THE CRYSTAL AND MOLECULAR STRUCTURE OF COBALT(III) *sym-fac*-N-(2-AMINOETHYL)-1,3-DIAMINOPROPANE-(*S*)-ASPARTATE PERCHLORATE, *sym-fac*-[Co-(aepn) (*S*)-Asp]ClO_4

Bohumil KRATOCHVÍL[a], Jan ONDRÁČEK[b], Jana ONDRÁČKOVÁ[c], Jiřina SOLDÁNOVÁ[d], František JURSÍK[c] and Bohumil HÁJEK[c]

[a] *Department of Mineralogy,*
[b] *Computer Centre,*
[c] *Department of Inorganic Chemistry,*
Prague Institute of Chemical Technology, 166 28 Prague 6 and
[d] *Department of Analytical Chemistry,*
Pharmaceutical Faculty, Komenský University, 832 32 Bratislava

Received May 13th, 1986

The crystal and molecular structure of *sym-fac*-[Co(aepn) (*S*)-Asp] ClO_4 was solved by the heavy atom method. The positions of the nonhydrogen atoms and their anisotropic temperature factors were refined. On the basis of 1 514 observed reflection intensities, a final reliability factor value of $R = 0{\cdot}096$ was obtained ($wR = 0{\cdot}101$). The substance crystallizes in the orthorhombic system in the $P2_12_12_1$ space group. The elementary cell contains four formula units and has dimensions of $a = 704{\cdot}0(6)$, $b = 939{\cdot}4(7)$, $c = 2\,369(2)$ pm. The secondary nitrogen atom of the triamine has S configuration. The five-membered ring has the λ conformation and the six-membered ring the flattened chair conformation. Selected structural parameters indicate that facial coordination of N-2-aminoethyl-1,3-diaminopropane leads to decreased strain in the coordinated, slightly deformed octahedron than meridional coordination and also that the chelate rings of the triamine are conformationally dependent. The bond lengths and angles of the part formed by (*S*)-aspartic acid agree with the corresponding values in $[Co((S)\text{-}Asp)_2]^-$.

Coordination of (*S*)-aspartic acid with diethylenetriamine (dien) in the ternary octahedral complex $[Co(S)\text{-}Asp(dien)]^+$ permits formation of three isomers differing in the rotation of one of the ligands by 120°. All three isomers, one symmetrical and two unsymmetrical, were isolated and characterized[1]. Lengthening of one half of the diethylenetriamine chain by one CH_2 leads to the conversion of the symmetric ligand to a heterotopic ligand. If this ligand, N-(2-aminoethyl)-1,3-diaminopropane (aepn), is coordinated together with (*S*)-aspartic acid in an octahedral complex, $[Co(aepn)\ (S)\text{-}Asp]^+$, then the number of isomers in the system $[Co(AAA)\ (S)\text{-}Asp]^+$ (AAA = linear triamine) increases from three to six. Only three isomers of $[Co(aepn)\text{-}(S)\text{-}Asp]^+$ were isolated[2]. The circular dichroism spectrum of the first of these, which should be the *sym-fac* isomer, exhibits[2] two components with opposite signs in the T_{1g} transition region, similarly to the *unsym-fac*-$[Co(S)\text{-}Asp(dien)]^+$ isomer. Although

the CD spectrum of the second isomer is roughly a mirror image, the two isomers have different absorption maxima. These facts prevent unambiguous determination of the structure of the $[Co(aepn)\text{-}(S)\text{-}Asp]^+$ isomer purely on the basis of the chiroptic properties, which reflect a number of effects, *e.g.* the contribution of the chirality of the donor atom of the ligand forming the condensed chelate rings or an increase in the size of the N—Co—N angle as a result of the presence of a condensed six-membered ring. Consequently, this work describes the crystal and molecular structure of the first of the three isomers of $[Co(aepn)\,(S)\text{-}Asp]^+$ solved on the basis of X-ray structural analysis.

EXPERIMENTAL

$[Co(aepn)\,(S)\text{-}Asp]ClO_4$ was prepared[2] by the Legg and Cook method[1] with chromatographic separation of the reaction mixture. Crystals for X-ray structural analysis were obtained by crystallization from water. For $C_9H_{20}ClCoN_4O_8$ (406·7) was calculated: 26·58% C, 4·95% H, 13·77% N and found: 26·60% C, 4·97% H, 13·48% N. The density of the substance was measured by the flotation method in an iodomethane–diethylether mixture at 20°C.

