CRYSTAL AND MOLECULAR STRUCTURE OF THE s-*fac*-[Co((*S*)-Asp)(medien)]ClO_4 . H_2O . $HClO_4$ ISOMER

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The crystal and molecular structure of s-*fac*-[Co((*S*)-Asp)(medien)]ClO_4 . H_2O . $HClO_4$ was elucidated by the heavy atom method. The positional parameters of the nonhydrogen atoms and their anisotropic temperature parameters were refined based on 2 474 observed reflections with final values of R = 0.0603 and wR = 0.0616. The substance crystallizes in the orthorhombic system in the space group $P2_12_12_1$, Z = 4, a = 8.536(1), b = 13.378(1), c = 16.899(2) Å. The structure comprises layers of the complex cation which alternate with layers containing two perchlorate anions and one hydroxonium cation. The five-membered chelate rings of 4-methyl-1,4,7-triazaheptane exist in the asymmetric λ, δ envelope conformations and the N–CH_3 group of the triamine has the *exo* orientation. The five-membered ring of (*S*)-aspartic acid assumes the symmetric envelope conformation, the six-membered chelate ring, the skew boat conformation.

Complexes of linear triamines are important from the stereochemical aspect because their chiroptical properties, in contrast to those of diamine complexes, exhibit many peculiarities. These include, e.g., intensity changes in the vicinal and configuration effect in dependence on the size of the triamine chelate rings[1 – 3].

Optical activity of complexes of the type of [Co((*S*)-Asp)(ABA)]$^+$((*S*)-Asp is (*S*)-aspartic acid), where ABA is a linear triamine, can comprise the configuration, conformation and vicinal contributions. The circular dichroism spectrum of [Co((*S*)-Asp)-(medien)]ClO_4 (medien = 4-methyl-1,4,7-triazaheptane) revealed[1] that the only existing of the three theoretically conceivable isomers has the s-*fac* arrangement with the C-vicinal contribution as the single source of optical activity.

Although the five-membered chelate rings of 4-methyl-1,4,7-triazaheptane can assume various conformations, the CD spectrum exhibits the C-vicinal effect solely, which implies that the conformation contributions compensate each other in this isomer. This is only possible (Dreiding models) if the N–CH_3 group has the equatorial character with a minimal steric repulsion. This is accomplished for the asymmetric λ, δ envelope conformations of the five-membered ring[1].

This work, which is part of a systematic study of the stereochemistry of heteroleptic cobalt(III) complexes of linear triamines, gives the complete crystal structure of the s-*fac*-[Co((*S*)-Asp)(medien)]ClO_4 . H_2O . $HClO_4$ isomer and compares the geometry of the structure with that of other complexes of linear triamines[4,5].

EXPERIMENTAL

The preparation of s-*fac*-[Co((*S*)-Asp)(medien)]ClO_4 . H_2O . $HClO_4$ has been described[1]. Its density was measured by the flotation method in a methyl iodide–diethyl ether mixture. For $C_9H_{23}Cl_2CoN_4O_{13}$ (524.1) calculated: 20.62% C, 4.23% H, 10.68% N; found: 20.44% C, 4.26% H, 10.39% N.

X-Ray diffraction measurements were performed on an Enraf–Nonius CAD4 four-ring diffractometer using a crystal 0.30 × 0.20 × 0.05 mm in size. MoK_α radiation (λ = 0.71073 Å) was monochromatized with a graphite monochromator. Lattice parameters were refined using 25 reflections within the $38° < 2\theta < 42°$ region. Intensities were measured within the region of $2\theta < 45°$ using the $\omega/2\theta$ scan applying a rate of 8.24 – 16.48° min^{-1}. A total of 3 050 reflections were measured at $0 \le h \le 9$, $0 \le k \le 14$, $-18 \le l \le 18$, with systematic extinction $h00$, $h = 2n$, $0k0$, $k = 2n$, $00l$, $l = 2n$, which corresponds to the space group $P2_12_12_1$. Elimination of reflections with negative intensities gave 2 878 reflections, out of which 2 474 were regarded as observed ($I > 1.96\ \sigma(I)$). The intensity of three standard reflections (2 1 16, 0 10 0, 8 0 0) was monitored in 2 h and a 3.7% decomposition was observed. Correction for the decomposition and empirical correction for absorption[4] were made; the minimum and maximum absorption coefficient values were 0.915 and 1.126, respectively.

