Co(2)–N(20)	90·2 (3)	C(34)–C(33)–O(31)	116·5 (7)
N(24)–Co(2)–N(21)	86·0 (3)	C(34)–C(33)–O(32)	116·9 (7)
C(2)–N(1)–Co(1)	109·0 (5)	O(36)–C(34)–O(35)	126·0 (8)
C(3)–N(4)–Co(1)	109·4 (5)	C(33)–C(34)–O(35)	116·9 (7)
C(7)–N(8)–Co(1)	109·0 (5)	C(33)–C(34)–O(36)	117·0 (7)

was $0\cdot 6$ e Å^{-3} located near the I(1) atom. At this stage, the attempts to assign the absolute chirality were not conclusive. Atomic scattering factors and corrections for anomalous dispersion taken from *International Tables for X-ray Crystallography* (1974). The geometrical calculations were performed with *XANADU* (Roberts & Sheldrick, 1975) and *DISTAN* (Burzlaff, Böhme & Gomm, 1977) and molecular illustrations were drawn with *PLUTO* (Motherwell & Clegg, 1978).

Discussion. The final positional parameters are given in Table 1, and bond angles and distances are listed in Table 2.* The structure consists of two crystallographically independent $[Co(en)_3]^{3+}$ complex ions, pairs of non-equivalent oxalate and iodide anions, and

* Lists of H-atom coordinates, anisotropic thermal parameters, intermolecular Co–Co, Co–I, Co–oxalate and Co–OW distances, and structure-factor amplitudes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44567 (20 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

crystallization water molecules. Fig. 1 shows a perspective drawing of the environment around each Co atom with the atomic numbering scheme, and Fig. 2 gives a stereoscopic view of the unit cell. The six coordinating nitrogens form a slightly distorted octahedron centred on each trivalent cobalt ion. Local symmetry is close to D_3 with a pseudo-threefold axis (A_3) passing through the basal triangles N(1)N(5)-N(9)–N(4)N(8)N(12) [Co(1)] and N(13)N(17)-N(21)–N(16)N(20)N(24) [Co(2)]. The chelation bite effects a small distortion by compressing to $86\cdot 1$ (5) [Co(1)] and $86\cdot 4$ (5)° [Co(2)] the average N–Co–N angle within each ligand [the normalized average chelate bite (Kepert, 1972) is $1\cdot 36$ in both cases (see Table 3)]. The distortions of both octahedra, as measured by ε (departure from the parallelism of the basal triangles) and φ (twist angle of these same triangles with respect to their antiprismatic position),

are very similar (see Table 3). The φ values found are in excellent agreement with calculations based on Kepert's theoretical correlation with the bite of the ligand (Kepert, 1972, 1977). The angles between the A_3 axis and the crystallographic c axis are 3·9 [Co(1)] and 5·3° [Co(2)], i.e. the basal triangles of both octahedra lie nearly parallel to the ab plane. Bond distances and angles within ethylenediamine ligands are as expected. Besides the crystallographic inequivalence, the local symmetry of the two oxalate groups differs {approximately C_{2h} for the oxalate ion having C(27)—C(28) as central bond [abbreviated as OX(1)] vs close to D_{2h} for the oxalate ion having C(33)—C(34) as central bond [abbreviated as OX(2)]}. This is consistent with the hydrogen-bonding scheme observed (see below).

Geometric data allowing the characterization of the conformational chirality of the chelate rings are given in Table 3. As can be noted, C—C ethylenediamine bonds are always paral*lel* to the respective A_3 axis. So, *lel lel lel* conformations result for the configurations of both cobalt complexes. Otherwise, it must be stressed that the helicity of all three rings surrounding each type of cobalt atom is the same, but this helicity is just the opposite for Co(1) with respect to Co(2). These two factors together imply that the configurations of the two [Co(en)₃]³⁺ ions are opposite (i.e. Δ and Λ). In other words, the structure contains the same number of dextrorotatory {[(+)Co(en)₃]³⁺, Λ configuration} and levorotatory {[(−)Co(en)₃]³⁺, Δ configuration} species.