Preliminary dimensions of the elementary cell and its symmetry were determined from oscillation, Weissenberg and equiinclination patterns. The lattice parameters were refined, space group determined and intensities of the reflections measured using a four-circle Syntex $P2_1$ diffractometer. Systematic absences of the reflections ($h00$, where $h = 2n + 1$, $0k0$, where $k = 2n + 1$) were found in the complete data set obtained from the diffractometer. The lattice parameters were refined on the basis of a set of 15 centred high-angle reflections. A single crystal with dimensions of 0·03 × 0·1 × 0·15 mm was selected for intensity measurements. Graphite monochromatized MoK_α, $\lambda = 71{\cdot}069$ pm radiation and the $\Theta/2\Theta$ scanning technique were employed. The measurements were carried out in the range $0 < 2\Theta < 60°$, with an automatically adjusted scanning rate in the range 4·88 to 29·3° min^{-1} at 2Θ. A total of 2 320 reflections were measured and the intensities of two standard diffractions were controlled after each 98 reflections. It was found after the measurement that the intensities of the standard diffractions decreased to 50% of the original value. Only 1 514 reflections were considered as observed as they fulfilled the condition $I > 1{\cdot}96\sigma\,(I)$. The intensities of the observed reflections were corrected using the Lorentz polarization factor; correction for absorption was neglected.

The phase problem was solved by the heavy atom method. The coordinates of the cobalt atom were determined from the Patterson map and the positions of the remaining nonhydrogen atoms were localized from Fourier maps. The structural parameters were refined by minimization of the function $\sum w(|F_0| - |F_c|)^2$ and the weighting scheme $w = 1{\cdot}8057/(\sigma^2(F_0) + 0{\cdot}00364F_0^2)$ was employed. A total of 46 parameters were refined: the scale factor and the positions and anisotropic temperature factors of the nonhydrogen atoms. The positions of the hydrogen atoms could not be found from the difference Fourier map and an attempt to refine their positions by generation from the known bonding geometry was also not successful. The highest maximum found on the final difference map has a height of 2·7 e/(100 pm)^3 at a distance of 96 pm from the cobalt atom. In the final refining cycle, the maximal value was $(\Delta/\sigma)_{max} = 0{\cdot}1$. The final values of the reliability factors* are $R = 0{\cdot}096$ and $wR = 0{\cdot}101$. The atomic scattering factor for cobalt, which is not

* The values of the observed and calculated structure factors and anisotropic temperature factors of the atoms are deposited with the authors and will be provided on request.

included in the SHELX 76 program was taken from tables[3]. All the calculations were carried out using the SHELX 76 program (ref.[4]) and TLSPLANE program (ref.[5]) using EC 1033 and ICL 4-72 computers. Fig. 1 was drawn using the PLUTO program (ref.[6]) on the graphical attachment of the IBM 370/135 computer.

RESULTS AND DISCUSSION

The basic crystallographic data for [Co(aepn) (*S*)-Asp]ClO_4 are listed in Table I and Table II contains the final atomic coordinates together with their equivalent isotropic temperature parameters.

The crystal structure of the studied substance consists of [Co(aepn) (*S*)-Asp]$^+$ and ClO_4^- ions (Fig. 1) bonded by electrostatic interactions. The [Co(aepn) (*S*)-Asp]$^+$ cations are connected by NH···O hydrogen bonds (Table III). In the [Co(aepn) (*S*)-Asp]$^+$ cation (Fig. 2), the cobalt atoms is coordinated to two tervalent ligands forming two five-membered, two six-membered and one seven-membered chelate rings. Their mutual positions correspond to symmetrical facial geometry and *S* chirality of the secondary nitrogen atom of the linear triamine. The studied complex is the first example of facially coordination of N-(2-aminoethyl)-1,3-diaminipropane. Table III lists the interatomic distances and angles.

The coordination octahedron around the cobalt atom is slightly distorted. The O(1)—Co—N(3) bonds are not colinear but rather enclose an angle of 174·1(4)°. This deviation can be the result of either nonbonding interactions or strain resulting from the condensed chelate rings. The Co—N triamine internuclear distances in the *sym-fac*-[Co(aepn) (*S*)-Asp]$^+$ cation are shorter than in [Co(en)$_3$]$^{3+}$ (ref.[7]), [Co(tn)$_3$]$^{3+}$ (ref.[8]) (tn = trimethylenediamine), *mer*-[Co(aepn)dien]$^{3+}$ (ref.[9]) and *unsym-fac*-[Co(dien)dpt]$^{3+}$ (ref.[10]) (dpt = dipropylenetriamine). In contrast, the N—C bonds are longer than in the given compared complexes. The Co—N(2) bond, which is shorter than the terminal Co—N(1) and Co—N(3) bonds, distinguishes between the meridional and facial arrangement of the linear triamine. The shortening of the internuclear Co—N(2) distance in the facial arrangement is apparently connected with the lower strain resulting in the six-membered ring compared with meridional coordination of the triamine. For comparison, the length of the Co—N(sec) bond in *mer*-[Co(aepn)dien]$^{3+}$ equals 199·4 pm (ref.[9]). In the second part of the [Co(aepn)-(*S*)-Asp]$^+$ cation, the bond lengths and bond angles of the portion formed by aspartic acid agree with the corresponding values for the *cis*(N)-*trans*(O_6)-[Co((*S*)-Asp)$_2$]$^-$ isomer (ref.[11]). Because of the covalent radii, the internuclear Co—N distances are greater than Co—O.

