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The Crystal Structure of Calcium *cis*(*N*)-*trans*(O_5)-Bis-(L-aspartato)cobaltate(III) *cis*(*N*)-*trans*(O_6)-Bis-(L-aspartato)cobaltate(III) Decahydrate

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Crystals of Ca *cis*(*N*)-*trans*(O_5)-[Co(L-asp)$_2$]*cis*(*N*)-*trans*(O_6)-[Co(L-asp)$_2$].$10H_2O$ are orthorhombic with space group $P2_12_12_1$: $a=18{\cdot}688$ (3), $b=10{\cdot}517$ (2), $c=17{\cdot}309$ (3) Å and $Z=4$. The structure was refined by least-squares methods with anisotropic temperature factors to give an R value of 0·041 on the basis of 3412 observed reflexions collected by the diffractometer method. The structure consists of two isomeric complex ions: *cis*(*N*)-*trans*(O_5) and *cis*(*N*)-*trans*(O_6) isomers, calcium ions and water molecules. Both complex cations exhibit distorted octahedral coordinations. The complex anions are held together by N–H···O hydrogen bonds to form a left-handed helix parallel to the b axis. A calcium ion is surrounded by three carboxylic oxygen atoms and four oxygen atoms of water molecules.

Introduction

There are three possible geometric isomers of the bis-(L-aspartato)cobaltate(III) ion when the ligand acts as a tridentate (Fig. 1). Two of the three isomers were isolated and characterized by Hosaka, Nishikawa & Shibata (1969). Later all three isomers were isolated and geometric configurations were assigned from absorption and circular dichroism spectra and nuclear magnetic resonance measurements (Yamada, Hidaka & Douglas, 1971; Froebe, Yamada, Hidaka & Douglas, 1971; Hidaka, Yamada & Douglas, 1972). Crystals of the calcium and lithium salts, having the composition $CaCo_2C_{16}H_{40}N_4O_{26}$ and $LiCoC_8H_{16}N_2O_{11}$, have been subjected to crystal-structure analysis in order to establish the absolute configurations and conformational details of the complex anions. The former crystals were obtained upon recrystallization of the blue-violet modification, which was considered to be the *cis*(*N*)-*trans* (O_5) isomer. The absorption and circular dichroism spectra of the compound in an aqueous solution are, however, not identical with those of the *cis*(*N*)-*trans*(O_5) isomer, but correspond to those of an equi-molar mixture of the two isomers, *cis*(*N*)-*trans*(O_5) and *cis*(*N*)-*trans*(O_6), indicating that the two isomers coexist in the crystal. On the other hand the latter crystals are expected to contain only one isomer. In the present paper the crystal structure of the calcium salt will be described.

Experimental

Crystal data

$CaCo_2C_{16}H_{40}N_4O_{26}$, M.W. 431.2

Orthorhombic

$a=18{\cdot}688$ (3), $b=10{\cdot}517$ (2) and $c=17{\cdot}309$ (3) Å, $U=3417{\cdot}9$ Å^3

$D_m=1{\cdot}73$, $D_x=1{\cdot}68$ g cm^{-3}, $Z=4$

Mo $K\alpha$ ($\lambda=0{\cdot}7107$ Å), $\mu=13{\cdot}7$ cm^{-1}

Space group: $P2_12_12_1$ (No. 20)

Elementary analysis gave: C 21·97, H 4·79, N 6·74%; $CaCo_2C_{16}H_{40}N_4O_{26}$ requires C 22·28, H 4·68, N 6·50%.

The intensities of the reflexions were measured on a Rigaku automated four-circle diffractometer. A crystal with approximate dimensions $0{\cdot}3\times0{\cdot}25\times0{\cdot}3$ mm was mounted on the goniostat with the b axis roughly parallel to the φ axis. Mo $K\alpha$ radiation was used. 4600 independent reflexions up to $2\theta=55°$ were measured by employing the ω–2θ scan technique, of which 3412 with $|F|>3\sigma$ were regarded as 'observed'. Three reflexions were measured as references every 50 reflexions: the net counts of these reflexions did not alter noticeably over the period of data collection. The

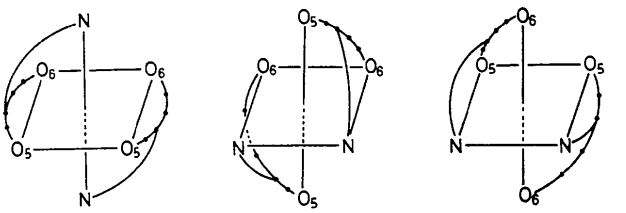

Fig. 1. Schematic drawings of (*a*) the *trans*(*N*), (*b*) the *cis*(*N*)-*trans*(O_5) and (*c*) the *cis*(*N*)-*trans*(O_6) isomers of the [Co(L-asp)$_2$]$^-$ ion.

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Table 1. *Observed and calculated structure amplitudes*

