THE CRYSTAL AND MOLECULAR STRUCTURE OF sym-*fac*-(1,4,7-TRIAZAHEPTANE)-(*S*)-ASPARTATOCOBALT(III) DIPERCHLORATE DIHYDRATE

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The crystal and molecular structure of s-*fac*-[Co((*S*)-Asp)(dien)]ClO_4 . $HClO_4$. 2 H_2O (dien = 1,4,7-triazaheptane) was solved by the heavy atom method. The position parameters of the non-hydrogen atoms and their anisotropic temperature parameters were refined based on 1 726 observed reflections with a final value of $R = 0.073$. The substance crystallizes in the orthorhombic system in the space group $P2_12_12_1$, $Z = 4$, $a = 8.506(1)$ Å, $b = 17.171(2)$ Å, $c = 13.277(1)$ Å. The structure involves hydrogen bonds between the O2, O4 and HN2 atoms of aspartic acid and the two molecules of water. The five-membered dien chelate rings take the asymmetric envelope conformations. The five-membered ring of (*S*)-aspartic acid possesses the symmetric envelope conformation whereas the six-membered ring exhibits the skew boat conformation.

This investigation of the structure of the s-*fac*-[Co((*S*)-Asp)(dien)]$^+$ complex (dien = 1,4,7-triazaheptane) is a continuation of the study of structures of complexes of cobalt(III) with aspartic acid (Asp) and linear triamines, viz. 4-methyl-1,4,7-triazaheptane[1] (medien), 1,4,8-triazaoctane[2,3] (aepn) and 1,5,9-triazanonane[4] (dpn). Three geometrical isomers, viz. s-*fac*, u_1-*fac* and u_2-*fac*, are conceivable for the title complex. Chromatographic separation of the reaction mixture revealed the presence of all of them in the ratio 71 : 20 : 9 but only the first was prepared in the crystalline form.

EXPERIMENTAL

The synthesis of s-*fac*-[Co((*S*)-Asp)(dien)]$^+$ has been described by Legg and Cooke[5]. Acidification of a solution containing the cation with perchloric acid resulted in the formation of crystals whose composition was s-*fac*-[Co((*S*)-Asp)(dien)]ClO_4 . $HClO_4$. 2 H_2O. For $C_8H_{23}N_4O_{14}Cl_2Co$ (529.1) calculated: 18.16% C, 4.38% H, 10.58% N; found: 16.09% C, 4.18% H, 9.35% N.

The phase problem was solved by the heavy atom method, and the structure was anisotropically refined in three blocks. The hydrogen atom positions calculated based on the expected geometry and their temperature parameters corresponding to the parent atoms were fixed. The positions of the perchlorate oxygen atoms were refined adopting the ideal geometry (rigid body) assumption. The highest peak in the final Fourier map, 1.7 e Å^{-3}, occurred near the chlorine atom. Absorption and extinction effects were disregarded. The basic crystallographic data and details concerning the measurement procedure and refinement are given in Table I.

TABLE I
Basic crystallographic data of s-*fac*-[Co((*S*)-Asp)(dien)]ClO_4 . $HClO_4$. 2 H_2O and their measuring and refinement parameters