Table 3. *Conformational characteristics of the complex ions* [Co(en)₃]³⁺

	Distance (Å) to N(1)N(5)N(9) [Co(1)] or N(16)N(20)N(24) [Co(2)] plane	C—C bond distance (Å)	Chelate ring conformation	Distance (Å) to ligand mean plane
Co(1) octahedron				
C(2)	0.400			+0.256
C(3)	1.903			−0.268
Δ|C(2)—C(3)|	1.503	1.514 (11)	lel, λ	
C(6)	0.351			+0.270
C(7)	1.869			−0.275
Δ|C(6)—C(7)|	1.518	1.525 (12)	lel, λ	
C(10)	0.424			+0.260
C(11)	1.943			−0.280
Δ|C(10)—C(11)|	1.519	1.525 (12)	lel, λ	
Average chelate bite: 1.364 (4)			c: 0.3°	
$\bar{d}_{Co-N}$ (Å): 1.959 (4)			φ: 6.5°	
Co(2) octahedron				
C(22)	1.817			−0.263
C(23)	0.298			+0.296
Δ|C(22)—C(23)|	1.519	1.527 (12)	lel, δ	
C(18)	1.936			−0.256
C(19)	0.500			+0.236
Δ|C(18)—C(19)|	1.436	1.491 (12)	lel, δ	
C(14)	1.927			−0.274
C(15)	0.401			+0.263
Δ|C(14)—C(15)|	1.526	1.532 (12)	lel, δ	
Average chelate bite: 1.369 (6)			c: 0.9°	
$\bar{d}_{Co-N}$ (Å): 1.964 (4)			φ: 6.3°	

In spite of that, owing to the crystallographic inequivalence of the two [Co(en)₃]³⁺ complex ions, the title compound is not purely racemic (as shown by its space group). At this point, given the relatively small dissimilarities between the complex ions, the configurations around both cobalt atoms must be arbitrarily assigned. In accordance with the positional parameters in Table 1 (see Fig. 1) Co(1) is $\Delta\lambda\lambda\lambda$ and Co(2) $\Lambda\delta\delta\delta$ (IUPAC, 1970).

From a chemical point of view, and taking into account the synthesis procedure, the yield of this 'active-racemic' compound is unique, considering the reported structures of [M(en)₃]L_m·xH₂O complexes. At first glance, only packing factors might explain the resulting asymmetry. Therefore, the 'asymmetry factor' will probably be better understood by considering the structure as a packing of large complex ions (Spinat, Brouty & Whuler, 1980; Shoemaker & Shoemaker, 1980) and then looking for the structural features resulting from the occupational pattern of the holes. Fig. 3 schematically shows the structural arrangement. According to Spinat, Brouty & Whuler (1980), [Co(en)₃]³⁺ ions have been approximated to spheres centred on Co atoms; two pairs of each type of non-equivalent oxalate and iodide anions are drawn; the position of the oxalate anions has been taken as the midpoint of the respective C—C bond.

A distorted body-centred cubic packing of [Co(en)₃]³⁺ ions clearly results. Eight of the fourteen nearest-neighbour complexes surrounding each Co(1) ion are Co(2) ions occupying the corners of a cube [$d_{Co(1)-Co(2)}$ ranges from 7·3 to 9·0 Å; $\bar{d}_{Co(1)-Co(2)}$
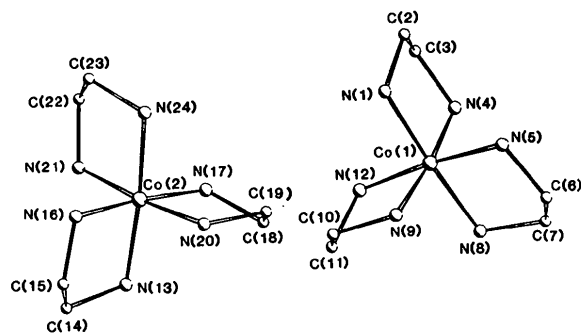

Fig. 1. Perspective view of the complex ions [Co(en)₃]³⁺ showing the configurations $\Delta\lambda\lambda\lambda$ [Co(1)] and $\Lambda\delta\delta\delta$ [Co(2)].
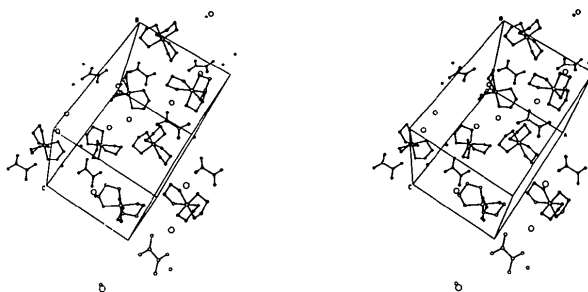

Fig. 2. Stereoscopic view of the unit cell.