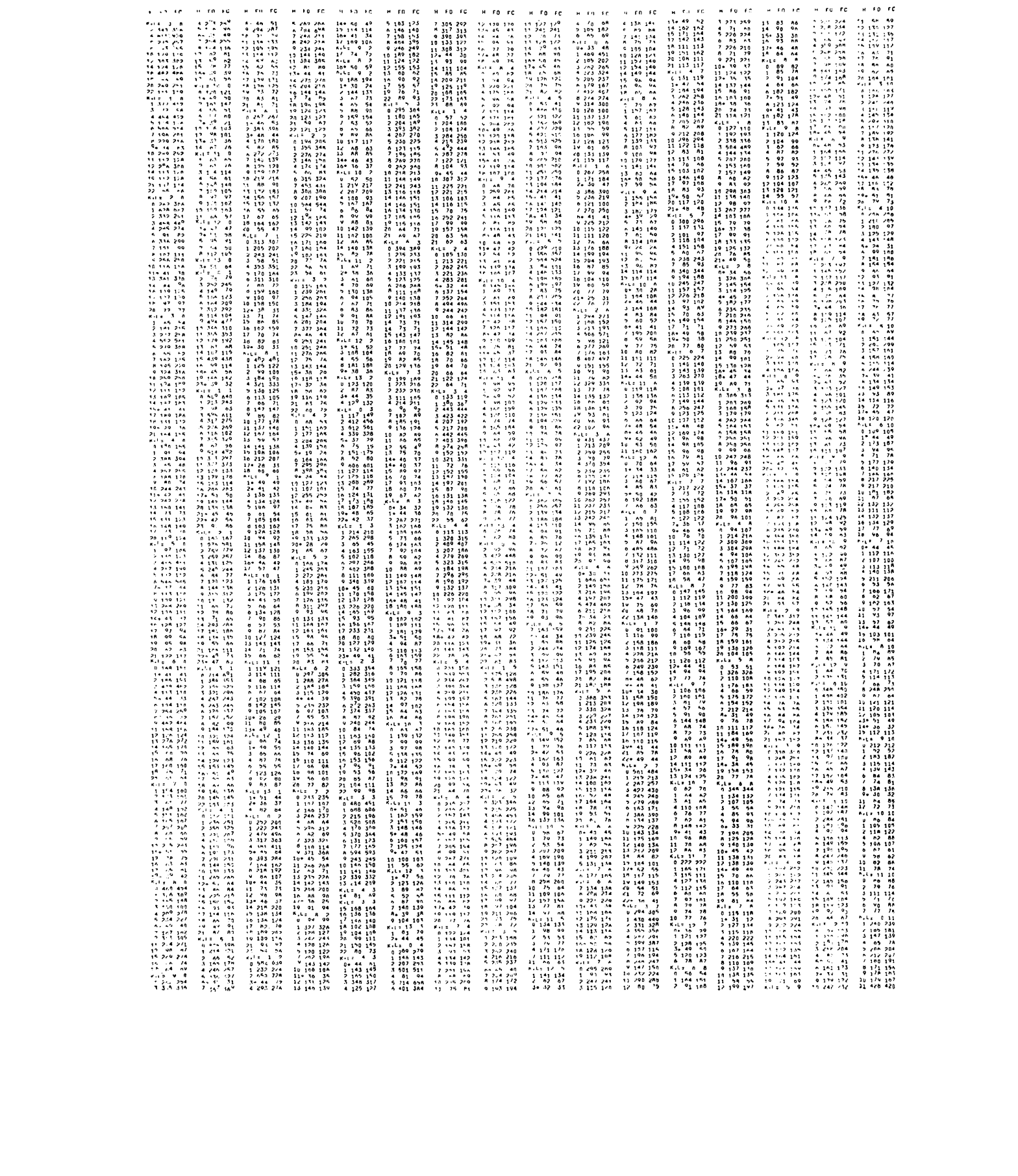
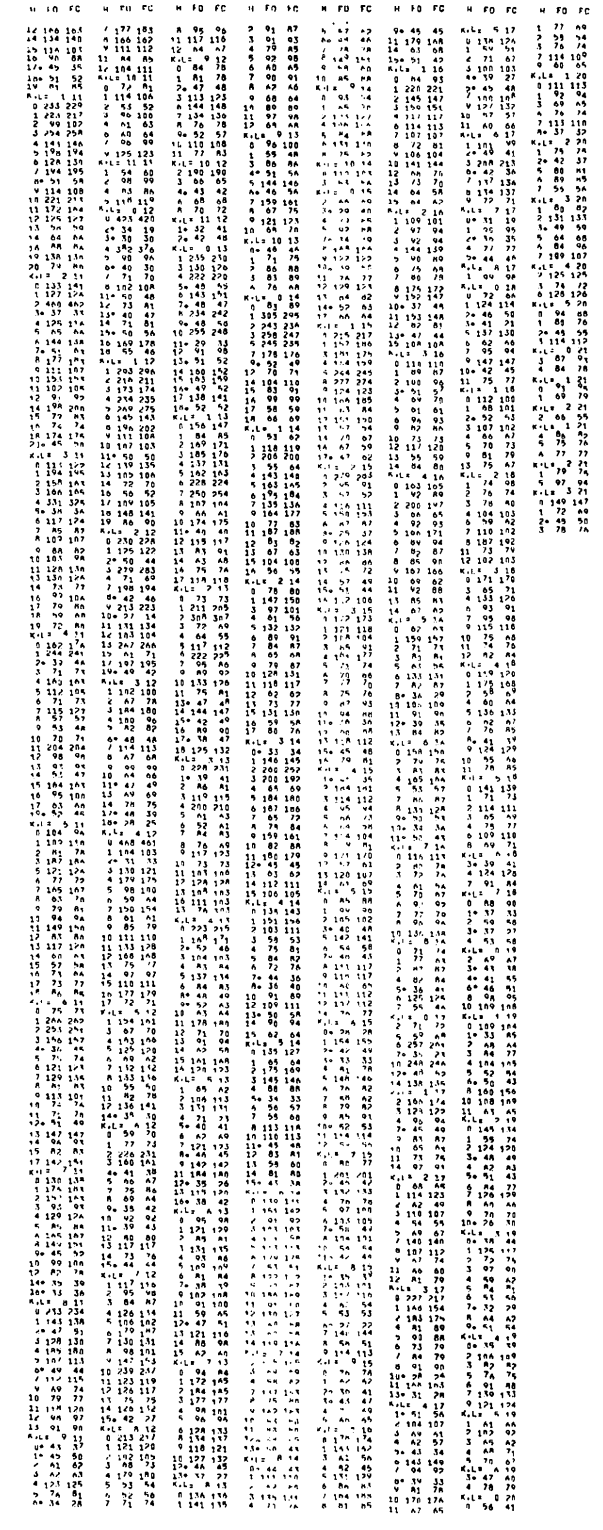


Table 1 (*cont.*)



intensities were corrected for Lorentz and polarization effects. No corrections for absorption and extinction were made.

