

bonds are 113.1° and 115.6° for the bidentate and bridging group respectively; these values show less of a difference than the values obtained by BW; 111.7° and 116.9° , respectively.

With the location of the hydrogen atoms, we have confirmed that hydrogen bonding occurs in accord with the water-oxygen contacts listed by BW as probable hydrogen bonds. The strong hydrogen bonds have nearly linear O-H...O angles, 167 to 176° , as well as short O...O and H...O distances; the H(4)...O(1) distance of 2.39 \AA with a O(8)-H(4)...O(1) angle of 136° implies that this is a very weak interaction. These findings are in agreement with a recent review on neutron-diffraction studies of H_2O molecules in various crystals (Ferraris & Franchini-Angela, 1972).

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The Crystal Structure of Calcium *cis(N)-trans(O₆)-Bis-(L-aspartato)cobaltate(III)-water(2/15)*

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Crystals of $2\{\text{Ca } cis(N)-trans(O_6)-[\text{Co}(L\text{-asp})_2]\} \cdot 15\text{H}_2\text{O}$ are hexagonal with space group $P6_3$: $a = 15.972(3)$, $c = 21.164(6) \text{ \AA}$ and $Z = 3$. The structure was refined by least-squares methods with anisotropic temperature factors to give an R value of 0.054 on the basis of the 2876 observed reflexions collected by diffractometry. The complex anions are held together by N-H...O hydrogen bonds to form left-handed triple helices parallel to the c axis. Calcium ions and water molecules are arranged in and among the helices.

Introduction

There are three isomers of the bis-(L-aspartato)cobaltate(III) ion, in which the ligand is tridentate. The stereochemistry of trifunctional aspartic acid is different from that of other bifunctional amino acids. The three rings join on the face of an octahedron at the asymmetric carbon atom in such a manner that the rings do not define the edges of the octahedron. The presence of such chelate rings leads to complexities

in the circular dichroism spectra which made it difficult to correlate the absolute configurations on the basis of circular dichroism. In fact, two opposite assignments have been made to the *cis(N)-trans(O₅)* and *cis(N)-trans(O₆)* isomers (Yamada, Hidaka & Douglas, 1971; Legg & Neal, 1973). In order to remove uncertainties about this point, crystals of the title compound have been subjected to crystal-structure analysis, although the structures of the two complex ions were known by the structure determination of a double salt,

Ca *cis(N)*-*trans(O₅)*-[Co(L-asp)₂].*cis(N)*-*trans(O₆)*-[Co(L-asp)₂].10H₂O (Oonishi, Shibata, Marumo & Saito, 1973).

Experimental

Bis-(L-aspartato)cobaltate salts were prepared according to the method of Hosaka, Nishikawa & Shibata (1969). The isomers were separated by ion-exchange column chromatography. Crystals of composition 2Ca[Co(L-asp)₂]₂.15H₂O were grown from the last

eluate by slow evaporation under 10°C, an aqueous solution of calcium chloride being used as an eluent. Several salts of alkali and alkaline earth metals were prepared and examined. Finally the present calcium salt was found to be most suitable for X-ray work.

Crystal data

Ca₂Co₄C₃₂H₇₀N₈O₄₇, F.W. 1634.8. Hexagonal, $a = 15.972$ (3), $c = 21.164$ (6) Å, $U = 4675.6$ Å³, $D_m = 1.78$, $D_x = 1.76$ g cm⁻³, $Z = 3$, $\mu(\text{Mo } K\alpha, \lambda = 0.7107 \text{ \AA}) = 14.0$ cm⁻¹. Space group: $P6_3$ (No. 173). Circular dichroism

Table 2. Atomic parameters

(a) Positional and thermal parameters for the non-hydrogen atoms ($\times 10^4$), with their e.s.d.'s in parentheses.

The β_{ij} 's are defined by $\exp[-h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23}]$.