Parameter	Data
Space group	$P2_12_12_1$, $Z = 4$
a, *b*, *c*, Å	8.506(1), 17.171(2), 13.277(1)
$\alpha = \beta = \gamma$, °	90
Cell volume *V*, Å^3	1 939.1(3)
$D_{(calc)}$, g cm^{-3}	1.813
μ(MoKα), cm^{-1}	12.35
F(000)	1 088
Crystal dimensions, mm	0.15 × 0.15 × 0.05
Diffractometer and radiation used	Enraf–Nonius CAD4, MoKα, $\lambda = 0.71073$ Å
Scan technique	$\omega/2\Theta$
No. and Θ range of reflections for lattice parameter refinement	17; 19 → 20 °
Range of *h*, *k* and *l*	0 → 8, 0 → 16, –12 → 12
Standard reflections	0 7 13, 0 12 3
Standard reflections monitored in interval; intensity fluctuaction	180 min; –4.3%
Total number of reflections measured; 2Θ range	2 582; $2\Theta \leq 40°$
Value of R_{int}	0.0729
No. of unique observed reflections	1 726
Criterion for observed reflections	$I \geq 1.96\ \sigma(I)$
Function minimized	$\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2$
Weighting scheme	unique
Parameters refined	261
Values of *R* and *S*	0.0726 and 3.06
Ratio of max. LS shift to e.s.d. in the last cycle	0.002
Max. and min. heights in final $\Delta\rho$ map	1.7, –1.4 eÅ^{-3}
Source of atomic scattering factors	refs[8,11]
Programs used	SDP (ref.[7]); SHELX76 (ref.[8]); PARST (ref.[9]); SHELXS86 (ref.[10])
Computer used	PDP11/73, PC AT

RESULTS AND DISCUSSION

The final coordinates of the non-hydrogen atoms and their equivalent temperature parameters are summarized in Table II, the bond angles and interatomic distances are listed in Table III, the possible hydrogen bonds are given in Table IV. The structure of

TABLE II
Positional parameters of non-hydrogen atoms in s-*fac*-[Co((*S*)-Asp)(dien)]ClO_4 . $HClO_4$. 2 H_2O (. 10^4) and their temperature parameters (. 10^3) with e.s.d.'s in parenthesis
$U_{eq} = (U_{11} + U_{22} + U_{33})/3$

Atom	x	y	z	U_{eq}, Å^2
Co	2326(2)	1696(1)	7747(1)	28.1(0.4)
Cl1	7213(4)	2967(2)	8822(3)	56.5(1.2)
Cl2	7530(5)	203(2)	555(3)	55.8(1.2)
OW1	–2699(11)	2031(5)	5586(7)	63(3)
OW2	–2371(17)	4135(6)	5143(7)	84(4)
O11	6023(12)	2701(6)	9391(7)	104(5)
O12	6639(15)	3260(7)	7960(6)	138(6)
O13	8204(17)	2380(9)	8614(13)	403(22)
O14	7983(19)	3528(10)	9325(8)	353(19)
O21	8007(17)	–387(4)	25(8)	289(13)
O22	8442(14)	796(5)	392(8)	188(9)
O23	7565(14	24(6)	1506(4)	99(5)
O24	6098(8)	379(9)	304(12)	366(24)
O1	703(9)	2007(5)	6842(7)	31(3)
O2	–356(10)	3084(6)	6194(9)	53(4)
O3	3928(10)	2122(6)	6854(7)	38(3)
O4	5230(11)	2970(6)	5936(7)	43(3)
N1	4063(13)	1352(7)	8610(10)	37(4)
N2	2509(12)	706(5)	7072(6)	31(3)
N3	691(13)	1204(7)	8549(10)	38(4)
N4	2042(12)	2733(5)	8330(7)	33(3)
C1	4802(27)	682(15)	8121(19)	138(11)
C2	4002(16)	325(9)	7405(17)	65(6)
C3	1109(18)	209(11	7290(16)	69(6)
C4	321(32)	450(14)	8131(18)	136(11
C5	547(15)	2738(9)	6778(12)	41(5)
C6	1605(13)	3254(8)	7484(9)	35(4)
C7	3108(14)	3468(8)	6919(10)	43(5)
C8	4121(15)	2812(8)	6551(11)	33(4)

the s-*fac*-[Co((*S*)-Asp)(dien)]$^+$ cation and the atom numbering are shown in Fig. 1, projection of the structure into the *xy* plane, along with the hydrogen bonds, is depicted in Fig. 2.

