Acta Cryst. (1977). B33, 70–76

The Crystal Structure and Absolute Configuration of $(-)_{589}$-*S,S*-6,9-Diaza-2,13-dithiatetradecane-5,10-dicarboxylatocobalt(III) Perchlorate

BY RODNEY J. GEUE AND MICHAEL R. SNOW

Department of Physical and Inorganic Chemistry, The University of Adelaide, Adelaide, S.A. 5001, *Australia*

(*Received* 26 *January* 1976; *accepted* 23 *June* 1976)

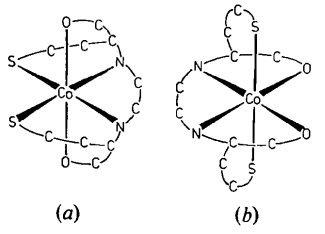
The structure of $(-)_{589}$-[Co(*S,S*-ebm)]ClO_4, where *S,S*-ebm denotes the dianion *S,S*-[$CH_3SCH_2CH_2CH(CO_2)CHNHCH_2^-]_2$, has been determined from 2451 photographically collected reflexions. The crystals are monoclinic with space group *C*2 and $a = 12{\cdot}34$ (2), $b = 7{\cdot}94$ (1), $c = 9{\cdot}46$ (1) Å, $\beta = 97{\cdot}45$ (8)° and $Z = 2$. The full-matrix least-squares refinement of the structure yielded a conventional *R* value of 0·060 (on *F*). The complex cation has crystallographic C_2 symmetry. The six-membered chelate rings have distorted chair forms and assume equatorial orientations with respect to the five-membered cobalt–diamine ring which has the δ conformation. The absolute configuration is $\Lambda\Delta\Lambda$ with respect to the skew ring chelate pairs and is formed as predicted from the stereospecific requirements of the optically active ligand. As a consequence, the prochiral configurations at the N and S atoms of the ligand both become *R* in the complex. The Co^{III} to thioether distance of 2·267 (3) Å is within the spectrum of values for this metal to negatively charged S ions.

Introduction

The ligand *S,S*-ebmH_2 {*S,S*-ebm is *S,S*-[$CH_3SCH_2CH_2CH(CO_2)CHNHCH_2^-]_2$} was synthesized from *S*-methionine and 1,2-dibromoethane by Mazurek & Phillip (Magee, Mazurek, O'Connor & Phillip, 1974) according to a method similar to that used for *S,S*-edds {*S,S*-edds is *S,S*-[$OOCCH_2$—$CH(CO_2)CHNHCH_2^-]_2$} formed from *S*-aspartic acid. Both the *S,S*-edds (Neal & Rose, 1968) and *S,S*-ebm (Magee *et al.*, 1974) ligands have been shown to act as sexidentate chelates on coordination to Co^{III}. In addition only one optically active isomer has been isolated in the preparation of both the Co^{III} complex of *S,S*-edds and that of *S,S*-ebm. Hence both ligands are stereospecific sexidentate chelating agents for Co^{III}, the donor atom sets being $N_2O_2S_2$ and N_2O_4 for *S,S*-ebm and *S,S*-edds respectively.

When the configuration about the asymmetric C atom is *S*, Dreiding molecular models indicate that for each of the above ligands, there are two possible configurational isomers for the Co^{III} complex (Fig. 1 for the *S,S*-ebm case). In the $\Lambda\Delta\Lambda$ (*IUPAC Information Bulletin*, 1968) or Λ configuration, the six-membered rings span equatorial sites, whereas in the Δ configuration they span axial coordination sites with respect to the cobalt–diamine ring. In view of the relatively strained nature of the equatorial five-membered cobalt–glycinato rings of $[Co(edta)]^-$ (Weakliem & Hoard, 1959) it was suggested (Neal & Rose, 1968) that the Λ configuration would be favoured for [Co(*S,S*-edds)]$^-$. Similar strain has been observed in the equatorially disposed five-membered rings of $[Co(pdta)]^-$ [pdta is 1,3-propylenediaminetetraacetic acid (Nagao, Marumo & Saito, 1972)] where the metal–diamine ring is six-membered. A recent report (Neal & Rose, 1973) of the structure of NH_4[Co(*S,S*-edds)] (Woodward, 1970) notes the equatorial disposition of the six-membered rings in the anion. These results, correlated with the similarity of the circular dichroism spectra of Na[Co(*S,S*-edds)] (Neal & Rose, 1968) and of $(-)_{589}$-[Co(*S,S*-ebm)]ClO_4 (Magee *et al.*, 1974), indicate that the complex ion in the latter compound has the Λ configuration with the S atoms occupying *cis* coordination sites. Several close non-bonded contacts in a molecular model of the Δ configuration enhance the favourability of Λ for [Co(*S,S*-ebm)]$^+$.

The six-membered chelate rings may adopt the chair, skew-boat or boat conformation in the crystal, although the lower-energy chair or skew-boat forms would be favoured unless they induce steric hindrance between chelate rings. Molecular models indicate no notable increase in inter-ring steric hindrance on changing from the boat to the chair or skew-boat conformation. In the crystal structures of Pt(*R,S*-MetH)Cl_2 and Pt(*S*-MetH)Cl_2 [MetH is methionine (Freeman & Golomb, 1970)], the carboxylate O atoms are not co-



(*a*) (*b*)

Fig. 1. (*a*) The Λ and (*b*) the Δ-isomers of [Co(*S,S*-ebm)]$^+$.

ordinated, and the six-membered chelate rings have chair conformations. However, in the structure of Pt(Glycyl-*S*-Met)Cl . H_2O (Freeman & Golomb, 1970) they are in the boat conformation. It was suggested that this was due to steric hindrance induced by the chair conformation in this compound. It may then be anticipated that the six-membered rings of $[Co(S,S\text{-ebm})]^+$ would prefer the chair or skew-boat conformation in the crystal when there are no strong counteracting lattice forces.