	<i>x</i>	<i>y</i>	<i>z</i>	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Co(1)	3323 (1)	1723 (1)	0	21 (1)	23 (1)	10 (1)	25 (1)	0 (1)	0 (1)
Co(2)	299 (1)	3125 (1)	2502 (1)	27 (1)	24 (1)	11 (1)	19 (1)	-3 (1)	5 (1)
Ca(1)	0	0	4427 (2)	20 (2)	20 (2)	9 (1)	0	0	0
Ca(2)	6667	3333	325 (2)	27 (2)	27 (2)	14 (1)	0	0	0
Ca(3)	3333	6667	953 (2)	16 (2)	16 (2)	13 (1)	0	0	0
O(1)	2862 (7)	711 (6)	622 (4)	48 (6)	29 (5)	12 (2)	42 (9)	11 (6)	7 (5)
O(2)	2495 (9)	-830 (7)	727 (5)	79 (8)	34 (6)	17 (3)	56 (12)	9 (8)	15 (6)
O(3)	5777 (6)	1610 (6)	-1 (5)	23 (4)	37 (5)	33 (3)	30 (8)	-12 (8)	-30 (8)
O(4)	4604 (6)	1925 (6)	60 (5)	26 (4)	23 (4)	20 (2)	29 (7)	-10 (6)	-11 (6)
O(5)	3649 (6)	2697 (6)	637 (4)	32 (5)	31 (5)	12 (2)	35 (8)	-1 (5)	-2 (5)
O(6)	3859 (7)	4190 (7)	728 (5)	46 (6)	34 (5)	20 (3)	51 (9)	-14 (6)	-19 (6)
O(7)	881 (6)	1748 (7)	-381 (5)	23 (5)	29 (5)	29 (3)	32 (8)	-12 (6)	-19 (6)
O(8)	2037 (6)	1496 (6)	-63 (5)	22 (4)	26 (4)	18 (3)	26 (7)	4 (5)	3 (6)
O(9)	1257 (6)	3339 (6)	3216 (5)	30 (5)	29 (5)	16 (2)	20 (8)	-11 (6)	0 (6)
O(10)	2844 (7)	3931 (8)	3182 (5)	31 (5)	55 (7)	19 (3)	25 (10)	-16 (6)	9 (7)
O(11)	2089 (6)	5639 (6)	1636 (5)	29 (5)	28 (5)	26 (3)	20 (8)	13 (6)	26 (6)
O(12)	1039 (6)	4438 (6)	2230 (5)	33 (5)	27 (5)	16 (2)	34 (8)	10 (5)	5 (5)
O(13)	-364 (6)	3503 (7)	3089 (5)	33 (5)	46 (6)	16 (3)	30 (9)	2 (6)	0 (6)
O(14)	-1883 (9)	3112 (12)	3314 (8)	48 (7)	129 (14)	37 (4)	95 (17)	26 (10)	-18 (13)
O(15)	-1680 (10)	368 (10)	2851 (11)	69 (9)	48 (8)	99 (9)	34 (14)	-123 (16)	79 (14)
O(16)	-449 (6)	1828 (6)	2784 (5)	31 (5)	31 (5)	22 (3)	6 (9)	-16 (6)	15 (6)
N(1)	2983 (6)	700 (7)	-598 (5)	25 (5)	23 (5)	8 (2)	21 (8)	-1 (5)	0 (5)
N(2)	3805 (7)	2796 (7)	-580 (5)	26 (5)	26 (5)	12 (2)	23 (9)	0 (6)	0 (6)
N(3)	1052 (8)	2763 (7)	1988 (6)	36 (6)	22 (5)	17 (3)	25 (9)	-5 (7)	0 (7)
N(4)	-703 (8)	2960 (8)	1928 (6)	37 (6)	29 (6)	16 (3)	31 (10)	-2 (7)	13 (7)
C(1)	2793 (9)	-92 (10)	411 (6)	28 (6)	42 (8)	10 (3)	34 (12)	4 (7)	12 (7)
C(2)	3160 (9)	-11 (8)	-274 (6)	25 (6)	19 (6)	16 (3)	16 (10)	-2 (7)	4 (7)
C(3)	4234 (9)	309 (9)	-270 (7)	30 (7)	32 (7)	21 (4)	39 (12)	-6 (8)	-13 (8)
C(4)	4921 (9)	1340 (9)	-53 (7)	28 (6)	36 (7)	19 (3)	44 (11)	-5 (8)	-6 (9)
C(5)	3693 (8)	3481 (9)	416 (6)	12 (5)	33 (6)	14 (3)	20 (10)	-3 (6)	-3 (7)
C(6)	3500 (9)	3454 (9)	-303 (6)	21 (6)	25 (6)	18 (3)	21 (10)	-3 (7)	-2 (7)
C(7)	2449 (9)	3120 (9)	-446 (7)	26 (6)	25 (6)	21 (4)	27 (11)	-7 (8)	0 (8)
C(8)	1744 (9)	2064 (9)	-275 (7)	21 (6)	27 (6)	13 (3)	20 (10)	-2 (7)	-12 (7)
C(9)	2081 (9)	3583 (9)	2871 (6)	32 (7)	25 (6)	12 (3)	28 (11)	-3 (7)	7 (7)
C(10)	2055 (9)	3423 (9)	2171 (7)	29 (6)	26 (6)	17 (3)	36 (11)	4 (7)	8 (7)
C(11)	2431 (10)	4394 (9)	1825 (7)	38 (7)	29 (7)	15 (3)	38 (12)	14 (8)	16 (8)
C(12)	1794 (9)	4839 (8)	1902 (6)	32 (7)	21 (6)	13 (3)	21 (10)	2 (7)	3 (7)
C(13)	-1271 (11)	3117 (13)	2946 (8)	37 (8)	68 (11)	23 (4)	48 (16)	5 (10)	13 (12)
C(14)	-1595 (10)	2585 (11)	2306 (7)	29 (7)	47 (9)	20 (4)	31 (13)	-4 (8)	17 (9)
C(15)	-2035 (10)	1522 (10)	2413 (8)	39 (8)	32 (7)	27 (5)	14 (12)	-12 (10)	21 (10)
C(16)	-1322 (12)	1223 (11)	2687 (9)	41 (9)	40 (9)	40 (7)	2 (14)	-38 (12)	45 (12)
W(1)	5412 (11)	3571 (11)	4105 (7)	111 (12)	97 (11)	24 (3)	149 (20)	0 (11)	-9 (10)
W(2)	5170 (11)	4538 (10)	1739 (8)	72 (10)	73 (10)	47 (6)	25 (16)	-53 (13)	-34 (13)
W(3)	4685 (16)	4529 (16)	2880 (14)	126 (18)	125 (18)	112 (12)	93 (30)	57 (25)	13 (26)
W(4)	3667 (10)	5727 (9)	279 (6)	88 (9)	72 (9)	28 (3)	119 (16)	6 (10)	-16 (9)
W(5)	621 (7)	1275 (6)	3643 (5)	36 (5)	40 (5)	15 (2)	43 (9)	9 (6)	21 (6)
W(6)	5491 (8)	3056 (8)	1173 (5)	48 (6)	51 (6)	18 (3)	46 (11)	8 (7)	6 (7)
W(7)	1428 (26)	1174 (26)	1376 (17)	101 (26)	113 (26)	44 (12)	100 (45)	19 (30)	16 (30)*
W(8)	1321 (34)	5554 (22)	3522 (14)	286 (50)	71 (20)	30 (9)	207 (53)	-105 (35)	-46 (22)*
W(9)	829 (50)	213 (33)	1265 (28)	556 (100)	90 (35)	139 (22)	341 (117)	276 (77)	44 (46)*