= 8·16 (19) Å]; the six next-nearest neighbours are Co(1) ions at the centres of the six adjacent cubes [$d_{Co(1)-Co(1)'}$ from 9·2 to 9·8 Å; $\bar{d}_{Co(1)-Co(1)'}$ = 9·44 (12) Å]. The equivalent environment is found for Co(2) [$d_{Co(2)-Co(2)'}$ ranges from 9·1 to 10·0 Å; $\bar{d}_{Co(2)-Co(2)'}$ = 9·44 (17) Å]. The ratio $\bar{d}_{Co(i)-Co(i)'}/\bar{d}_{Co(i)-Co(j)}$ fits the expected value (1·15) nicely.

Given the considerable size of the anions, it might be thought that octahedral holes would be preferentially occupied (Spinat, Brouty & Whuler, 1980). Although the number of this type of holes in the non-closest-packed arrangement found is higher than that required to accommodate all the anions, both electrostatic and steric factors would work against the exclusive occupation of octahedral holes by these bulky anions. In fact, iodide anions are better described as occupying tetrahedral sites. These are defined by two Co(1) and two Co(2) ions [$\bar{d}_{I(1)-Co(1)}$ = 5·4 (2); $\bar{d}_{I(1)-Co(2)}$ = 5·5 (7); $\bar{d}_{I(2)-Co(1)}$ = 5·5 (8); $\bar{d}_{I(2)-Co(2)}$ = 5·18 (2) Å] (see Fig. 3). Oxalate anions are actually placed in distorted octahedral sites. With regard to the structural unit in Fig. 3, OX(1) are found at the centres of cube faces whereas OX(2) are at the midpoints of cube edges. Four nearly coplanar Co(2) [$\bar{d}_{OX(1)-Co(2)}$ = 6·7 (5) Å] and two axial Co(1) [$\bar{d}_{OX(1)-Co(1)}$ = 4·736 (6) Å] form the environment of the OX(1) anions whose oxygen atoms point approximately towards the Co(2) ions. OX(2), in turn, shows the equivalent situation [four coplanar Co(1), $\bar{d}_{OX(2)-Co(1)}$ = 6·8 (6); two axial Co(2), $\bar{d}_{OX(2)-Co(2)}$ = 4·80 (3) Å].

So far, no evident 'asymmetry' cause has arisen. Because the only additional factor to be analysed is the structural role of water molecules, this and the hydrogen-bonding network implied must constitute the 'asymmetry factor'. With regard to the cobalt ion packing arrangements, two structural types of water molecules can be recognized: five complex ions surround O(W1) in a nearly square-pyramidal geometry; the same holds for O(W2), but the polyhedron around O(W3) formed by the complex ions is roughly tetrahedral [two Co(1) and two Co(2); $\bar{d}_{O(W3)-Co(1)}$ = 5·3 (4), $\bar{d}_{O(W3)-Co(2)}$ = 5·70 (16) Å]. In the pyramidal
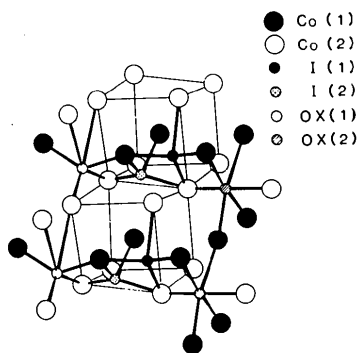

Legend:
● Co (1)
○ Co (2)
● I (1)
⊘ I (2)
○ OX(1)
⊘ OX(2)

Fig. 3. Schematic structural arrangement.