The phase problem was solved by the heavy atom method. The positions of the nonhydrogen atoms were derived from Fourier maps, the positions of the hydrogen atoms were calculated assuming the ideal geometry, and the positions of the water hydrogen atoms were derived from the differential Fourier map. A total of 262 parameters were refined in three blocks: the scale factor and the positional and anisotropic temperature parameters of the nonhydrogen atoms, by minimization of the function $\sum w(|F_o| - |F_c|)^2$ using the weight scheme of $1.5318/(\sigma^2|F_o| + 0.0009\ F_o^2)$. The temperature parameters of the hydrogen atoms were taken as the 1.3-fold multiple of the equivalent temperature parameter of the parent atom. In the last cycle, $(\Delta/\sigma)_{max}$ was 0.001, the reliability factors were $R_{int} = 0.035$, $R = 0.0603$, $wR = 0.0616$, $S = 1.61$ (for the opposite enantiomer, $R = 0.0656$, $wR = 0.0672$, $S = 1.87$). The maximum and minimum electron densities on the final differential Fourier map were 0.648 and −0.488 e $Å^{-3}$. The calculations were performed on PDP11/73 and PC AT 286 computers using the programs SHELX 76 (ref.[5]) and PARST 88 (ref.[6]) and the SDP system[7]. The atomic scattering factor values for cobalt were taken from ref.[8].

RESULTS AND DISCUSSION

From among the three conceivable stereoisomers, viz. s-*fac*, u_1-*fac* and u_2-*fac*, only s-*fac*-[Co((*S*)-Asp)(medien)]$^+$ was prepared. Preparation of the remaining two diastereoisomers failed due to the possible interactions between the CH_2 group of (*S*)-aspartic acid and the $N-CH_3$ group (for the u_2-*fac* isomer) or between the hydrogen atom of the NH_2 group and the $N-CH_3$ group (for the u_1-*fac* isomer).

The basic crystallographic data are given in Table I. The positional parameters of the nonhydrogen atoms along with their temperature coefficients are given in Table II, the interatomic distances and angles, in Table III. The coordinates of the hydrogen atoms, anisotropic temperature parameters of nonhydrogen atoms, and equations of planes used in this paper are deposited with the authors. The maximum Cl–O distances in the ClO_4^- anion are 1.344(12) and 1.461(7) Å, the minimum and maximum values of the O–Cl–O angle are 104.1(5)° and 117.2(7)°.

The structure of the s-*fac*-[Co((*S*)-Asp)(medien)]$^+$ cation and the numbering of the atoms are shown in Fig. 1. The crystal structure (Fig. 2) consists of repeating layers of the complex s-*fac*-[Co((*S*)-Asp)(medien)]$^+$ cation and two ClO_4^- anions and one H_3O^+ ion, which, in contrast to the analogous complexes[9,10], are not linked by a system of hydrogen bonds.

As in other complexes with linear triamines[9,10], the coordination polyhedron has the shape of a distorted octahedron whose distortion is due to the strain originating in the condensed chelate rings, bringing about departure of the donor atoms from the corresponding octahedron planes. The results show that the degree of distortion depends on the size of the triamine chelate ring and, in the case of complexes of the s-*fac*-[Co((*S*)-Asp)(ABA)]$^+$ type, decreases in order 6-6 ≥ 5-6 > 5-5 (dpt: s-*fac* 171.3°≥ aepn: s-*fac* 171.0°, u-*fac* 172.6° > medien: s-*fac* 176.2°, where aepn = 1,4,8-triaza-