Solution and refinement of the structure

The positions of the cobalt and calcium atoms were deduced from the Patterson maps. These coordinates were used to calculate the structure factors. The R value was 0·35. Three-dimensional electron density maps were then calculated with all the terms, the phases of which were calculated on the basis of the cobalt and calcium atoms. The maps revealed the positions of all the remaining non-hydrogen atoms of the complex ions. The atomic positions and isotropic temperature factors were refined by the least-squares method with the block-diagonal program *HBLS*-4 written by Dr Ashida. A weighting scheme, $w=0{\cdot}2$ for $|F_o| \leq 15$ and $w=1$ for all other F_o's was employed. The scattering factor for Co, Ca, O, N, C and H atoms were taken from *International Tables for X-ray Crystallography* (1962). After several refinement cycles the structure converged with $R=0{\cdot}10$. A difference Fourier synthesis was then calculated, which revealed the positions of 10 oxygen atoms of water molecules. After inclusion of the water oxygen atoms, further cycles of least-squares refinement were carried out with anisotropic modes. R then decreased to 0·045. A difference synthesis at this stage revealed all the positions of hydrogen atoms except those of water molecules. In this difference synthesis and electron density synthesis, there was one well defined peak with a height of about one half that of an oxygen atom. The maps were well explained if one of the 10 oxygen atoms is distributed over this new position and its original position with equal probability. This disorder of water molecules was taken into account in subsequent refinement. Further refinement cycles were carried out with anisotropic temperature factors for non-hydrogen atoms and with isotropic temperature factors for hydrogen atoms. The final R value was 0·041 for all the 3412 observed reflexions. At the final stage of the refinement all the parameter shifts of non-hydrogen atoms were

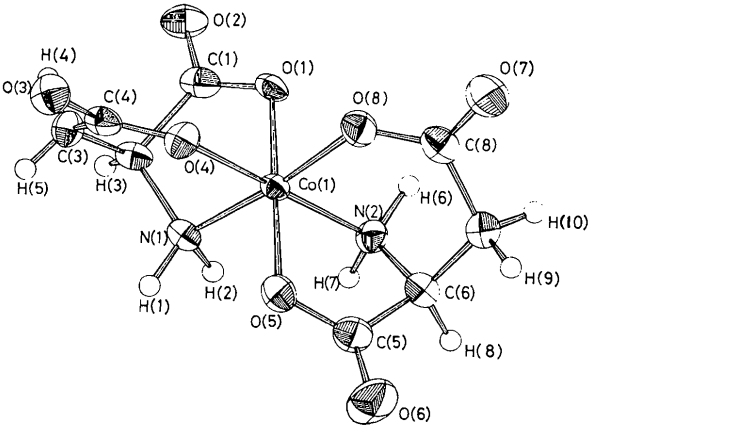


Fig. 2. A perspective drawing of *cis*(*N*)-*trans*(O_5)-[Co(L-asp)$_2$]$^-$ and the numbering scheme of the atoms. The ellipsoids show the thermal motions of the atoms with a probability of 50%.

well within the corresponding standard deviations. Table 1 gives the observed and calculated structure factors. The atomic parameters and their standard deviations are listed in Table 2.

Determination of the absolute configuration

Equi-inclination Weissenberg photographs of the first layer around the *b* axis were taken using Cu $K\alpha$ radiation. Differences between intensities of some reflexions and those of their counter-reflexions were clearly discernible, as shown in Table 3. Comparison of the observed and calculated differences shows that the complex ions have the absolute configurations illustrated in Figs. 2 and 3.

Description of the structure and discussion

The crystal is essentially ionic and is built up of *cis*(N)-*trans*(O_5)-[Co(L-asp)$_2$]$^-$, *cis*(*N*)-*trans*(O_6)-[Co(L-asp)$_2$]$^-$ Ca^{2+} and water molecules. Thermal ellipsoids of the complex ions, the *cis*(*N*)-*trans*(O_5) isomer (complex *A*), and *cis*(*N*)-*trans*(O_6) isomer (complex *B*) are illustrated in Figs. 2 and 3, which correctly represent the absolute

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 $\exp[-(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+2hk\beta_{12}+2hl\beta_{13}+2kl\beta_{23})]$.