* Population 0.5.

Table 2 (cont.)

(b) Positional parameters for the hydrogen atoms ($\times 10^3$). Mean isotropic temperature factor for the hydrogen atoms is 4.0 \AA^2 .

	<i>x</i>	<i>y</i>	<i>z</i>
H(1)	338	95	-127
H(2)	244	52	-100
H(3)	292	-64	-72
H(4)	443	21	-98
H(5)	440	-16	-37
H(6)	352	258	-129
H(7)	432	324	-81
H(8)	403	418	-64
H(9)	240	356	-43
H(10)	222	311	-120
H(11)	95	284	124
H(12)	83	210	172
H(13)	256	343	190
H(14)	307	472	165
H(15)	251	416	110
H(16)	-58	260	125
H(17)	-33	361	150
H(18)	-217	272	190
H(19)	-253	106	236
H(20)	-206	117	166

spectrum: $\Delta\varepsilon = +3.8, 17100 \text{ cm}^{-1}$; $\Delta\varepsilon = -1.72, 20300 \text{ cm}^{-1}$.

The intensities of reflexions were measured on a Rigaku automated four-circle diffractometer using

Mo $K\alpha$ radiation monochromated by a graphite plate, the ω - 2θ scan technique being employed. The crystal was approximately in the form of a cylinder 0.2 mm in diameter and 0.25 mm in length. 3500 accessible reflexions with $2\theta \leq 55^\circ$ were measured. Reflexion intensities were corrected in the usual way for Lorentz and polarization effects but not for absorption and extinc-

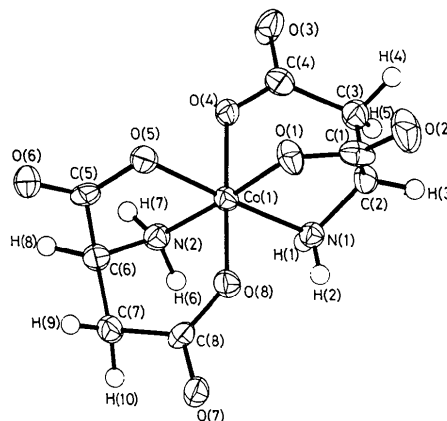


Fig. 1. A perspective drawing of $cis(N)\text{-}trans(O_6)\text{-}[\text{Co}(\text{L-asp})_2]^-$ [complex ion (I)] and the numbering scheme of the atoms. The ellipsoids show the thermal motion of the atoms with a probability of 50%.