Table 4. *Hydrogen-bond distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

A–H*···B	A···B	H···B	A–H···B
N(1)–H(1L)···O(32ⁱ)	2·905 (9)	2·18 (8)	145 (8)
N(1)–H(1L)···O(36ⁱ)	2·989 (9)	2·31 (8)	138 (8)
N(1)–H(1B)···O(26ⁱⁱ)	2·965 (9)	2·11 (8)	162 (8)
N(4)–H(4L)···O(31ⁱⁱⁱ)	2·968 (9)	2·14 (8)	147 (8)
N(4)–H(4B)···O(W2ⁱˣ)	2·923 (9)	2·02 (8)	174 (8)
N(5)–H(5L)···O(36ⁱ)	2·883 (9)	2·18 (8)	133 (8)
N(5)–H(5B)···O(W2ⁱˣ)	3·007 (9)	2·07 (8)	155 (8)
N(8)–H(8L)···O(31ⁱⁱⁱ)	2·979 (9)	2·21 (8)	138 (8)
N(8)–H(8L)···O(35ⁱⁱⁱ)	2·889 (9)	2·09 (8)	141 (8)
N(8)–H(8B)···I(2ⁱⁱ)	3·688 (6)	2·74 (1)	156 (3)
N(9)–H(9L)···O(32ⁱ)	2·922 (9)	2·08 (8)	148 (8)
N(9)–H(9B)···I(2ⁱⁱⁱ)	3·611 (7)	2·89 (1)	144 (3)
N(12)–H(12L)···O(35ⁱⁱⁱ)	2·907 (9)	2·17 (8)	128 (8)
N(12)–H(12B)···O(25ⁱⁱ)	2·980 (9)	2·10 (8)	163 (8)
N(13)–H(13L)···O(26ᵛ)	3·118 (9)	2·34 (8)	137 (8)
N(13)–H(13L)···O(29ᵛ)	2·880 (9)	2·03 (8)	146 (8)
N(13)–H(13B)···I(1ᵛ)	3·655 (7)	2·73 (1)	147 (3)
N(16)–H(16L)···O(30ⁱⁱ)	3·110 (9)	2·34 (8)	136 (8)
N(16)–H(16B)···O(31ᵛⁱ)	2·876 (9)	1·96 (8)	152 (8)
N(17)–H(17L)···O(29ᵛ)	2·802 (9)	1·91 (8)	147 (8)
N(17)–H(17B)···O(W1ᵛⁱⁱ)	3·009 (9)	2·17 (8)	164 (8)
N(20)–H(20L)···O(35ᵛ)	3·018 (9)	2·15 (8)	143 (8)
N(20)–H(20B)···I(1ᵛ)	3·855 (7)	2·88 (1)	138 (4)
N(21)–H(21L)···O(26ᵛ)	3·035 (9)	2·19 (8)	138 (8)
N(21)–H(21B)···O(32ᵛⁱ)	2·877 (9)	1·97 (8)	164 (8)
N(24)–H(24L)···O(30ⁱⁱ)	2·719 (9)	1·81 (8)	151 (8)
N(24)–H(24B)···O(W1ᵛⁱⁱ)	2·929 (9)	2·06 (8)	149 (8)
O(W1)–H(W11)···O(35ᵛ)	2·784 (9)	2·17 (8)	116 (8)
O(W2)–H(W20)···O(30ᵛⁱⁱⁱ)	2·827 (9)	2·34 (8)	117 (8)
O(W3)–H(W30)···O(36ᵛ)	2·909 (10)	2·16 (8)	148 (9)
O(W3)–H(W31)···O(25ᵛⁱⁱⁱ)	2·947 (10)	1·95 (8)	175 (9)

Symmetry code: (i) $1-x$, $\frac{1}{2}+y$, $\frac{3}{2}-z$; (ii) $\frac{1}{2}-x$, $1-y$, $\frac{1}{2}+z$; (iii) $\frac{1}{2}+x$, $\frac{1}{2}-y$, $1-z$; (iv) $\frac{3}{2}-x$, $1-y$, $-\frac{1}{2}+z$; (v) x, y, z; (vi) $-\frac{1}{2}+x$, $\frac{1}{2}-y$, $1-z$; (vii) $\frac{1}{2}-x$, $1-y$, $-\frac{1}{2}+z$; (viii) x, y, $1+z$.

* For amine hydrogens, L and B indicate *lel* and *ob*, respectively (Cramer & Huneke, 1978).

cases, the four basal cobalt ions are Co(1) for O(W1) [$\bar{d}_{O(W1)-Co(1)}$ = 6·8 (4) Å] and Co(2) for O(W2) [$\bar{d}_{O(W2)-Co(2)}$ = 6·8 (5) Å]. Apical cobalt ions are Co(2) for O(W1) [$d_{O(W1)-Co(2)}$ = 6·270 (7) Å] and Co(1) for O(W2) [$d_{O(W2)-Co(1)}$ = 6·114 (8) Å]. Thus, water by itself does not show the 'asymmetry'.