	x	*y*	*z*	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Co(1)	2270 (1)	6100 (1)	3790 (1)	13 (1)	34 (1)	15 (1)	3 (1)	− 6 (1)	−2 (1)
Co(2)	342 (1)	3511 (1)	2077 (1)	10 (1)	23 (1)	13 (1)	− 1 (1)	1 (1)	−2 (1)
Ca	2242 (1)	9622 (1)	892 (1)	18 (1)	39 (1)	20 (1)	2 (1)	12 (1)	10 (1)
O(1)	1268 (2)	6228 (5)	3730 (3)	11 (1)	67 (5)	16 (2)	11 (4)	−9 (3)	7 (5)
O(2)	286 (3)	5832 (6)	4420 (3)	11 (1)	85 (6)	34 (2)	8 (5)	−4 (3)	6 (6)
O(3)	2144 (3)	8423 (5)	5641 (3)	22 (2)	58 (5)	25 (2)	−10 (6)	−7 (3)	−24 (6)
O(4)	2321 (3)	7452 (5)	4542 (3)	21 (2)	40 (4)	21 (2)	−12 (5)	2 (3)	−12 (5)
O(5)	3278 (3)	5866 (5)	3843 (3)	15 (1)	80 (6)	20 (2)	− 5 (5)	−8 (3)	−10 (6)
O(6)	4161 (3)	5129 (8)	3139 (3)	14 (2)	178 (11)	44 (3)	19 (7)	−1 (4)	−58 (10)
O(7)	2524 (4)	8206 (6)	1876 (4)	46 (3)	95 (7)	30 (3)	40 (8)	14 (4)	52 (7)
O(8)	2336 (3)	7391 (5)	3015 (3)	28 (2)	50 (5)	21 (2)	14 (5)	1 (3)	15 (5)
O(9)	1027 (3)	4786 (5)	1767 (3)	11 (1)	33 (4)	17 (2)	− 4 (4)	6 (2)	−5 (4)
O(10)	1755 (3)	5209 (5)	787 (3)	19 (2)	52 (5)	24 (2)	−19 (5)	17 (3)	−3 (5)
O(11)	− 667 (3)	4074 (6)	61 (3)	19 (2)	115 (8)	22 (2)	13 (6)	−11 (3)	10 (7)
O(12)	− 280 (2)	3942 (4)	1251 (3)	12 (1)	45 (4)	14 (1)	10 (4)	1 (3)	7 (5)
O(13)	− 208 (2)	4664 (4)	2695 (3)	16 (2)	24 (4)	16 (2)	− 6 (4)	6 (2)	−1 (4)
O(14)	−1033 (3)	4634 (5)	3618 (3)	14 (1)	43 (5)	28 (2)	0 (4)	14 (3)	−8 (5)
O(15)	1256 (3)	2756 (6)	4109 (3)	26 (2)	66 (6)	25 (2)	−11 (6)	−24 (3)	14 (6)
O(16)	964 (3)	3151 (5)	2915 (3)	15 (1)	44 (5)	17 (2)	− 3 (4)	−1 (3)	6 (5)
N(1)	2094 (4)	4892 (6)	4607 (4)	16 (2)	39 (6)	18 (2)	− 1 (6)	−8 (4)	−2 (6)
N(2)	2290 (4)	4825 (6)	2995 (4)	18 (2)	51 (6)	17 (2)	3 (6)	3 (4)	−10 (7)
N(3)	879 (4)	2408 (6)	1427 (4)	15 (2)	28 (6)	20 (2)	− 2 (6)	2 (4)	−5 (6)
N(4)	− 315 (4)	2248 (6)	2414 (4)	12 (2)	30 (5)	14 (2)	− 9 (6)	−1 (4)	−5 (5)
C(1)	946 (4)	5828 (7)	4334 (5)	15 (2)	43 (7)	26 (3)	− 3 (7)	−12 (4)	−16 (8)
C(2)	1432 (4)	5347 (8)	4979 (5)	13 (2)	41 (7)	21 (3)	1 (6)	−6 (4)	1 (8)
C(3)	1597 (4)	6440 (8)	5523 (4)	20 (2)	50 (7)	16 (3)	− 7 (7)	−3 (4)	−13 (8)
C(4)	2051 (4)	7516 (8)	5212 (5)	14 (2)	44 (7)	22 (3)	4 (7)	−15 (4)	−15 (8)
C(5)	3539 (5)	5345 (9)	3242 (5)	14 (2)	80 (9)	26 (3)	8 (8)	−6 (5)	−6 (9)
C(6)	2995 (4)	5019 (8)	2605 (5)	20 (2)	63 (8)	20 (3)	7 (8)	−3 (4)	4 (8)
C(7)	2955 (5)	6121 (9)	2034 (5)	26 (3)	74 (9)	19 (3)	19 (8)	5 (5)	6 (9)
C(8)	2575 (5)	7327 (9)	2329 (5)	22 (3)	61 (8)	23 (3)	2 (8)	−3 (5)	8 (9)
C(9)	1331 (4)	4502 (7)	1131 (5)	9 (2)	36 (6)	22 (3)	8 (6)	−4 (4)	7 (7)
C(10)	1130 (4)	3232 (7)	786 (4)	11 (2)	42 (7)	16 (2)	3 (6)	4 (4)	0 (7)
C(11)	537 (4)	3407 (9)	184 (4)	9 (2)	79 (8)	13 (2)	−10 (7)	0 (3)	−9 (8)
C(12)	− 183 (4)	3833 (8)	519 (4)	14 (2)	49 (7)	17 (2)	1 (7)	−5 (4)	7 (7)
C(13)	− 623 (4)	4089 (7)	3183 (4)	13 (2)	31 (6)	16 (3)	2 (6)	−1 (4)	−10 (7)
C(14)	− 540 (4)	2639 (7)	3206 (4)	18 (2)	25 (6)	15 (2)	− 2 (6)	1 (4)	−3 (6)
C(15)	58 (4)	2296 (7)	3780 (4)	21 (2)	40 (7)	16 (3)	− 7 (7)	−2 (4)	2 (8)
C(16)	800 (4)	2776 (7)	3593 (5)	20 (2)	22 (6)	24 (3)	15 (6)	−11 (4)	−12 (7)
W(1)	3364 (4)	9048 (7)	268 (5)	28 (2)	76 (8)	47 (3)	− 2 (8)	33 (5)	−24 (9)
W(2)	1690 (5)	471 (8)	− 222 (5)	38 (3)	113 (9)	39 (4)	−20 (10)	27 (5)	−35 (10)
W(3)	1845 (5)	7702 (7)	274 (5)	48 (3)	58 (7)	39 (3)	−17 (8)	4 (6)	−19 (8)
W(4)	2164 (4)	1059 (6)	2025 (4)	23 (2)	76 (6)	26 (2)	4 (7)	1 (4)	−7 (7)
W(5)	1744 (4)	9860 (7)	3369 (4)	32 (3)	97 (8)	34 (3)	14 (8)	14 (5)	21 (8)
W(6)	2780 (6)	2341 (9)	3670 (6)	58 (4)	120 (11)	54 (4)	32 (13)	−21 (8)	1 (12)
W(7)*	4440 (10)	7822 (21)	1292 (15)	47 (7)	216 (30)	111 (14)	−19 (26)	−54 (18)	127 (38)
W(8)	4596 (5)	1424 (13)	1500 (5)	45 (4)	277 (19)	37 (3)	90 (17)	−11 (6)	−17 (15)
W(9)	4860 (10)	3852 (19)	1938 (10)	134 (9)	369 (41)	119 (17)	−36 (34)	122 (22)	−157 (49)
W(10)	4619 (6)	191 (16)	4293 (7)	46 (10)	386 (34)	70 (10)	11 (32)	1 (18)	142 (34)
W(11)*	3599 (6)	1275 (28)	2539 (8)	11 (4)	571 (57)	34 (6)	− 9 (26)	15 (8)	−173 (34)

* Population 0·5.