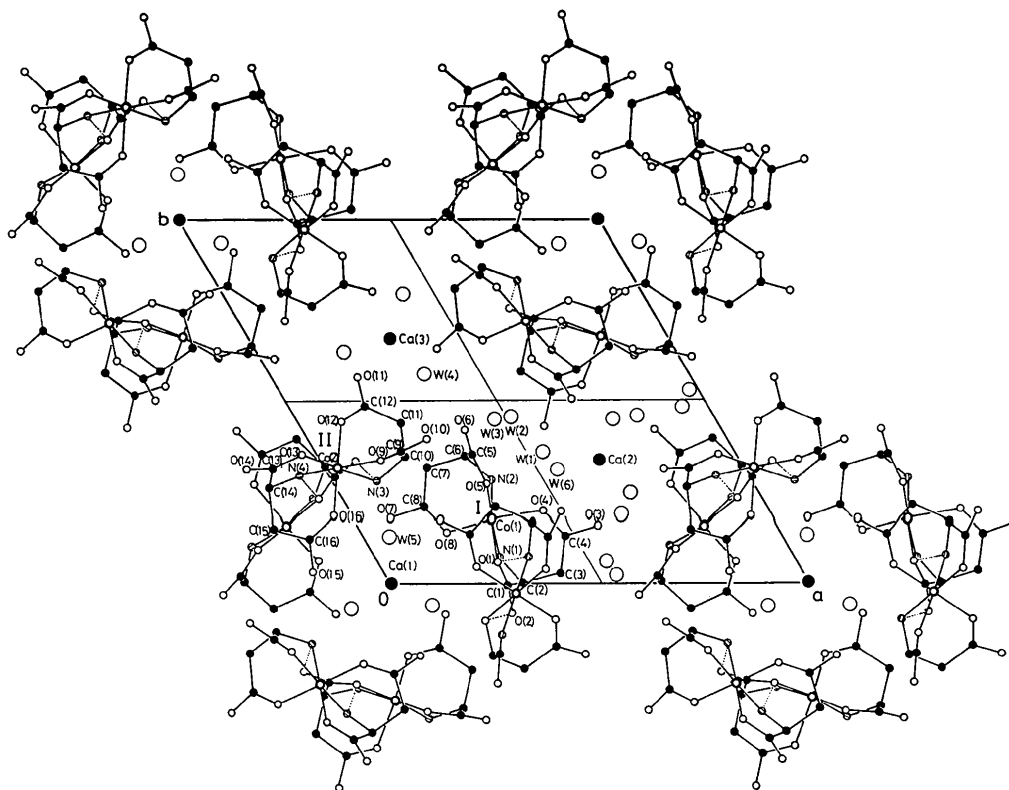


Fig. 2. A projection of the structure along the *c* axis.

tion. Those reflexions for which $|F|$ is smaller than 3σ were rejected. The remaining 2876 unique non-zero data were used for solution and refinement of the structure.

Solution and refinement

The arrangement of the cobalt atoms could be readily deduced from Patterson syntheses. The positions of other lighter atoms, except those of the oxygen atoms of the water molecules, could be located by successive Fourier syntheses of electron density. With the aid of difference syntheses the positions of the water oxygen

atoms were found at a later stage of the refinement. With $R=0.07$ a difference synthesis revealed all the hydrogen atoms (except those of the water molecules) in plausible positions. The final refinement cycles were carried out including the hydrogen atoms, of which the thermal parameters were assumed to be isotropic. A block-diagonal least-squares program was used throughout. The final R value was 0.054. Unit weight was given to all the reflexions. Atomic scattering factors for Ca, Co, C, N, O and H were taken from *International Tables for X-ray Crystallography* (1962). Observed and calculated structure amplitudes are compared in Table 1.* The final atomic parameters are given in Table 2.

Determination of the absolute configuration

A Weissenberg photograph was taken around the [010] axis for the zeroth layer, using Cu $K\alpha$ radiation. The 60 recorded pairs of hkl and $h\bar{k}l$ were examined. Ten pairs for which $|F_c(hkl)|$ and $|F(h\bar{k}l)|$ differed by more than 15% are shown in Table 3. Accordance between the observed and calculated differences indicates that the complex cation has the absolute configuration shown in Fig. 1, in agreement with the previous result (Oonishi *et al.*, 1973).

Description of the structure and discussion

The crystal is built up of complex cations, calcium ions and water molecules. Fig. 2 shows a projection of the structure along the c axis. There are two crystallographically independent but chemically equivalent complex

