Table 3. *Principal interatomic distances* (Å), *angles* (°) *and torsion angles* (°) *in* $M(C_3H_4O_6P)_2.2H_2O$

	M = Zn	M = Mg	M = Mn	M = Ca
P—O(1)	1.564 (2)	1.564 (2)	1.568 (2)	1.573 (3)
P—O(2)	1.496 (2)	1.496 (2)	1.495 (2)	1.499 (2)
P—O(3)	1.474 (2)	1.477 (2)	1.474 (2)	1.477 (2)
P—O(4)	1.615 (2)	1.615 (2)	1.618 (2)	1.616 (2)
O(4)—C(2)	1.378 (3)	1.390 (3)	1.380 (3)	1.383 (4)
O(5)—C(1)	1.269 (3)	1.283 (3)	1.247 (4)	1.237 (4)
O(6)—C(1)	1.249 (3)	1.246 (4)	1.289 (4)	1.296 (4)
C(1)—C(2)	1.487 (3)	1.484 (4)	1.487 (4)	1.486 (5)
C(2)—C(3)	1.318 (3)	1.320 (4)	1.319 (4)	1.320 (5)
M—O(2)	2.065 (2)	2.059 (2)	2.155 (2)	2.326 (3)
M—O(3^{i})	2.033 (2)	2.016 (2)	2.106 (2)	2.259 (3)
M—O(7)	2.180 (2)	2.154 (2)	2.290 (2)	2.451 (3)
O(1)—P—O(2)	107.0 (1)	107.4 (1)	107.5 (2)	107.9 (2)
O(1)—P—O(3)	111.1 (1)	111.3 (1)	111.0 (2)	111.4 (2)
O(1)—P—O(4)	103.9 (1)	103.5 (1)	103.9 (2)	104.0 (2)
O(2)—P—O(3)	120.7 (1)	120.5 (1)	120.3 (2)	119.9 (2)
O(2)—P—O(4)	102.3 (1)	102.3 (1)	102.5 (2)	102.4 (2)
O(3)—P—O(4)	110.3 (1)	110.3 (1)	110.1 (2)	109.8 (2)
P—O(4)—C(2)	123.1 (2)	123.3 (3)	123.3 (2)	124.0 (3)
O(5)—C(1)—O(6)	124.7 (3)	124.1 (3)	124.4 (3)	124.1 (4)
O(5)—C(1)—C(2)	117.6 (3)	117.6 (3)	120.3 (3)	121.4 (3)
O(6)—C(1)—C(2)	117.7 (3)	118.3 (3)	115.3 (3)	114.5 (3)
O(4)—C(2)—C(1)	112.1 (2)	112.4 (3)	111.0 (3)	110.7 (3)
O(4)—C(2)—C(3)	127.3 (3)	126.6 (3)	127.2 (3)	126.7 (4)
C(1)—C(2)—C(3)	120.6 (3)	121.0 (3)	121.7 (3)	122.5 (4)
O(2)—M—O(3^{i})	89.2 (1)	89.3 (1)	89.0 (1)	87.0 (1)
O(2)—M—O(7)	92.4 (1)	91.7 (1)	91.7 (1)	89.2 (1)
O(3^{i})—M—O(7)	91.9 (1)	91.3 (1)	92.8 (1)	93.8 (1)
P—O(2)—M	134.9 (1)	136.8 (1)	134.7 (2)	133.4 (2)
P—O(3)—M^{ii}	176.1 (2)	177.2 (2)	175.6 (2)	175.0 (2)
O(1)—P—O(4)—C(2)	69.2 (7)	70.4 (4)	71.2 (5)	74.1 (5)
O(2)—P—O(4)—C(2)	− 179.6 (6)	− 178.0 (4)	− 176.9 (4)	− 173.6 (5)
O(3)—P—O(4)—C(2)	− 50.0 (7)	− 48.7 (5)	− 47.8 (5)	− 45.2 (5)
P—O(4)—C(2)—C(1)	165.9 (8)	164.5 (5)	165.7 (5)	163.8 (5)
P—O(4)—C(2)—C(3)	− 14.5 (9)	− 16.6 (6)	− 15.4 (6)	− 17.4 (7)
C(3)—C(2)—C(1)—O(5)	− 174.7 (9)	− 174.7 (6)	− 173.8 (7)	− 174.7 (7)
C(3)—C(2)—C(1)—O(6)	5.5 (10)	5.5 (7)	7.7 (7)	5.6 (8)
O(4)—C(2)—C(1)—O(5)	5.0 (9)	4.2 (6)	5.1 (6)	4.2 (7)
O(4)—C(2)—C(1)—O(6)	− 174.8 (9)	− 175.6 (6)	− 173.4 (6)	− 175.5 (7)