Table 2 (*cont.*)

(*b*) Positional parameters for the hydrogen atoms ($\times 10^3$)

Mean isotropic temperature factor of the hydrogen atoms is 5·2 Å^2.

	x	*y*	*z*
H(1)	254 (8)	486 (16)	493 (8)
H(2)	212 (6)	401 (11)	438 (11)
H(3)	117 (8)	465 (15)	519 (8)
H(4)	116 (6)	682 (10)	562 (6)
H(5)	189 (7)	623 (14)	598 (8)
H(6)	194 (6)	491 (11)	269 (10)
H(7)	227 (7)	401 (10)	319 (6)
H(8)	307 (7)	411 (13)	245 (8)
H(9)	344 (6)	645 (12)	192 (7)
H(10)	274 (8)	594 (13)	152 (8)
H(11)	60 (9)	177 (16)	119 (10)
H(12)	124 (7)	185 (13)	170 (7)
H(13)	152 (6)	288 (10)	46 (6)
H(14)	68 (6)	415 (10)	− 23 (6)
H(15)	51 (6)	266 (13)	− 13 (7)
H(16)	− 14 (8)	155 (15)	243 (9)
H(17)	− 68 (6)	230 (10)	207 (7)
H(18)	− 96 (7)	230 (13)	343 (8)
H(19)	− 13 (6)	256 (12)	428 (7)
H(20)	4 (5)	134 (10)	376 (6)

Table 3. *Determination of the absolute configuration*

h	*k*	*l*	$\lvert F_c(hkl)\rvert^2$	Obs.	$\lvert F_c(\bar{h}kl)\rvert^2$
1	1	$\bar{2}$	4096	>	3996
1	1	$\bar{3}$	4844	>	2652
1	1	$\bar{4}$	2016	<	3410
1	1	$\bar{12}$	7327	>	6384
3	1	$\bar{3}$	640	>	408
3	1	$\bar{5}$	756	<	1156
3	1	$\bar{7}$	790	<	1616
3	1	$\bar{15}$	1998	<	2362
4	1	$\bar{2}$	4396	<	6384
4	1	$\bar{3}$	2540	>	986
6	1	$\bar{1}$	1436	>	829

configurations. Two aspartic acid residues are octahedrally coordinated to a cobalt atom as a tridentate ligand through two amino nitrogen atoms and four carboxylic oxygen atoms. A five-membered, a six-membered and a seven-membered chelate ring are formed. Two nitrogen atoms are in *cis*-positions in both of the complex ions. In the complex *A*, two oxygen atoms of the five-membered chelate rings are in *trans*-positions and those of the six-membered chelate rings are in *cis*-positions, whereas in the complex *B* oxygen atoms of the five-membered chelate rings and those of the six-membered chelate rings are in *cis*- and *trans*-positions, respectively.

The bond distances and angles within the complex ions are listed in Tables 4 and 5, together with their estimated standard deviations. The Co–N distances are 1·929 and 1·922 Å in the complex *A* and 1·902 and 1·901 Å in the complex *B*, all shorter than those observed in other cobalt(III) complexes. The Co–O distances range from 1·879 to 1·931 Å in the complex *A* and from 1·897 to 1·929 Å in the complex *B*. As can be seen from Figs. 2 and 3 and Table 4 the two Co–O distances are longer for those in *cis*-positions than for those in *trans*-positions. The deviations from 90° of N–Co–O angles in the chelate rings range from +3·9 to −4·7° in the complex *A* and from +5·5 to −5·2° in the complex *B*. The coordination octahedrons are slightly distorted. For example, the Co–N(1) and Co(1)–O(8) bonds in the complex *A* are not collinear but make an angle of 173·1°. Likewise the angles N(2)–Co(1)–O(4) and O(1)–Co(1)–O(5) are 174·9 and 176·7° respectively. These distortions seem to be due to the non-bonded hydrogen interaction as well as to formation of the strained chelate rings. The deviations of the carbon atoms from the plane formed by cobalt, nitrogen and oxygen atoms are listed in Table 6. As can be seen from the table, the conformations of the four five-membered chelate rings in the complex ions *A* and *B* are the symmetric envelope form, and those of the six-membered chelate rings are all asymmetric skew-boat.

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

Complex *A*	
Co(1)···N(1)	1·929 (7) Å
Co(1)···N(2)	1·922 (7)
Co(1)···O(1)	1·879 (5)
Co(1)···O(4)	1·931 (5)
Co(1)···O(5)	1·903 (5)
Co(1)···O(8)	1·912 (5)
N(1)····C(2)	1·475 (10)
C(1)····C(2)	1·526 (11)
C(2)····C(3)	1·517 (11)
C(3)····C(4)	1·513 (11)
C(1)····O(1)	1·278 (10)
C(1)····O(2)	1·241 (10)
C(4)····O(3)	1·222 (10)
C(4)····O(4)	1·266 (9)
N(2)····C(6)	1·495 (11)
C(5)····C(6)	1·539 (12)
C(6)····C(7)	1·525 (12)
C(7)····C(8)	1·541 (13)
C(5)····O(5)	1·273 (11)
C(5)····O(6)	1·197 (10)
C(8)····O(7)	1·216 (12)
C(8)····O(8)	1·271 (10)
Complex *B*	
Co(2)···N(3)	1·902 (7) Å
Co(2)···N(4)	1·901 (6)
Co(2)···O(9)	1·929 (5)
Co(2)···O(12)	1·897 (5)
Co(2)···O(13)	1·917 (5)
Co(2)···O(16)	1·897 (5)
N(3)····C(10)	1·485 (10)
C(9)····C(10)	1·511 (11)
C(10)···C(11)	1·531 (10)
C(11)···C(12)	1·533 (10)
C(9)····O(9)	1·274 (9)
C(9)····O(10)	1·239 (9)
C(12)···O(11)	1·229 (10)
C(12)···O(12)	1·284 (9)
N(4)····C(14)	1·492 (10)
C(13)···C(14)	1·533 (10)
C(14)···C(15)	1·537 (11)
C(15)···C(16)	1·511 (11)
C(13)···O(13)	1·295 (9)
C(13)···O(14)	1·217 (9)
C(16)···O(15)	1·235 (10)
C(16)···O(16)	1·275 (10)