Examination of the data listed in Table 4 reveals a complex hydrogen-bonding scheme involving a variety of interactions. Focusing our attention on the water molecules, we note the following: (i) as proton donors, O(W1) and O(W2) interact through one oxygen atom from oxalate groups [OX(2) and OX(1), respectively] with one cobalt-complex ion [Co(1) and Co(2), respectively]; (ii) as proton acceptors, each OW (1 and 2) interacts with two –NH(ob) groups (Cramer & Huneke, 1978) from two different ethylenediamine rings [O(W1) with Co(2) and O(W2) with Co(1)]; (iii) O(W3) is involved in the more asymmetric local hydrogen-bonding system. O(W3) does not act as a Lewis base but only as a two-proton donor. Thus, it forms single bridges with oxygen atoms from one OX(2) and one OX(1). In turn, the OX(2) interacts with two –NH(lel) groups from Co(1) and the OX(1) interacts with one –NH(ob) group from Co(1) and one –NH (lel) group from Co(2).

Regarding again the full hydrogen-bonding network (Table 4), it can be noted that these subtle differences in the intermolecular forces involving crystallization water

[O(W3) mainly] propagate across all the structure. Thus, the number, kind and strength of hydrogen bonds formed by [Co(1)(en)₃]³⁺ differs from that formed by [Co(2)(en)₃]³⁺. A common feature for both is that iodide anions are bonded to —NH(ob) groups, in agreement with the steric criterion of Raymond, Corfield & Ibers (1968) developed by Spinat, Whuler & Brouty (1979). On the other hand, it can be assumed that the presence of four base sites in the planar oxalate anions makes possible the stabilization of $\Lambda\delta\delta\delta$ or $\Delta\lambda\lambda\lambda$ configurations instead of other configurations, such as $\Lambda\lambda\lambda\lambda$ or $\Delta\delta\delta\delta$, which are usually stabilized when an extensive hydrogen-bonding network exists (Haque, Caughlan & Emerson, 1970; Duesler & Raymond, 1971; Cramer & Huneke, 1978).

The structure reported here provides a nice example of how packing factors can lead to unexpected results, hydrogen bonding lying behind the observed asymmetry.

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Structure de l'Uranophane Alpha, Ca(UO₂)₂(SiO₃OH)₂.5H₂O

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Abstract. $M_r = 856$, monoclinic, $P2_1$, $a = 15\cdot909$ (6), $b = 7\cdot002$ (3), $c = 6\cdot665$ (3) Å, $\beta = 97\cdot27$ (4)°, $V = 736$ Å³, $Z = 2$, $D_x = 3\cdot78$ Mg m⁻³, λ(Mo $K\alpha$) = $0\cdot7107$ Å, $\mu = 21\cdot0$ mm⁻¹, $F(000) = 760$, $T = 295$ K, $R(F) = 0\cdot030$ for 4422 reflexions. Uranophane alpha has five water molecules rather than the four previously announced. The structure has $P2_1/a$ pseudosymmetry for 16 atoms and $P2_1$ symmetry for the Ca atom and the water molecules. The localization of H atoms leads to the conclusion that the charges of the compound are balanced by (OH)⁻ in (SiO₃OH) tetrahedra and not by oxonium (H₃O)⁺. So the formula is Ca(UO₂)₂(SiO₃-OH)₂.5H₂O.

Introduction. L'échantillon d'uranophane alpha utilisé provient des Bois Noirs du Puy-de-Dôme. La formule chimique CaO.2UO₃.2SiO₂.5H₂O est celle d'un composé ayant deux formes cristallines différentes connues, l'uranophane alpha et l'uranophane beta.

La structure de l'uranophane alpha avait été étudiée d'abord par Smith, Gruner & Lipscomb (1957) ensuite par Stohl & Smith (1981). Ces auteurs faute d'avoir localisé les atomes d'hydrogène ont suggéré la possibilité d'une présence d'ions oxonium (H₃O)⁺ pour balancer les charges, la formule proposée était Ca-(H₃O)₂(UO₂)₂(SiO₄)₂.2H₂O La formule que nous avons obtenue après avoir localisé les atomes d'hydrogène est