TABLE I
Basic crystallographic data

Space group, $P2_12_12_1$
$Z = 4$
a = 8.536(1) Å
b = 13.378(1) Å
c = 16.899(2) Å

V = 1 929.9(6) Å^3
ρ_o = 1 802 kg m^{-3}
ρ_c = 1 807 kg m^{-3}
$\mu(MoK_\alpha)$ = 1.24 mm^{-1}
$F(000)$ = 1 080

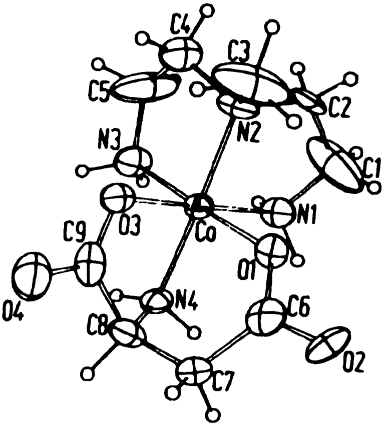

FIG. 1
Structure of the s-*fac*-[Co((*S*)-Asp)(medien)]$^+$ cation

TABLE II
Positional parameters of non-hydrogen atoms (. 10^4) and their temperature coefficients (. 10^3), $U_{eq} = (U_{11} + U_{22} + U_{33})/3$

Atom	x	y	z	U_{eq}, Å^2
Co	124.7(1.2)	-208.1(0.7)	791.9(0.5)	26(1)
Cl(1)	4726(3)	3591(2)	5499(1)	43(1)
Cl(2)	4996(3)	2001(1)	2702(1)	48(1)
O(11)	3590(10)	2967(6)	5132(5)	95(6)
O(12)	5133(13)	3060(5)	6226(4)	111(6)
O(13)	3959(14)	4443(6)	5732(6)	136(8)
O(14)	6014(13)	3706(10)	5051(7)	185(11)
O(21)	6145(10)	1941(9)	3295(5)	102(7)
O(22)	3509(10)	2194(9)	2994(8)	162(11)
O(23)	4926(14)	1004(6)	2434(7)	148(8)
O(24)	5501(16)	2596(10)	2126(7)	220(12)
O(1)	-1410(6)	685(4)	321(3)	30(3)
O(2)	-2652(6)	1545(4)	-603(4)	39(3)
O(3)	1798(6)	621(5)	468(3)	35(3)
O(4)	2926(7)	1219(5)	-630(4)	56(4)
O(w)	213(7)	2978(4)	-317(3)	59(4)
N(1)	-1671(8)	-993(6)	1139(4)	37(4)
N(2)	-76(9)	504(4)	1812(3)	37(3)
N(3)	1717(8)	-1044(6)	1298(4)	41(5)
N(4)	431(7)	-848(4)	-233(3)	29(3)
C(1)	-2539(16)	-479(10)	1735(8)	104(10)
C(2)	-1533(11)	129(12)	2195(6)	86(9)
C(3)	-106(17)	1596(6)	1731(5)	90(7)
C(4)	1328(11)	220(8)	2300(6)	53(6)
C(5)	1887(17)	-751(10)	2119(7)	112(11)
C(6)	-1547(10)	949(7)	-396(5)	38(5)
C(7)	520(9)	558(6)	-1037(4)	38(5)
C(8)	895(9)	-6(6)	-764(5)	39(5)
C(9)	1959(10)	681(7)	-281(6)	40(5)