Table 5. *Bond angles within the complex ions with their estimated standard deviations in parentheses*

Complex *A*	
N(1)—Co(1)–N(2)	93·9 (2)°
N(1)—Co(1)–O(1)	85·3 (2)
N(1)—Co(1)–O(4)	89·9 (2)
N(1)—Co(1)–O(5)	92·7 (2)
N(2)—Co(1)–O(1)	91·7 (2)
N(2)—Co(1)–O(5)	85·7 (2)
N(2)—Co(1)–O(8)	89·5 (2)
O(1)—Co(1)–O(4)	92·0 (2)
O(1)—Co(1)–O(8)	88·6 (2)
O(4)—Co(1)–O(5)	90·8 (2)
O(4)—Co(1)–O(8)	87·0 (2)
O(5)—Co(1)–O(8)	93·5 (2)
Co(1)–N(1)—C(2)	104·4 (3)
Co(1)–O(1)—C(1)	113·6 (5)
O(1)—C(1)—C(2)	115·3 (7)
O(1)—C(1)—O(2)	124·4 (7)
O(2)—C(1)—C(2)	120·3 (7)
C(1)—C(2)—N(1)	106·7 (6)
C(1)—C(2)—C(3)	108·9 (4)
N(1)—C(2)—C(3)	110·2 (5)
C(2)—C(3)—C(4)	117·4 (6)
C(3)—C(4)—O(4)	120·7 (4)
C(3)—C(4)—O(3)	116·6 (6)
O(4)—C(4)—O(3)	122·7 (5)
C(4)—O(4)—Co(1)	129·5 (4)
Co(1)–N(2)—C(6)	104·2 (4)
Co(1)–O(5)—C(5)	113·3 (5)
O(5)—C(5)—C(6)	115·4 (7)
O(5)—C(5)—O(6)	125·1 (8)
O(6)—C(5)—C(6)	119·5 (7)
C(5)—C(6)—N(2)	106·8 (7)
C(5)—C(6)—C(7)	109·2 (5)
N(2)—C(6)—C(7)	110·7 (6)
C(6)—C(7)—C(8)	115·7 (6)
C(7)—C(8)—O(8)	121·0 (5)
C(7)—C(8)—O(7)	116·6 (7)
O(7)—C(8)—O(8)	122·4 (6)
C(8)—O(8)—Co(1)	129·9 (4)

Table 5 (*cont.*)

Complex *B*	
N(3)—Co(2)–N(4)	95·5 (2)°
N(3)—Co(2)–O(9)	84·8 (2)
N(3)—Co(2)–O(12)	91·3 (2)
N(3)—Co(2)–O(16)	90·4 (2)
N(4)—Co(2)–O(12)	90·1 (2)
N(4)—Co(2)–O(13)	85·6 (2)
N(4)—Co(2)–O(16)	91·2 (2)
O(9)—Co(2)–O(12)	91·8 (2)
O(9)—Co(2)–O(13)	94·1 (2)
O(9)—Co(2)–O(16)	86·8 (2)
O(12)–Co(2)–O(13)	86·6 (2)
O(13)–Co(2)–O(16)	91·6 (2)
Co(2)–N(3)—C(10)	104·6 (3)
Co(2)–O(9)—C(9)	111·9 (4)
O(9)—C(9)—C(10)	115·9 (4)
O(9)—C(9)—O(10)	124·1 (4)
O(10)–C(9)—C(10)	120·0 (6)
C(9)—C(10)–N(3)	107·4 (5)
C(9)—C(10)–C(11)	110·1 (4)
N(3)—C(10)–C(11)	110·5 (5)
C(10)–C(11)–C(12)	114·4 (6)
C(11)–C(12)–O(12)	121·5 (6)
C(11)–C(12)–O(11)	117·5 (6)
O(11)–C(12)–O(12)	121·0 (7)
C(12)–O(12)–Co(2)	129·5 (4)
Co(2)–N(4)—C(14)	105·8 (3)
Co(2)–O(13)–C(13)	112·9 (3)
O(13)–C(13)–C(14)	114·9 (5)
O(13)–C(13)–O(14)	124·1 (3)
O(14)–C(13)–C(14)	121·0 (5)
C(13)–C(14)–N(4)	106·1 (4)
C(13)–C(14)–C(15)	108·9 (5)
N(4)—C(14)–C(15)	108·9 (6)
C(14)–C(15)–C(16)	116·8 (6)
C(15)–C(16)–O(16)	121·4 (7)
C(15)–C(16)–O(15)	118·2 (7)
O(15)–C(16)–O(16)	120·4 (7)
C(16)–O(16)–Co(2)	128·2 (5)

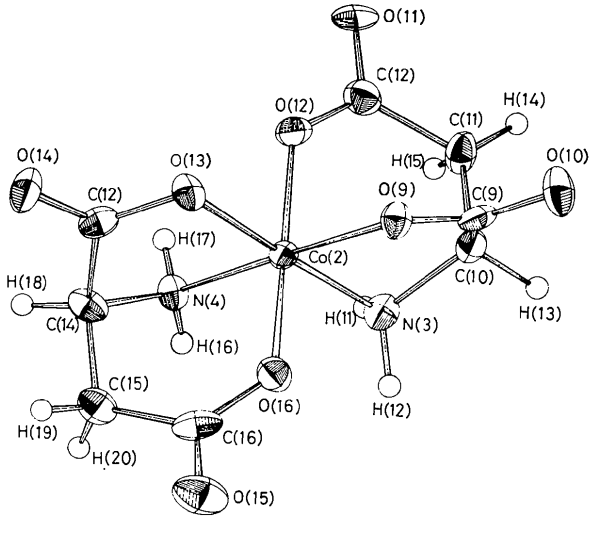


Fig. 3. A perspective drawing of *cis*(*N*)-*trans*(*O*$_6$)-[Co(L-asp)$_2$]$^-$ and numbering scheme of atoms. The ellipsoids show the thermal motions of the atoms with a probability of 50%.