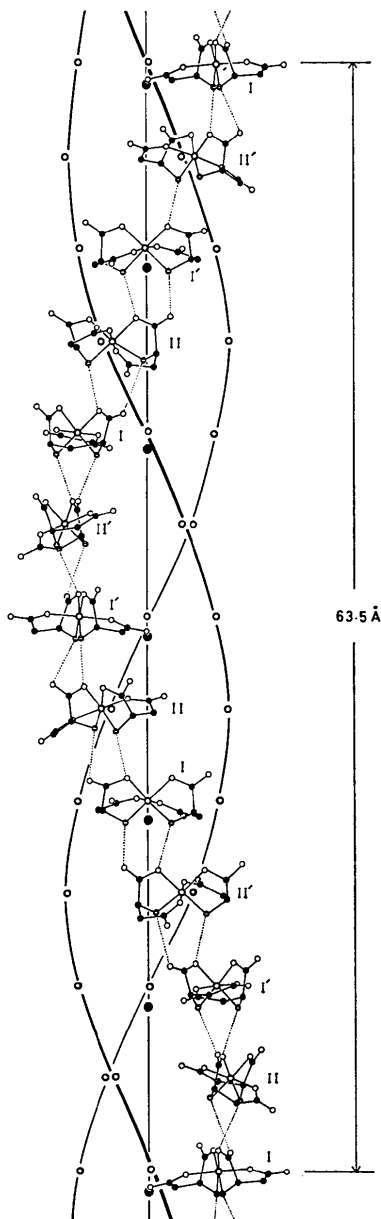


Fig. 3. A side view of the triple helix formed by the complex ions. The repeat distance of the helix along its axis is $3 \times c$, 63.5 Å.

Table 3. Determination of the absolute configuration

h	k	l	$ F_c(hkl) $	Obs.	$ F_c(h\bar{k}l) $
0	0	8	65	<	93
0	0	12	96	<	123
0	0	18	19	>	13
2	$\bar{1}$	9	50	<	63
2	$\bar{1}$	13	39	<	49
4	$\bar{2}$	2	97	>	76
4	$\bar{2}$	11	36	<	45
4	$\bar{2}$	16	50	>	42
6	$\bar{3}$	3	27	<	33
6	$\bar{3}$	13	28	<	34

ions, which are designated (I) and (II). The complex cations correspond to the *cis(N)-trans(O₆)* isomer. Tables 4 and 5 contain all the bond lengths and angles within the complex ions (I) and (II) together with their estimated standard deviations. The corresponding bond lengths and angles observed for the *cis(N)-trans(O₆)* isomer in the double salt are listed for comparison under the heading 'Complex B'.

* This table has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30847 (15 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 4. *Interatomic distances within the complex ion with their estimated standard deviations in parentheses*

Complex I		Complex II		Complex B*
Co(1)—N(1)	1.92 (1) Å	Co(2)—N(3)	1.91 (1) Å	1.902 (7) Å
Co(1)—N(2)	1.93 (1)	Co(2)—N(4)	1.92 (1)	1.901 (6)
Co(1)—O(1)	1.92 (1)	Co(2)—O(9)	1.92 (1)	1.929 (5)
Co(1)—O(4)	1.91 (1)	Co(2)—O(12)	1.91 (1)	1.897 (5)
Co(1)—O(5)	1.92 (1)	Co(2)—O(13)	1.92 (1)	1.917 (5)
Co(1)—O(8)	1.91 (1)	Co(2)—O(16)	1.90 (1)	1.897 (5)
N(1)—C(2)	1.47 (2)	N(3)—C(10)	1.46 (2)	1.485 (10)
C(1)—C(2)	1.54 (2)	C(9)—C(10)	1.50 (2)	1.511 (11)
C(2)—C(3)	1.53 (2)	C(10)—C(11)	1.54 (2)	1.531 (10)
C(3)—C(4)	1.52 (2)	C(11)—C(12)	1.51 (2)	1.533 (10)
C(1)—O(1)	1.31 (2)	C(9)—O(9)	1.29 (2)	1.274 (9)
C(1)—O(2)	1.23 (2)	C(9)—O(10)	1.24 (2)	1.239 (9)
C(4)—O(3)	1.22 (2)	C(12)—O(11)	1.25 (2)	1.229 (10)
C(4)—O(4)	1.29 (2)	C(12)—O(12)	1.26 (2)	1.284 (9)
N(2)—C(6)	1.48 (2)	N(4)—C(14)	1.48 (2)	1.492 (10)
C(5)—C(6)	1.55 (2)	C(13)—C(14)	1.54 (3)	1.533 (10)
C(6)—C(7)	1.52 (2)	C(14)—C(15)	1.50 (3)	1.537 (11)
C(7)—C(8)	1.53 (2)	C(15)—C(16)	1.55 (3)	1.511 (11)
C(5)—O(5)	1.31 (2)	C(13)—O(13)	1.30 (2)	1.295 (9)
C(5)—O(6)	1.22 (2)	C(13)—O(14)	1.25 (3)	1.217 (9)
C(8)—O(7)	1.23 (2)	C(16)—O(15)	1.24 (3)	1.235 (10)
C(8)—O(8)	1.29 (2)	C(16)—O(16)	1.25 (2)	1.275 (10)

* *cis(N)-trans(O₆)* isomer in Ca *cis(N)-trans(O₆)-[Co(L-asp)₂]* *cis(N)-trans(O₆)-[Co(L-asp)₂]*. 10H₂O (Oonishi, Shibata, Marumo & Saito, 1973).