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

Atoms	Value	Atoms	Value
		Distances	
Co–N(1)	1.948(7)	N(4)–C(8)	1.494(10)
Co–N(2)	1.977(5)	C(1)–C(2)	1.415(18)
Co–N(3)	1.957(7)	C(4)–C(5)	1.417(17)
Co–N(4)	1.950(5)	C(6)–C(7)	1.489(11)
Co–O(1)	1.943(5)	C(7)–C(8)	1.497(11)
Co–O(3)	1.890(6)	C(8)–C(9)	1.528(12)
N(1)–C(1)	1.427(15)	O(1)–C(6)	1.268(10)
N(2)–C(2)	1.489(13)	O(2)–C(6)	1.284(10)
N(2)–C(3)	1.468(10)	O(3)–C(9)	1.276(11)
N(2)–C(4)	1.504(12)	O(4)–C(9)	1.244(11)
N(3)–C(5)	1.449(14)		
		Angles	
N(2)–Co–N(4)	176.2(3)	Co–N(1)–C(1)	111.2(7)
N(1)–Co–O(3)	176.7(3)	N(1)–C(1)–C(2)	110.5(10)
N(3)–Co–O(1)	176.8(3)	C(1)–C(2)–N(2)	117.5(9)
N(2)–Co–N(3)	89.4(3)	N(2)–C(4)–C(5)	112.4(8)
N(1)–Co–N(2)	86.0(3)	C(4)–C(5)–N(3)	114.9(10)
N(1)–Co–N(3)	96.1(3)	Co–N(3)–C(5)	109.5(6)
N(3)–Co–N(4)	92.5(3)	Co–N(2)–C(4)	106.7(5)
N(1)–Co–N(4)	97.8(3)	Co–N(2)–C(3)	113.6(4)
O(3)–Co–N(4)	84.2(2)	Co–N(2)–C(2)	106.8(5)
O(3)–Co–N(3)	86.4(3)	C(3)–N(2)–C(4)	108.5(7)
O(3)–Co–N(2)	92.0(2)	C(2)–N(2)–C(4)	110.0(7)
O(1)–Co–N(4)	89.8(2)	C(2)–N(2)–C(3)	111.2(8)
O(1)–Co–N(2)	90.1(2)	Co–O(1)–C(6)	128.7(5)
O(1)–Co–N(1)	85.7(3)	Co–O(3)–C(9)	113.9(5)
O(1)–Co–O(3)	91.7(2)	Co–N(4)–C(8)	103.8(4)
O(1)–C(6)–O(2)	120.1(7)	C(7)–C(8)–C(9)	109.9(7)
O(2)–C(6)–C(7)	116.9(7)	N(4)–C(8)–C(9)	106.9(7)
O(1)–C(6)–C(7)	122.9(8)	O(4)–C(9)–C(8)	119.3(8)
C(6)–C(7)–C(8)	115.3(6)	O(3)–C(9)–C(8)	115.3(8)
N(4)–C(8)–C(7)	110.6(6)	O(3)–C(9)–O(9)	125.3(9)

octane, 1,6-diamine-3-azahexane, and dpt = 1,5,9-triazanonane, 1,7-diamine-4-azaheptane).

As to the interatomic distances, the Co–N_{sec} and Co–N_4 distances are longest whereas the O(4)–C(9) and O(1)–C(6) distances are shortest (Table III). The Co–N_{sec} distance is longer than the Co–N_{term} (Co–N(1), Co–N(3)) distances, as is the case with the s-*fac*-[Co((*S*)-Asp)(dpt)]$^+$ cation[11] but not with the s-*fac*-[Co((*S*)-Asp)(aepn)]$^+$ cation[9]. The Co–N_{sec} distance is consistent with that in the isolated chelate ring[9] (1.974(4) Å whereas the Co–N_{term} distances are shorter.

The N–C and C–C distances in the five-membered rings of medien are shorter than both in the five-membered ring of aepn and in the six-membered ring of dpt. The C–C distances in medien are shorter than in the isolated five-membered chelate ring (1.510(10) Å, ref.[12]).