Symmetry code: (i) $x, y-1, z$; (ii) $x, 1+y, z$.

Table 4. *Hydrogen-bonding data in* $M(C_3H_4O_6P)_2.2H_2O$ *crystals* (Å, °)

O—H···O	M	O···O	H···O	O—H···O
O(1)—H(1)···O(7^{i})	Zn	2.693 (3)	1.75 (3)	162 (4)
	Mg	2.712 (3)	1.77 (3)	161 (4)
	Mn	2.704 (3)	1.75 (3)	169 (3)
	Ca	2.734 (3)	1.79 (4)	163 (5)
O(5)—H(5)···O(6^{ii})	Zn	2.638 (3)	1.69 (5)	163 (4)
	Mg	2.636 (3)	1.69 (5)	164 (5)
O(6)—H(6)···O(5^{ii})	Mn	2.633 (4)	1.67 (6)	169 (6)
	Ca	2.641 (5)	1.69 (5)	167 (5)
O(7)—H(71)···O(2^{iii})	Zn	2.753 (3)	1.78 (2)	179 (3)
	Mg	2.768 (3)	1.80 (3)	173 (3)
	Mn	2.758 (3)	1.87 (4)	150 (4)
	Ca	2.741 (3)	1.83 (4)	155 (4)
O(7)—H(7)···O(4)	Zn	3.044 (4)	2.24 (4)	139 (3)
	Mg	3.072 (4)	2.27 (5)	140 (4)
	Mn	3.107 (4)	2.29 (5)	142 (4)
	Ca	3.213 (4)	2.51 (5)	129 (4)
O(7)—H(7)···O(5)	Zn	3.310 (4)	2.46 (3)	146 (3)
	Mg	3.364 (4)	2.47 (5)	153 (4)
	Mn	3.279 (4)	2.43 (4)	146 (4)
	Ca	3.211 (4)	2.29 (4)	158 (4)

Symmetry code: (i) $x-1, y+1, z$; (ii) $2-x, 2-y, -z$; (iii) $1+x, y, z$.

second [H(7)] water atom is utilized in weak bifurcated hydrogen bonds. There are only small differences between the analogous strong hydrogen bonded oxygen–oxygen distances in the four structures. The largest differences are observed in the weak bifurcated hydrogen bonds.

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Structure of [(*S*)-Alaninato]tetraamminecobalt(III) Sulfate

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Abstract. $[Co(C_3H_6NO_2)(NH_3)_4]SO_4$, $M_r = 311.20$, monoclinic, $P2_1$, $a = 9.769\ (1)$, $b = 9.080\ (1)$, $c = 12.474\ (2)$ Å, $\beta = 100.98\ (8)°$, $V = 1086.2\ (2)$ Å^3, $Z = 4$, $D_x = 1.90$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, $\mu = 1.78$ mm^{-1}, $F(000) = 648.0$, $T = 293$ K, final $R = 0.035$, $wR = 0.044$ for 2194 unique observed re-

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flexions. The structure contains two independent complex cations and two independent SO_4 anions joined together by Coulombic forces and hydrogen bonds. The coordination around the Co atom in both complex cations is distorted octahedral. The (*S*)-alaninato ligands are bidentate and bound to the metal atoms through carboxylato O and amino N atoms forming five-membered chelate rings with asymmetric envelope conformations. The position of the methyl groups with respect to the Co—O—N plane of the chelate rings is more equatorial than axial.