Table 5. *Bond angles (°) within the complex ion with their estimated standard deviations in parentheses*

Complex I		Complex II		Complex B
N(1)—Co(1)—N(2)	98.9 (5)	N(3)—Co(2)—N(4)	101.8 (6)	95.5 (2)
N(1)—Co(1)—O(1)	84.8 (5)	N(3)—Co(2)—O(9)	83.1 (5)	84.8 (2)
N(1)—Co(1)—O(4)	90.7 (5)	N(3)—Co(2)—O(12)	91.3 (5)	91.3 (2)
N(1)—Co(1)—O(8)	88.5 (5)	N(3)—Co(2)—O(16)	89.8 (5)	90.4 (2)
N(2)—Co(1)—O(4)	88.5 (5)	N(4)—Co(2)—O(12)	88.6 (5)	90.1 (2)
N(2)—Co(1)—O(5)	84.3 (5)	N(4)—Co(2)—O(13)	84.3 (5)	85.6 (2)
N(2)—Co(1)—O(8)	92.2 (5)	N(4)—Co(2)—O(16)	91.3 (5)	91.2 (2)
O(1)—Co(1)—O(4)	91.4 (5)	O(9)—Co(2)—O(12)	90.7 (5)	91.8 (2)
O(1)—Co(1)—O(5)	92.0 (5)	O(9)—Co(2)—O(13)	90.9 (5)	94.1 (2)
O(1)—Co(1)—O(8)	88.0 (5)	O(9)—Co(2)—O(16)	89.4 (5)	86.8 (2)
O(4)—Co(1)—O(5)	89.0 (5)	O(12)—Co(2)—O(13)	89.2 (5)	86.6 (2)
O(5)—Co(1)—O(8)	91.8 (5)	O(13)—Co(2)—O(16)	89.7 (5)	91.6 (2)
Co(1)—N(1)—C(2)	105.5 (8)	Co(2)—N(3)—C(10)	105.0 (9)	104.6 (3)
Co(1)—O(1)—C(1)	113.5 (10)	Co(2)—O(9)—C(9)	111.7 (9)	111.9 (4)
O(1)—C(1)—C(2)	113.3 (13)	O(9)—C(9)—C(10)	115.1 (12)	115.9 (4)
O(1)—C(1)—O(2)	123.8 (15)	O(9)—C(9)—O(10)	122.5 (14)	124.1 (4)
O(2)—C(1)—C(2)	122.9 (14)	O(10)—C(9)—C(10)	122.5 (13)	120.0 (6)
C(1)—C(2)—N(1)	107.0 (11)	C(9)—C(10)—N(3)	108.2 (12)	107.4 (5)
C(1)—C(2)—C(3)	109.8 (12)	C(9)—C(10)—C(11)	109.6 (12)	110.1 (4)
N(1)—C(2)—C(3)	111.2 (12)	N(3)—C(10)—C(11)	109.5 (12)	110.5 (5)
C(2)—C(3)—C(14)	116.4 (13)	C(10)—C(11)—C(12)	114.0 (13)	114.4 (6)
C(3)—C(4)—O(4)	120.6 (13)	C(11)—C(12)—O(12)	121.3 (13)	121.5 (6)
C(3)—C(4)—O(3)	119.0 (14)	C(11)—C(12)—O(11)	115.7 (13)	117.5 (6)
O(3)—C(4)—O(4)	120.4 (14)	O(11)—C(12)—O(12)	123.0 (13)	121.0 (7)
C(4)—O(4)—Co(1)	129.9 (10)	C(12)—O(12)—Co(2)	129.6 (10)	129.5 (4)
Co(1)—N(2)—C(6)	104.6 (8)	Co(2)—N(4)—C(14)	106.4 (10)	105.8 (3)
Co(1)—O(5)—C(5)	112.9 (9)	Co(2)—O(13)—C(13)	111.2 (12)	112.9 (3)
O(5)—C(5)—C(6)	114.2 (12)	O(13)—C(13)—C(14)	117.1 (16)	114.9 (5)
O(5)—C(5)—O(6)	125.4 (14)	O(13)—C(13)—O(14)	122.9 (19)	124.1 (3)
O(6)—C(5)—C(6)	120.4 (13)	O(14)—C(13)—C(14)	120.0 (19)	121.0 (5)
C(5)—C(6)—N(2)	106.1 (11)	C(13)—C(14)—N(4)	105.2 (14)	106.1 (4)
C(5)—C(6)—C(7)	112.1 (12)	C(13)—C(14)—C(15)	109.2 (15)	108.9 (5)
N(2)—C(6)—C(7)	111.7 (12)	N(4)—C(14)—C(15)	110.6 (14)	108.9 (6)
C(6)—C(7)—C(8)	114.6 (12)	C(14)—C(15)—C(16)	114.0 (15)	116.8 (6)
C(7)—C(8)—O(8)	122.0 (12)	C(15)—C(16)—O(16)	121.8 (16)	121.4 (7)
C(7)—C(8)—O(7)	117.8 (13)	C(15)—C(16)—O(15)	116.1 (18)	118.2 (7)
O(7)—C(8)—O(8)	120.1 (13)	O(15)—C(16)—O(16)	121.9 (20)	120.4 (7)
C(8)—O(8)—Co(1)	128.8 (9)	C(16)—O(16)—Co(2)	129.9 (12)	128.2 (5)