Except for the C=O and C–O bonds, there are no substantial differences in the interatomic distances for the coordination of (*S*)-aspartic acid. Table III demonstrates that for the six-membered ring, the O(6)–O(2) distance is longer than the C(6)–O(1) distance, while in the five-membered ring of (*S*)-aspartic acid this is not observed. The extension of the C=O bond is appreciable in the five-membered ring of the s-*fac*-[Co((*S*)-Asp)(dpt)]$^+$ cation[11] but not in the s-*fac*-[Co((*S*)-Asp)(aepn)]$^+$ cation[9]. Table IV demonstrates that the N_{prim}–Co–N_{prim} angle in the triamine is independent of the size of the chelate rings in the complexes examined[9,11].

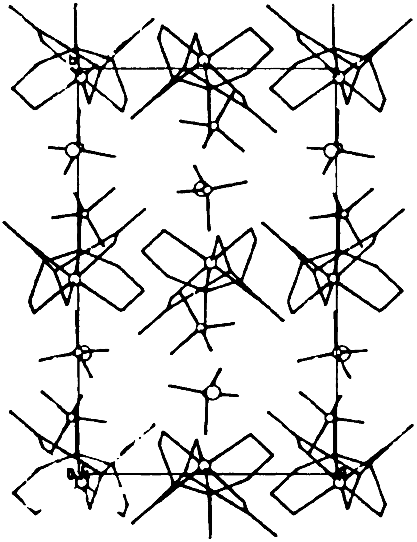

FIG. 2

Elementary cell of s-*fac*-[Co((*S*)-Asp)(medien)]ClO_4 . H_2O . $HClO_4$, projection into the *xy* plane

TABLE IV
Angles (in °) between the donor atoms in the triamine molecule in the s-*fac*-[Co((*S*)-Asp)(ABA)]$^+$ cations

ABA	Angle			Ref.
	N(1)–Co–N(2)	N(2)–Co–N(3)	N(1)–Co–N(3)	
acpn	95.0(5)	86.4(5)	94.7(5)	9
dpt	92.4(7)	99.1(7)	93.2(6)	11
medien	85.9(3)	87.4(3)	96.1(3)	1

TABLE V
Departures (Å) of atoms from the optimum planes constructed through atoms of chelate rings in the s-*fac*-[Co((*S*)-Asp)(medien)]$^+$ cation

Atom	Distance, Å	Atom	Distance, Å
Co^a	0	Co^a	0
N(3)^a	0	N(1)^a	0
N(2)^a	0	N(2)^a	0
C(4)	−0.370(10)	C(1)	0.482(14)
C(5)	0.041(14)	C(2)	0.159(13)
N(4)^a	0	N(4)^a	0
Co^a	0	Co^a	0
O(3)^a	0	O(1)^a	0
C(8)	0.829(8)	C(8)	−1.216(8)
C(9)	0.484(9)	C(7)	−0.931(8)
		C(6)	−0.405(9)
N(2)^a	−0.038(8)		
Co^a	0.001(10)		
N(4)^a	−0.026(6)		
C(8)^a	0.003(8)		
C(3)	0.289(14)		
C(2)	0.916(10)		
C(4)	−1.438(10)		

^{a} Atom through which the plane was constructed. Plane equations are deposited with the authors.

The dihedral angle of the coordinated chelate ring of the triamine N–C–C–N for the s-*fac*-[Co((*S*)-Asp)(medien)]$^+$ cation is on average more than 50% smaller than as corresponds to the isolated five-membered ring[12].

Table V documents that the C(1), C(2) and C(4), C(5) carbon atoms of the chelate rings depart from the planes constructed through the N(1)–Co–N(2)–C(1)–C(2) and N(2)–Co–N(3)–C(4)–C(5) atoms. The deviations indicate that the five-membered rings of 4-methyl-1,4,7-triazaheptane occur in the λ, δ asymmetric envelope conformations. The N–CH_3 group is oriented in the *exo* position (i.e. between the O(5) and O(6) oxygen atoms of (*S*)-aspartic acid). The five-membered ring of (*S*)-aspartic acid takes the symmetric envelope conformation and the six-membered chelate ring the skew boat conformation, which are typical of (*S*)-aspartic acid coordinated as a three-donor ligand[9,11].

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