The N(2)—Co—N(3) bond angle in the five-membered ring is less than 90°, but is 1% larger than for the isolated five-membered ethylenediamine ring[7] and meridionally coordinated N-(2-aminoethyl)-1,3-diaminopropane[9]. Similarly, the N(1)—Co—N(2) angle in the six-membered triamine ring, with a value of 95°, is 5° larger than

that in the six-membered ring in $[Co(tn)_3]^{3+}$ (ref.[8]) and in *mer*-$[Co(aepn)dien]^{3+}$ (ref.[9]).

TABLE I

Basic crystallographic data for *sym-fac*-[Co(aepn) (*S*)-Asp]ClO_4

a = 704·0(6) pm	ϱ_0 = 1 746 kg m^{-3}
b = 939·4(7)	ϱ_c = 1 723 kg m^{-3}
c = 2 369(2)	space group: $P2_12_12_1$
V = 1 567(2) . 10^6 pm^3	$\mu(MoK_\alpha)$ = 1·70 mm^{-1}
Z = 4	F(000) = 840

TABLE II

Coordinates of atoms and their equivalent isotropic temperature parameters (.10^4) in *sym-fac*-[Co(aepn) (*S*)-Asp]ClO_4. $U_{eq} = 1/3(U_{11} + U_{22} + U_{33})$

Atom	x	y	z	U_{eq}(.10^4 pm^2)
Co	3 555(2)	−381(2)	5 813(1)	281(7)
O(1)	5 220(13)	813(10)	5 387(4)	341(49)
O(2)	6 345(19)	2 009(10)	4 664(4)	549(65)
O(3)	3 708(15)	−2 725(10)	4 440(4)	412(55)
O(4)	4 073(14)	−1 968(10)	5 332(4)	374(53)
N(1)	2 910(18)	1 274(12)	6 274(5)	399(66)
N(2)	5 722(15)	−940(13)	6 268(5)	349(58)
N(3)	2 070(16)	−1 733(11)	6 271(5)	368(62)
N(4)	1 463(17)	−60(10)	5 271(4)	340(56)
C(1)	4 511(27)	2 209(15)	6 489(8)	574(104)
C(2)	5 929(23)	1 331(17)	6 851(7)	457(90)
C(3)	7 005(20)	282(17)	6 490(8)	525(88)
C(4)	5 142(5)	−1 949(18)	6 753(7)	485(95)
C(5)	3 423(28)	−2 762(14)	6 520(7)	524(91)
C(6)	5 138(26)	1 189(14)	4 879(6)	420(82)
C(7)	3 576(25)	671(15)	4 473(6)	461(84)
C(8)	2 289(19)	−526(13)	4 720(6)	314(63)
C(9)	3 412(23)	−1 846(13)	4 827(6)	363(72)
Cl	1 023(6)	79(4)	7 875(2)	512(22)
O(11)	949(21)	50(17)	7 289(5)	956(111)
O(22)	624(25)	1 522(21)	8 088(8)	1 241(144)
O(33)	2 888(23)	−224(16)	8 062(7)	947(104)
O(44)	−291(28)	−836(19)	8 109(7)	1 137(138)

It follows from the deviations of the C(4) and C(5) atoms by $-14{\cdot}1(1{\cdot}7)$ and $+52{\cdot}1(1{\cdot}4)$ pm from the best-fit plane through the N(2)—Co—N(3) atoms (Table IV), the five-membered chelate ring of triamine assumes the λ conformation. Study of the Dreiding models indicates that the conformation of the five-membered ring is not completely independent of the conformation of the condensed six-membered