Table 6. Deviations (Å) of the carbon atoms from the plane formed by N, Co and O atoms

Five-membered chelate rings			Distances of the atoms from the plane					
Atoms defining plane								
Complex I	Co(1)	N(1) O(1)	C(1)	0.36	C(2)	0.77		
	Co(1)	N(2) O(5)	C(5)	0.46	C(6)	0.85		
Complex II	Co(2)	N(3) O(9)	C(9)	0.59	C(10)	0.84		
	Co(2)	N(4) O(13)	C(13)	0.53	C(14)	0.84		
Complex B	Co(2)	N(3) O(9)	C(9)	0.45	C(10)	0.80		
	Co(2)	N(4) O(13)	C(13)	0.33	C(14)	0.75		
Six-membered chelate rings			Distances of the atoms from the plane					
Atoms defining plane								
Complex I	Co(1)	N(1) O(4)	C(2)	1.20	C(3)	0.99	C(4)	0.40
	Co(1)	N(2) O(8)	C(6)	1.18	C(7)	0.88	C(8)	0.29
Complex II	Co(2)	N(3) O(12)	C(10)	1.14	C(11)	0.74	C(12)	0.13
	Co(2)	N(4) O(16)	C(14)	1.14	C(15)	0.77	C(16)	0.19
Complex B	Co(2)	N(3) O(12)	C(10)	1.22	C(11)	0.95	C(12)	0.34
	Co(2)	N(4) O(16)	C(14)	1.24	C(15)	1.02	C(16)	0.53

Table 7. Pertinent interatomic distances

Key to symmetry operations			
	x	y	z
1	x	y	z
2	y	y-x	½+z
3	y-x	-x	z
4	-x	-y	½+z
5	-y	x-y	z
6	x-y	x	½+z
Ca(1)-O(7)	2.45 (1)	4	
Ca(1)-W(5)	2.42 (1)	1	
Ca(2)-O(3)	2.48 (1)	1	
Ca(2)-W(6)	2.47 (1)	1	
Ca(3)-O(11)	2.34 (1)	1	
Ca(3)-W(4)	2.32 (1)	1	
O(4)-W(6)	2.87 (2)	1	
O(5)-W(6)	2.93 (2)	1	
O(6)-W(2)	2.85 (2)	1	
O(6)-W(4)	2.79 (2)	1	
O(7)-N(1)	3.08 (2)	5	
O(9)-W(5)	3.12 (2)	1	
O(9)-N(2)	2.92 (2)	6	
O(10)-W(3)	2.68 (3)	1	
O(10)-N(1)	2.90 (2)	6	
O(14)-W(1)	2.95 (2)	5	
O(15)-W(5)	2.64 (2)	5	
O(16)-W(5)	2.92 (2)	1	
N(3)-O(2)	2.89 (2)	5	
N(4)-O(1)	3.05 (2)	5	
W(2)-W(6)	2.92 (2)	1	
W(5)-O(7)	3.02 (2)	2	
W(5)-W(5)	3.06 (2)	5	
W(5)-O(7)	2.97 (2)	6	
W(5)-O(8)	3.03 (2)	6	
W(5)-N(1)	3.14 (2)	6	

As shown in the tables, the shapes and the sizes of the complex ions (I) and (II) are very much alike, and similar to those of the complex ion B, of which a detailed description of the structure has already been given (Oonishi *et al.*, 1973).

The deviations of the carbon atoms from the plane formed by cobalt, nitrogen and oxygen atoms are listed in Table 6. Pertinent interatomic distances outside the complex ions are listed in Table 7. The complex ions (I) and (II) are held together by four

N-H...O hydrogen bonds between carboxylic oxygen atoms in the five-membered chelate rings and the amino group. Thus the complex ions form a left-handed triple helix parallel to the *c* axis, as illustrated in Fig. 3. As shown in Fig. 2, the helices of the complex anions are packed intimately by electrostatic interactions between carboxylic oxygen atoms not coordinated to the cobalt atoms and the calcium ions located among the helices. Other calcium ions lie on the threefold axes of rotation and are distributed in the helices. Every calcium ion is coordinated to the three carboxylic oxygen atoms and the three oxygen atoms of the water molecules in a distorted octahedral coordination. The rest of the molecules of water of crystallization are arranged in a channel formed by the three triple helices of the complex anions. They are held together by N-H...O and O-H...O hydrogen bonds.