TABLE III
Interatomic distances (Å) and bond angles (°) in the s-*fac*-[Co((*S*)-Asp)(dien)]$^+$ cation

Atoms	Distances	Atoms	Distances
Co–O1	1.907(9)	N1–C1	1.464(28)
Co–O3	1.949(9)	N2–C2	1.495(18)
Co–N1	1.960(12)	N2–C3	1.493(19)
Co–N2	1.928(9)	N3–C4	1.443(27)
Co–N3	1.944(12)	N4–C6	1.483(16)
Co–N4	1.957(9)	C1–C2	1.319(31)
O1–C5	1.265(18)	C3–C4	1.367(32)
O2–C5	1.243(18)	C5–C6	1.573(19)
O3–C8	1.262(17)	C6–C7	1.527(17)
O4–C8	1.276(17)	C7–C8	1.500(19)

Atoms	Angles	Atoms	Angles
N3–Co–N4	95.2(5)	Co–N2–C2	108.5(8)
N2–Co–N4	175.0(4)	C2–N2–C3	111.7(11)
N2–Co–N3	86.0(4)	Co–N3–C4	109.6(12)
N1–Co–N4	97.8(5)	Co–N4–C6	106.3(7)
N1–Co–N3	95.1(5)	N1–C1–C2	117.6(19)
N1–Co–N2	86.9(5)	N2–C2–C1	116.6(15)
O3–Co–N4	89.2(4)	N2–C3–C4	112.1(16)
O3–Co–N3	175.1(5)	N3–C4–C3	118.6(19)
O3–Co–N2	89.5(4)	O1–C5–O2	125.5(14)
O3–Co–N1	86.7(4)	O2–C5–C6	117.1(13)
O1–Co–N4	84.5(4)	O1–C5–C6	117.3(12)
O1–Co–N3	87.1(4)	N4–C6–C5	104.8(10)
O1–Co–N2	90.7(4)	C5–C6–C7	108.8(10)
O1–Co–N1	176.6(5)	N4–C6–C7	107.9(10)
O1–Co–O3	91.0(4)	C6–C7–C8	117.4(11)
Co–O1–C5	113.4(8)	O4–C8–C7	118.3(12)
Co–O3–C8	129.6(9)	O3–C8–C7	121.7(12)
Co–N1–C1	107.5(12)	O3–C8–O4	120.0(12)
Co–N2–C3	110.5(8)		

TABLE IV
Possible hydrogen bonds in s-*fac*-[Co((*S*)-Asp)(dien)]ClO_4 . $HClO_4$. 2 H_2O. Symmetry code: (i) $x - 1$, y, z; (ii) $x - 1/2$, $-y + 1/2$, $-z + 1$.

Atoms	Distances	Atoms	Angles
OW1–O2	2.791(13)	O2–OW1–$O4^i$	91.9(4)
OW1–$O4^i$	2.451(13)	C5–O2–OW1	89.4(8)
		$C8^i$–$O4^i$–OW1	80.4(7)
OW2–O2	2.853(16)	O2–OW2–$HN2^{ii}$	123.7(5)
OW2–$O4^i$	3.045(16)	$O4^i$–OW2–$HN2^{ii}$	111.5(6)
OW2–$N2^{ii}$	2.955(15)	O2–OW2–$O4^i$	79.5(4)
OW2–$HN2^{ii}$	1.957(12)	C5–O2–OW2	168.2(10)
		$C8^i$–$O4^i$–OW2	148.9(9)
		$N2^{ii}$–$HN2^{ii}$–OW2	176.4(9)