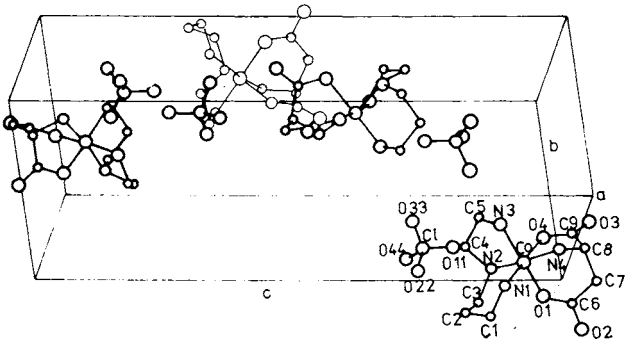

FIG. 1

The elementary cell of *sym-fac*-[Co(aepn) (*S*)-Asp]ClO_4

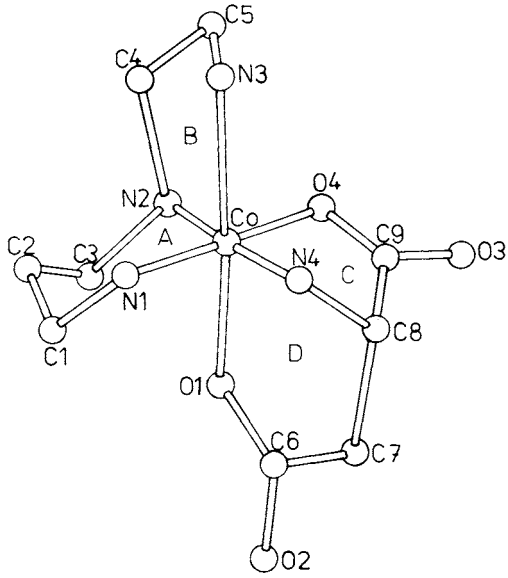

FIG. 2

The structure of the *sym-fac*-[Co-(aepn) (*S*)-Asp]$^+$cation

TABLE III

Interatomic distances (pm) and angles (°) in *sym-fac*-[Co(aepn) (*S*)-Asp]ClO_4

Bond length	Bond angle
The cobalt environment	
Co—N(1) : 195·5(1·1)	N(1)—Co—N(2) : 95·0(5)
—N(2) : 194·0(1·1)	N(2)—Co—O(4) : 88·3(5)
—N(3) : 197·1(1·2)	O(4)—Co—N(4) : 82·7(4)
—N(4) : 197·8(1·1)	N(4)—Co—N(1) : 94·0(5)
—O(1) : 191·1(0·9)	N(3)—Co—N(1) : 94·7(5)
—O(4) : 191·2(1·0)	N(3)—Co—N(2) : 86·4(5)
	N(3)—Co—O(4) : 85·8(4)
	N(3)—Co—N(4) : 93·5(5)
	O(1)—Co—N(1) : 88·3(4)
	O(1)—Co—N(2) : 88·3(4)
	O(1)—Co—O(4) : 91·4(4)
	O(1)—Co—N(4) : 91·3(4)
Ring A	
N(1)—C(1) : 151·7(2·1)	Co—N(1)—C(1) : 118·4(1·0)
C(1)—C(2) : 155·2(2·4)	N(1)—C(1)—C(2) : 110·8(1·2)
C(2)—C(3) : 150·9(2·2)	C(1)—C(2)—C(3) : 110·9(1·3)
C(3)—N(2) : 155·2(1·9)	C(2)—C(3)—N(2) : 112·5(1·1)
	C(3)—N(2)—Co : 116·4(0·9)
	C(3)—N(2)—C(4) : 110·9(1·1)
Ring B	
N(2)—C(4) : 154·4(2·0)	Co—N(2)—C(4) : 111·8(0·9)
C(4)—C(5) : 153·4(2·5)	N(2)—C(4)—C(5) : 104·3(1·2)
C(5)—N(3) : 147·9(2·0)	C(4)—C(5)—N(3) : 109·0(1·1)
	C(5)—N(3)—Co : 107·4(9)
Ring C	
O(4)—C(9) : 128·7(1·7)	Co—O(4)—C(9) : 114·6(8)
C(9)—O(3) : 125·1(1·6)	O(4)—C(9)—O(3) : 124·1(1·2)
C(9)—C(8) : 149·3(1·8)	O(4)—C(9)—C(8) : 115·1(1·1)
	O(3)—C(9)—C(8) : 120·7(1·2)
	C(9)—C(8)—N(4) : 107·5(1·0)
	C(9)—C(8)—C(7) : 110·8(1·2)
Ring D	
O(1)—C(6) :125·4(1·6)	Co—N(4)—C(8) : 103·5(8)
C(6)—O(2) : 125·5(2·0)	N(4)—C(8)—C(7) : 110·0(1·0)
C(6)—C(7) : 154·0(2·3)	C(8)—C(7)—C(6) : 114·2(1·1)