Yamada, Hidaka & Douglas (1971) first prepared and separated all three possible isomers of [Co(L-asp)₂]⁻ by ion-exchange column chromatography. They assigned the first, second and third eluates as the *trans(N)*, *cis(N)-trans(O₆)* and *cis(N)-trans(O₅)* isomers, respectively, on the basis of absorption, circular dichroism and p.m.r. (Froebe, Yamada, Hidaka & Douglas, 1971) studies of related compounds such as (+)₅₄₆⁻ and (-)₅₄₆⁻[Co(edta)]⁻. On the other hand Legg & Neal (1973) made opposite assignments with respect to the two *cis(N)* isomers on the basis of C.D. and p.m.r. studies of the closely related *S,S*-ethylenediamine-*N,N'*-disuccinic acid complex of cobalt(III), [Co(edds)]⁻, in which three chelate rings join on the face of an octahedron at non-coordinating atoms. The present X-ray study has verified the assignment of Legg & Neal (1973) for the two *cis(N)* isomers. In both of the assignments, pretty good correlations are recognized between the circular dichroism spectra of the reference compounds and those of the isomers in question. Thus correlation between stereochemistries with circular dichroism spectra requires some prudence. A check on the correlation by X-ray analysis is needed at important points.

All the calculations were carried out on the FACOM 270-30 of this Institute and on the HITAC 8700/8800 at the Computer Centre of this University with a local version of the Universal Crystallographic Computation Program System (Crystallographic Society of Japan).

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The Crystal and Molecular Structure of Proflavine Hemisulphate Hydrate

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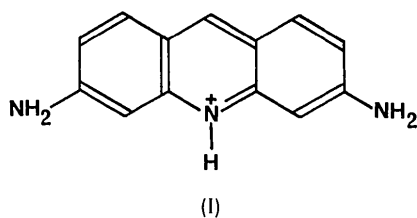
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Proflavine hemisulphate (3,6-diaminoacridine hemisulphate hydrate), crystallizes in the monoclinic space group $P2_1/c$, with $a = 12.703$ (1), $b = 19.940$ (2), $c = 21.487$ (2) Å, $\beta = 92.24$ (2)°, and $Z = 16$. The structure was solved by direct and search methods. The asymmetric unit contains four proflavine molecules, two sulphate ions and seven water molecules. The structure was refined to a final R of 0.074 for 4738 statistically significant reflexions, out of a total of 5601 measured on a diffractometer. The proflavine rings have slight deviations from equivalent geometry. They are not highly stacked. There are strong intermolecular interactions involving the positively-charged central nitrogens of the proflavine rings, and the sulphate anions, which tend to dominate the crystal structure. The complex hydrogen-bonding pattern in the structure involves all but three hydrogen-bond donors.

Introduction

The acridines derive much of their biological interest from the fact that they often show mutagenic and anti-tumour properties (Albert, 1966). Many of these compounds interact with nucleic acids; it is believed that these interactions are intimately related to the biological properties (Peacocke, 1973). The mode of binding to DNA has been well established for proflavine [(I), 3,6-diaminoacridine], which is perhaps the most extensively studied of all acridine-nucleic acid systems (Peacocke, 1973). Binding is of two types, a strong stacking interaction between planar aminoacridine rings and purine-pyrimidine base pairs (Lerman, 1961; Pritchard, Blake & Peacocke, 1966), and weaker electrostatic binding between aminoacridine cations and the charged phosphates on the exterior of the DNA double helix. One of the purposes of the present study was to obtain information relevant to the precise stereochemistry of these processes.



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The structure of acridine itself has been established by Phillips (1956) and Phillips, Ahmed & Barnes (1960); several substituted acridines have also been studied (Talacki, Carrell & Glusker, 1974, and references therein; Courseille, Busetta & Hospital, 1973). Obendorf, Carrell & Glusker (1974) have recently reported the crystal structure of proflavine dihydrochloride in which the aminoacridine moiety is diprotonated. Proflavine is, however, normally studied and used medicinally as the hemisulphate, and it is this compound that is reported here. A preliminary account has been published (Neidle & Jones, 1975).

Experimental

Commercial proflavine hemisulphate (British Drug Houses Ltd) was crystallized from water in the dark. Large prismatic needles were obtained, which showed oblique extinction. Preliminary Weissenberg and precession photographs showed the crystals to be monoclinic. Systematic absences $h0l: l=2n+1$ and $0k0: k=2n+1$, showed the space group to be $P2_1/c$. Cell dimensions were obtained by least-squares refinement of 2θ values measured on a diffractometer.

Crystal data

$\text{C}_{13}\text{H}_{12}\text{N}_3^+ \cdot 0.5(\text{SO}_4^{2-}) \cdot 1.75\text{H}_2\text{O}$, F.W.289.7. Monoclinic needles, elongated along **a**. $a = 12.703$ (1), $b =$