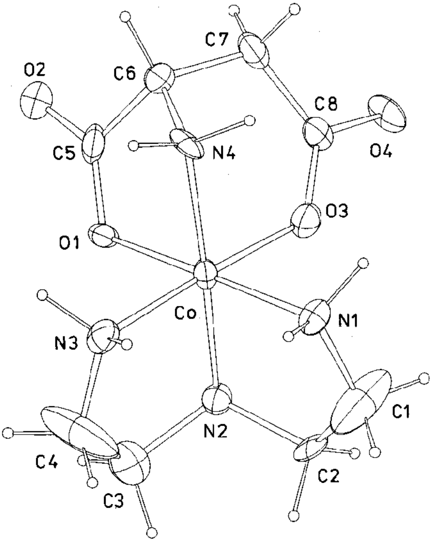

FIG. 1
Structure of the s-*fac*-[Co((*S*)-Asp)(dien)]$^+$ cation

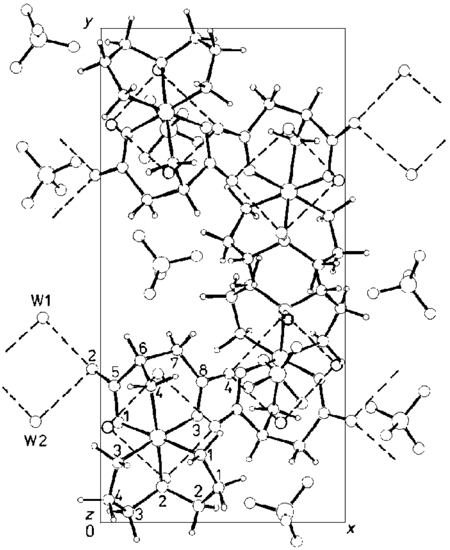

FIG. 2
Projection of the s-*fac*-[Co((*S*)-Asp)(dien)]ClO_4 . $HClO_4$. 2 H_2O structure in the *xy* plane. Dashed lines indicate hydrogen bonds

As in the other complexes involving linear triamines[1 – 4], the coordination octahedron is distorted due to tension which goes from the condensed rings; as a result, the donor atoms depart from the octahedral planes. The distortion depends on the size of the triamine chelate ring[1], and for complexes of the $[Co((S)\text{-}Asp)(ABA)]^+$ type decreases in order 6,6 ≥ 5,6 ≥ 5,5 ring. In $[Co((S)\text{-}Asp)(dien)]^+$ the N4–Co–N2 angle is 175.0(4)° (Table III). As for the bond lengths, the Co–N1 and Co–N4 bonds are longest whereas the O1–C5 and O3–C8 bonds are shortest. The Co–N2 bond is shorter than the Co–N3 and Co–N1 bonds, as in s-*fac*-$[Co((S)\text{-}Asp)(aepn)]^+$ (ref.[2]) and in contrast to s-*fac*-$[Co((S)\text{-}Asp)(dpn)]^+$ (ref.[4]); also, it is shorter than as corresponds to the isolated chelate ring[6] (1.974(4) Å).

The 1,4,7-triazaheptane five-membered chelate rings take the asymmetric envelope conformations. Their definition is affected by the enormously high temperature parameters of the C1 and C4 atoms. The high temperature motion of those atoms brings about a pronounced apparent shortening of the N1–C1, N3–C4, C1–C2, and C3–C4 bonds (Table III). The five-membered ring of (*S*)-aspartic acid takes the symmetric envelope conformation whereas the six-membered ring possesses the skew boat conformation.

In all the structures of the $[Co((S)\text{-}Asp)(ABA)]^+$ type investigated, where ABA is a linear triamine[1 – 4], the bond lengths and angles of aspartic acid are the same within the error of determination, unaffected by the triamine chelate ring type. The carboxy C–O bond lengths, which can be affected by the hydrogen bond systems, are an exception. Remarkable is the apparent shortening of the C1–C2 and C3–C4 bonds in the structures with triazaheptanes[1]. High temperature parameters of the C1 and C4 carbons were observed in both of them. Their temperature ellipsoids are elongated markedly, indicating appreciable tension in the rings.

Noteworthy is the dependence of the crystal composition and structure on the solution pH: acid solutions give structures which are entirely different from those separating from neutral solutions[1 – 4].

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