The structure projected along the *b* axis is shown in Fig. 4. The important molecular contacts are listed in Table 7. A complex *B* and the one related by a twofold screw axis parallel to the *b* axis are held together by two N–H···O hydrogen bonds formed between amino nitrogen atoms and carboxylic oxygen atoms of the five-membered chelate rings. A complex *A* is linked to two complexes *B* that are related to each other by a twofold screw axis parallel to the *b* axis by four N–H···O hydrogen bonds; two of them are formed between carboxylic oxygen atoms in the six-membered chelate rings of the complex *B* and amino nitrogen atoms of the complex *A*, and the other two are between the amino nitrogen atoms of the complex *B* and oxygen atoms in the five-membered chelate rings of the complex *A*. By these hydrogen bonds, the complex ions form a left-handed helix parallel to the *b* axis, as shown in Fig. 5. These helices are held together by electrostatic forces between calcium ions and the carboxylic oxygen atoms not used to form hydrogen bonds. A calcium ion is coordinated to three carboxylic oxygen atoms and four oxygen atoms of the water molecules. The coordination polyhedron is a distorted pentagonal bipyramid. The rest of the water of crystallization molecules are arranged in a channel formed by four

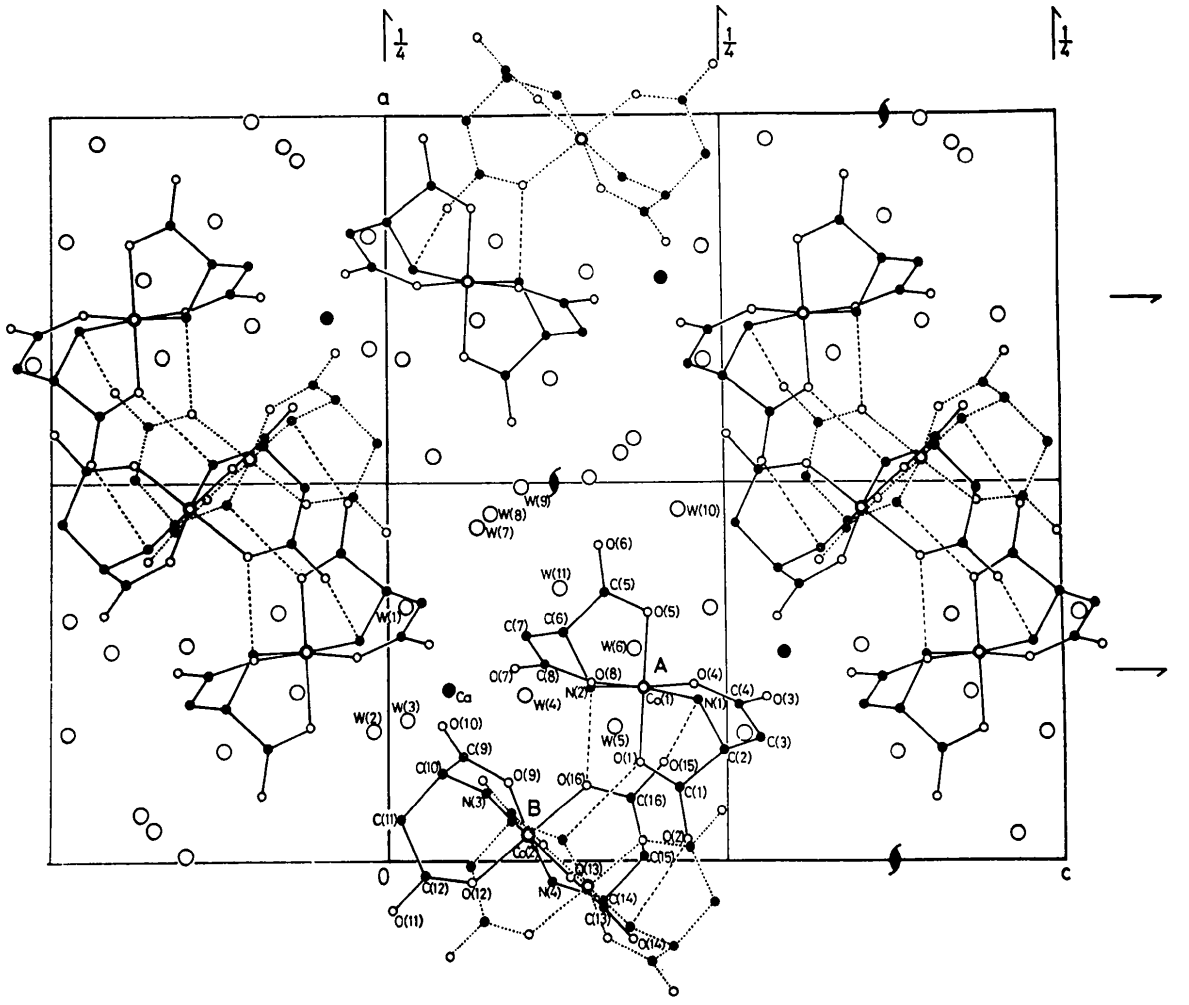


Fig. 4. A projection of the structure along the *b* axis.