Introduction. Cobalt(III) complex ions of the type $[Co(am)(NH_3)_4]^{2+}$, containing one optically active amino acidato chelate ligand (am), have been considered as model systems for investigation of vicinal optical activity in octahedral complexes (Hawkins, 1971). For such investigations it is important to establish how the observed optical activity of a complex depends on the relative positions of the atoms of the amino acid and the cobalt(III) centre. However, no crystal structure analysis of a $[Co(am)(NH_3)_4]^{2+}$ complex ion has been reported. We have determined the crystal structure of the sulfate salt of the cation [(*S*)-alaninato]tetraamminecobalt(III).

Experimental. The compound was prepared by a known synthetic procedure which starts from (*S*)-alanine and tetraamminecarbonatocobalt(III) nitrate (Yasui, Hidaka & Shimura, 1966). The crystal specimen had dimensions of 0.15 × 0.18 × 0.26 mm. An Enraf–Nonius CAD-4 diffractometer with graphite monochromator was used.

Unit-cell dimensions from a least-squares fit of 21 reflexions with $13 < \theta < 24^\circ$. Intensities from $\theta/2\theta$ scans of $(0.90 + 0.35\tan\theta)^\circ$ in θ. Background estimated by extending scans at both ends by 25%. Scan speeds adjusted to give $\sigma(I)/I > 0.03$ subject to a time limit of 90 s. Two standard reflexions; no sign of decay over period of the data collection. 2765 independent reflexions ($0 \le h \le 12$, $0 \le k \le 11$, $-15 \le l \le 15$) collected with $2 \le \theta \le 27^\circ$, 2194 observed with $I > 3\sigma(I)$. Final agreement factors: $R = 0.035$, $wR = 0.044$ [$w = 1/\sigma^2(F_o)$], for 288 independent parameters; $(\Delta/\sigma)_{\max} = 0.02$; $\Delta\rho_{\max} = 0.22$, $\Delta\rho_{\min} = -0.24$ e Å^{-3}.

Data corrected for Lp, not for absorption. The structure was solved by heavy-atom and difference Fourier methods. Full-matrix least-squares refinement on *F* with anisotropic thermal parameters for all non-H atoms. A difference Fourier map revealed some of the H-atom positions; remaining H atoms included in calculated positions (at C—H and N—H distances of 0.95 Å). All H atoms included in the final structure factor calculation as riding atoms with fixed isotropic *B* values of 1.3 times the B_{eq} value of the attached N or C atoms. Atomic scattering factors and anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974, Vol. IV). Computer programs of *SDP* system (Frenz, 1982). Model constrained to give known absolute stereochemistry of (*S*)-alanine.

Discussion. The structure consists of two crystallographically independent complex cations and SO_4 anions joined together by Coulombic forces and by N—H···O hydrogen bonds. The absolute configuration of the complex cations and the atomic numbering scheme used are shown in Fig. 1. The atomic coordinates and B_{eq} values for non-H atoms are given in Table 1* and the bond lengths and angles within independent cation–anion pairs designated *A* and *B* are listed in Table 2. Since the crystal structure exhibits a pseudo inversion centre the geometries of the *A* and *B* units are similar, except for the amino acidato ligands.

The coordination around the Co atoms in both complex cations is distorted octahedral. The (*S*)-alaninato ligand is bidentate and binds to the metal atom through carboxylato O and amino N atoms to form a five-membered chelate ring. The remaining octahedral positions are occupied by N atoms belonging to four NH_3 groups. Bond lengths and angles are in good agreement with those found in other compounds containing five-membered amino acidato rings (Freeman, 1967; Watson, Johnson, Ćelap & Kamberi, 1972; Herak, Prelesnik, Manojlović-Muir & Muir, 1974; Herak & Prelesnik, 1976; Herak, Prelesnik & Krstanović, 1978; Vasić,