TABLE III
(*Continued*)

Bond length	Bond angle
C(7)—C(8) : 155·8(2·0)	C(7)—C(6)—O(2) : 115·1(1·2)
C(8)—N(4) : 149·4(1·6)	C(7)—C(6)—O(1) : 122·8(1·4)
	O(2)—C(6)—O(1) : 122·1(1·5)
	C(6)—O(1)—Co : 130·1(1·0)
The chlorine environment	N—O distances indicating
Cl—O(11) : 139·0(1·3)	possible hydrogen bonds
—O(22) : 147·4(2·0)	(i: $x - 1/2, 1/2 - y, 1 - z$
—O(33) : 141·4(1·7)	ii: $x - 1/2, -1/2 - y, 1 - z$)
—O(44) : 137·8(1·9)	N(1)—O(2^{i}) : 295·8(1·5)
	N(3)—O(3^{ii}) : 294·9(1·6)
	N(4)—O(2^{i}) : 287·1(1·5)
	N(4)—O(3^{ii}) : 292·6(1·4)

ring. The ethylenediamine ring of the linear triamine can also assume an δ-asymmetric envelope conformation, but not the δ conformation. The latter conformation can be assumed by the five-membered ring only when the six-membered condensed chelate ring has the twist-boat conformation. From the point of view of steric interactions, both the δ conformation and the δ-asymmetric conformation envelope are less suitable than the λ conformation. A conformational dependence in the condensed ring system appears also in the degree of bending of the chelate ring. The N(2)—C(4)—C(5)—N(3) torsion angle defining the conformation of the chelate ring equals 48·3°, almost 7° less than in the isolated five-membered ethylenediamine ring[7].

The six-membered ring has the chair conformation with the cobalt and carbon C(2) atoms lying above and below the best-fit plane formed by the N(1)—C(1)—C(3)—N(2) atoms (Table IV) at distances of 76·9(0·2) and −75·8(1·7) pm. The bond angles in the six-membered ring, Co—N(1)—C(1) 118·4° and Co—N(2)—C(3) 116·4° differ from the tetrahedral value, indicating that the chair formed by the six-membered ring is rather flattened. The torsion angle Co—N(1)—C(1)—C(2): −38·3° also corresponds to this deformation, as it is smaller than the torsion angle in the six-membered chelate ring of the *unsym-fac*-$[Co(dien)dpt]^{3+}$ isomer (ref.[10]). The decrease in the size of the torsion angle is apparently the result of strain introduced into the system of conformationally interdependent condensed chelate rings by the rigid five-membered ring. Deformation of the six-membered ring has also been observed in other complexes with isolated[8] and condensed chelate rings[9,10]. The distortion of the bond angles can be a result of nonbonding apical interactions of the axial

TABLE IV

Deviations of atoms from the optimal plane fitted through the atoms of the five- and six-membered chelate rings of N-(2-aminoethyl)-1,3-diaminopropane in *sym-fac*-[Co(aepn) (*S*)-Asp]$^+$. Each plane is defined as $AX + BY + CZ + D = 0$

Atom[a]	Distance, pm	Atom[b]	Distance, pm
N(2)	0	N(1)	−0·2(1·2)
Co	0	C(1)	0·2(1·9)
N(3)	0	C(3)	−0·2(1·9)
C(4)	−14·1(1·7)	N(2)	0·1(1·2)
C(5)	52·1(1·4)	Co	76·9(0·2)
		C(2)	−75·8(1·7)

[a] The plane fitted through the N(2)—Co—(N(3) atoms: $0{\cdot}20896X - 0{\cdot}72976Y - 0{\cdot}65099Z + 8{\cdot}18067 = 0$; $\chi^2 = 0$; [b] the plane fitted through the N(1)—C(1)—C(3)—N(2) atoms: $0{\cdot}24291X - 0{\cdot}94079Z + 13{\cdot}20177 = 0$; $\chi^2 = 0{\cdot}04$.

hydrogen atoms located on the C(1) and C(2) carbon atoms, and the O(1) oxygen atoms of β-carboxyl(*S*)-aspartic acid or of strain resulting from coordination of the ligand forming the condensed five- and six-membered rings. The magnitude of the observed deviations is slightly less than for *mer*-[Co(aepn)dien]$^{3+}$ (ref.[9]), indicating greater strain of the facially coordinated unsymmetric triamine compared with the meridional arrangement.

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Translated by M. Štulíková.