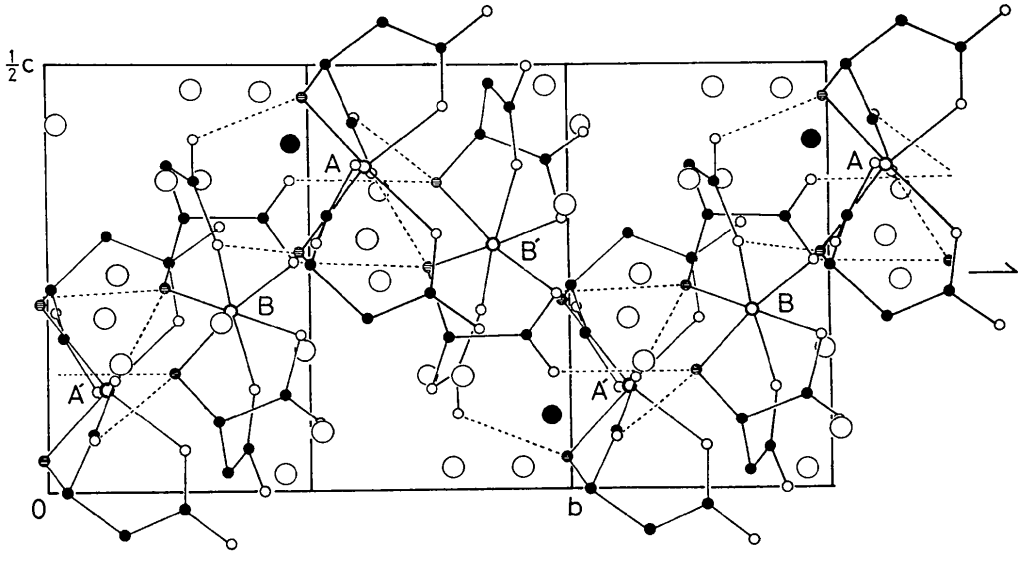


Fig. 5. A projection of the structure along the *a* axis, showing a helix formed by the complex ions.

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

Five-membered chelate rings

Plane determined by:			Distances of the atoms from the planes in Å:			
Co(1)	N(1)	O(1)	C(1) 0·38		C(2)	0·77
Co(1)	N(2)	O(5)	C(5) 0·39		C(6)	0·78
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

Plane determined by:			Distances of the atoms from the planes in Å:					
Co(1)	N(1)	O(4)	C(2)	1·23	C(3)	1·01	C(4)	0·40
Co(1)	N(2)	O(8)	C(6)	1·27	C(7)	1·10	C(8)	0·38
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

helices of complex anions. They are held together by O–H···O hydrogen bonds and are linked to the carboxylic oxygen atoms.

Table 7. *Interatomic distances less than* 3·4 Å

Key to symmetry operations

1	x	y	z
2	$-x$	$\frac{1}{2}+y$	$\frac{1}{2}-z$
3	$1-x$	$\frac{1}{2}+y$	$\frac{1}{2}-z$
4	$\frac{1}{2}-x$	$1-y$	$\frac{1}{2}+z$
5	$\frac{1}{2}+x$	$\frac{1}{2}-y$	$1-z$
6	x	$1+y$	z

Ca···O(3)	2·394 (6) Å	4
Ca···O(7)	2·322 (9)	1
Ca···O(14)	2·413 (5)	2
O(1)····N(4)	2·871 (8)	2
O(2)····O(13)	3·358 (7)	1
O(2)····O(14)	3·097 (8)	1
O(2)····N(3)	3·104 (9)	2
O(2)····C(11)	3·189 (10)	2
O(2)····C(12)	3·164 (10)	2
O(3)····O(11)	3·093 (8)	2
O(5)····C(11)	3·297 (9)	4
O(6)····*W*(8)	2·764 (13)	3
O(6)····*W*(9)	2·799 (19)	1
O(8)····*W*(5)	2·888 (9)	1
O(9)····N(2)	3·176 (8)	1
O(9)····N(4)	3·239 (8)	2
O(9)····C(14)	3·136 (9)	2
O(10)···C(7)	3·258 (10)	1
O(10)···*W*(3)	2·773 (9)	1
O(13)···N(4)	2·895 (7)	2
O(14)···N(3)	2·933 (2)	2
O(15)···*W*(1)	2·851 (10)	4
O(15)···*W*(6)	2·981 (12)	1
O(15)···N(1)	2·871 (9)	1
O(15)···C(1)	3·305 (10)	1
O(16)···N(2)	3·043 (8)	1
Ca···*W*(1)	2·435 (8) Å	1
Ca···*W*(2)	2·362 (8)	6
Ca···*W*(3)	2·403 (8)	1
Ca···*W*(4)	2·480 (7)	6

Table 7 (*cont.*)

N(1) ····*W*(6)	3·388 (12)	1
N(1) ····O(10)	2·968 (9)	4
N(2) ····*W*(6)	3·004 (12)	1
N(3) ····*W*(4)	2·974 (9)	1
C(4) ····O(11)	3·098 (10)	2
C(4) ····*W*(2)	3·252 (12)	1
C(6) ····*W*(6)	3·390 (13)	1
W(1)····*W*(3)	3·171 (11)	1
W(1)····*W*(7)	2·975 (23)	1
W(2)····*W*(10)	2·678 (15)	6
W(4)····*W*(7)	3·353 (12)	1
W(4)····*W*(11)	2·835 (23)	1
W(5)····O(12)	2·975 (9)	2
W(5)····*W*(4)	2·760 (10)	6
W(5)····*W*(6)	3·291 (13)	6
W(6)····*W*(3)	2·864 (13)	4
W(6)····*W*(11)	2·725 (22)	1
W(8)····*W*(9)	2·709 (23)	1
W(8)····*W*(11)	2·595 (21)	1
W(9)····*W*(10)	2·732 (22)	3
W(10)···O(2)	2·771 (14)	5

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