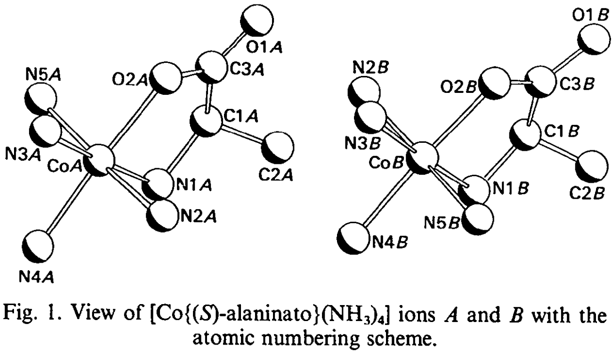

Fig. 1. View of [Co{(*S*)-alaninato}$(NH_3)_4$] ions *A* and *B* with the atomic numbering scheme.

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* Lists of structure factors, anisotropic thermal parameters for non-H atoms, equations of planes, atomic parameters for H atoms and hydrogen-bond geometries, and a molecular packing diagram have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54550 (29 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: MU0224]

Table 1. *Positional parameters with e.s.d.'s in parentheses*

$$B_{\mathrm{eq}} = (4/3)\textstyle\sum_i\sum_j \beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}(Å^2)
Molecule *A*				
Co	0.29854 (8)	0.28000	0.46721 (7)	0.97 (1)
S	−0.1851 (2)	0.2391 (2)	0.4105 (1)	1.31 (3)
O1	0.4426 (6)	0.0517 (6)	0.7298 (4)	2.0 (1)
O2	0.4149 (5)	0.1539 (5)	0.5683 (4)	1.43 (8)
O3	−0.2603 (6)	0.1169 (6)	0.3432 (5)	2.2 (1)
O4	−0.1199 (6)	0.3312 (7)	0.3373 (5)	2.6 (1)
O5	−0.0774 (5)	0.1747 (7)	0.4972 (5)	2.5 (1)
O6	−0.2857 (6)	0.3245 (7)	0.4607 (4)	2.5 (1)
N1	0.1902 (5)	0.3026 (6)	0.5828 (4)	1.12 (9)
N2	0.4233 (6)	0.4374 (7)	0.5298 (5)	1.9 (1)
N3	0.4160 (6)	0.2510 (8)	0.3556 (5)	2.1 (1)
N4	0.1766 (6)	0.4139 (7)	0.3721 (5)	1.6 (1)
N5	0.1786 (6)	0.1122 (7)	0.4099 (4)	1.4 (1)
C1	0.2355 (7)	0.1906 (8)	0.6692 (5)	1.3 (1)
C2	0.2393 (9)	0.2535 (10)	0.7812 (6)	2.5 (1)
C3	0.3752 (7)	0.1253 (7)	0.6581 (6)	1.3 (1)
Molecule *B*				
Co	−0.29585 (8)	0.22689 (10)	0.03322 (7)	1.03 (1)
S	0.1874 (2)	0.2701 (2)	0.0892 (1)	1.32 (3)
O1	−0.4322 (7)	0.4418 (7)	−0.2417 (5)	2.9 (1)
O2	−0.4080 (5)	0.3545 (6)	−0.0700 (4)	1.78 (9)
O3	0.0810 (5)	0.3387 (7)	0.0032 (4)	2.2 (1)
O4	0.1178 (6)	0.1774 (7)	0.1600 (4)	2.6 (1)
O5	−0.2634 (6)	0.3905 (6)	0.1549 (4)	2.0 (1)
O6	−0.2857 (6)	0.1862 (7)	0.0406 (5)	2.8 (1)
N1	−0.1874 (6)	0.1929 (6)	−0.0799 (5)	1.5 (1)
N2	−0.4181 (6)	0.0627 (6)	−0.0241 (4)	1.3 (1)
N3	−0.4160 (6)	0.2625 (6)	0.1408 (4)	1.2 (1)
N4	−0.1686 (6)	0.0967 (7)	0.1310 (4)	1.4 (1)
N5	−0.1817 (6)	0.3939 (7)	0.0938 (6)	2.1 (1)
C1	−0.2656 (7)	0.2461 (8)	−0.1851 (6)	1.7 (1)
C2	−0.1687 (9)	0.2971 (11)	−0.2620 (7)	3.0 (2)
C3	−0.3762 (8)	0.3587 (8)	−0.1653 (6)	1.8 (1)

Herak & Djurić, 1976). Chelate rings in both complex molecules, *A* and *B*, have asymmetric envelope conformations. For consideration of vicinal optical activity of the complex the position of the side methyl group with respect to the coordination plane of the chelate (plane formed by Co, O2 and N1) is important (Juranić *et al.*, 1988; Bosnich & Harrowfield, 1972). The atoms C1*A*, C2*A* and C3*A* lie at 0.296, −0.532 and 0.110 Å respectively from the plane formed by O2*A*, Co*A* and N1*A*. The corresponding deviations of C1*B*, C2*B* and C3*B* from the plane defined by O2*B*, Co*B* and N1*B* are 0.348, −0.292 and 0.084 Å. Therefore the position of the methyl groups with respect to the coordination planes is more equatorial than axial.

From the aforesaid it may be concluded that in both crystallographically independent complex ions the ligand conformation is such that the ring side group is found in the region where it would induce only slight optical activity (Juranić *et al.*, 1988). This is in accordance with the optical activity of the complex observed in solution (Hawkins, 1971).

The ions which comprise the structure are linked by an extensive network of weak and slightly bent hydrogen bonds in which all possible donors and acceptors participate. There is no intramolecular hydrogen bonding.

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

	Molecule *A*	Molecule *B*
Cations		
Co—O2	1.910 (4)	1.914 (5)
Co—N1	1.956 (6)	1.944 (6)
Co—N2	1.944 (6)	1.958 (5)
Co—N3	1.983 (7)	1.970 (6)
Co—N4	1.941 (5)	1.963 (5)
Co—N5	1.972 (6)	1.948 (6)
O2—C3	1.280 (9)	1.285 (9)
C3—O1	1.206 (8)	1.257 (9)
N1—C1	1.487 (8)	1.470 (9)
C1—C2	1.508 (10)	1.542 (12)
C1—C3	1.518 (10)	1.542 (11)
O2—Co—N1	85.1 (2)	85.9 (2)
O2—Co—N2	85.8 (2)	89.2 (2)
O2—Co—N3	91.9 (2)	91.1 (2)
O2—Co—N4	176.5 (2)	175.0 (2)
O2—Co—N5	90.8 (2)	90.1 (2)
N1—Co—N2	90.8 (3)	89.6 (2)
N1—Co—N3	176.9 (2)	176.5 (2)
N1—Co—N4	91.7 (2)	89.3 (2)
N1—Co—N5	89.0 (2)	93.1 (3)
N2—Co—N3	88.7 (3)	88.4 (2)
N2—Co—N4	92.9 (2)	92.3 (2)
N2—Co—N5	176.6 (2)	177.2 (3)
N3—Co—N4	91.4 (3)	93.8 (2)
N3—Co—N5	91.5 (3)	88.8 (3)
N4—Co—N5	90.5 (3)	88.8 (2)
Co—N1—C1	109.5 (4)	109.6 (4)
N1—C1—C2	111.4 (6)	112.2 (5)
N1—C1—C3	110.5 (6)	109.7 (6)
C2—C1—C3	111.8 (5)	115.7 (7)
O1—C3—O2	123.2 (7)	125.0 (7)
O2—C3—C1	115.4 (5)	115.5 (6)
Co—O2—C3	117.3 (4)	115.7 (5)
SO_4 groups		
O3—S	1.497 (6)	1.481 (5)
O4—S	1.469 (7)	1.476 (6)
O5—S	1.478 (5)	1.479 (5)
O6—S	1.481 (6)	1.447 (7)
O3—S—O4	107.4 (3)	109.5 (4)
O3—S—O5	108.9 (3)	107.4 (3)
O3—S—O6	109.4 (3)	110.4 (3)
O4—S—O5	110.3 (3)	109.3 (3)
O4—S—O6	111.4 (4)	111.6 (4)
O5—S—O6	109.5 (3)	108.5 (3)

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