Because of the strong connectivity between all chelate rings in this sexidentate complex, a Dreiding model of the Λ configuration of $[Co(S,S\text{-ebm})]^+$ also indicates conformational preferences for the cobalt–glycinato and cobalt–diamine rings. Thus, for a six-membered ring chair conformation, the λ and δ conformations of cobalt–glycinato and cobalt–diamine rings, respectively, appear to be favoured. For the skew-boat conformation of the six-membered rings, the λ conformation of the cobalt–diamine ring is favoured with the envelope conformation of the cobalt–glycinato rings.

Most of the presentiments discussed above have been confirmed by the X-ray structural analysis of $(-)_{589}$-$[Co(S,S\text{-ebm})]ClO_4$.

Experimental

Crystals of $(-)_{589}$-$[Co(S,S\text{-ebm})]ClO_4$ were supplied by W. Mazurek and A. T. Phillip. The deep-crimson crystals were pseudo-hexagonal platelets which exhibited the forms {100}, {010}, {001}, {010}, {110} and $\{1\bar{1}0\}$. Preliminary precession photographs recorded with Mo $K\alpha$ radiation were used to determine the space group and unit-cell dimensions; the crystal data are collected in Table 1.

Integrated intensity data were recorded on film using a Supper–Buerger precession camera for the reciprocal layers $h0l$–$h3l$ and $hk0$–$hk4$. Three photographs per layer were recorded with Mo $K\alpha$ using a Zr filter. Triple film packs and a Nonius Weissenberg camera were used to record the layers $0kl$–$10kl$ of integrated data by the equi-inclination Weissenberg technique. The crystal used for intensity data collection measured 0·45 × 0·45 × 0·15 mm, and was mounted along the a^* axis for the precession photographs and the a axis for the Weissenberg photographs.

Table 1. *Crystal data*

$(-)_{589}$-$C_{12}H_{22}N_2O_4S_2.ClO_4$	Space group $C2$
F. W. 480·83	$F(000) = 496$
Monoclinic	$D_m = 1\cdot73\ (2)$ g cm^{-3}
$a = 12\cdot34\ (2)$ Å	$D_c = 1\cdot737$
$b = 7\cdot94\ (1)$	$Z = 2$
$c = 9\cdot46\ (1)$	μ(Mo $K\alpha$) = 13·4 cm^{-1}
$\beta = 97\cdot45\ (8)°$	[λ(Mo $K\alpha$) = 0·7107 Å]
$U = 919\ (4)$ Å^3	

Intensities were determined photometrically with a Nonius II microdensitometer attached to a digital voltmeter, and a paper-tape punch. The response linearity of the system was confirmed using intensity strips and silica discs of known optical density over a range of 0 → 2. For each observed reflexion, a value for the relative intensity of the light transmitted by the plateau region of the spot was punched on paper tape, followed by an average value of the background intensity. A reflexion which could not be detected on the film of maximum exposure was designated unobserved, and the background value only was recorded. Reflexions which could not be measured reliably were also recorded. Both unobserved and unreliable reflexions were assigned identifiers and precluded from least-squares procedures.

The interfilm and interlayer scale factors were determined by a non-iterative least-squares procedure (Rae, 1965) and standard deviations were assigned to the reflexions as previously described (Snow, 1970). The intensities were corrected for the Lorentz and polarization effects, but not for absorption. The final data set included 2451 reflexions including 265 non-equivalent Friedel pairs.

Solution and refinement of the structure

The complex cation $[Co(S,S\text{-ebm})]^+$ has crystallographic site symmetry in the structure since $Z = 2$ and space group $C2$ has four general asymmetric sites per cell. Of the two possible independent sites with twofold symmetry, the one on the C_2 axis through the origin of the conventional cell was chosen for the cation. Since the y coordinate for one atom may be assigned arbitrarily in this space group, the Co atom was placed at the origin of the cell. A Patterson synthesis revealed the position of the S atom. A subsequent Fourier map, phased on the Co and S coordinates, located the N and O positions in the coordination sphere around Co and the Cl atom of the ClO_4 anion. The anion resided on the C_2 axis at $x = 0$, $z = \frac{1}{2}$, which is not symmetry related to that constraining the cation $x = 0$, $z = 0$. A second Fourier synthesis established the sites of all other non-hydrogen atoms in the structure. The refinement by full-matrix least squares of the scale factor, positional parameters and individual isotropic thermal parameters converged with an R_1 value of 0·109. Subsequent refinement with anisotropic thermal parameters for all atoms reduced R_1 to 0·080 and incorporated the anomalous components in the scattering factors of Co, Cl and S. A comparison of the observed and calculated values for the 265 Friedel pairs then established the S configuration for the asymmetric C atoms and the Λ configuration for the complex cation.

H atom positions, with the exception of the methyl H

atoms, were calculated for C—H and N—H distances of 1·02 and 0·95 Å assuming tetrahedral H—N—H and H—C—H angles. The H atoms were then included in the refinement with fixed coordinates and isotropic thermal parameters of 3·0 Å^2. Refinement of the scale factor and the non-hydrogen atom parameters finally converged with $R_1 = 0{\cdot}060$ and $R_2 = 0{\cdot}060$. The error in an observation of unit weight was estimated as 3·24 from a structure factor calculation after the final refinement cycle. This indicates that the σF and w_{hkl} are not on an absolute scale. The average $w(|F_o| - |F_c|)^2$ determined in ranges of $|F_o|$ varied from 3·6 to 8·6 (excluding the terminal ranges) in a random manner. The terminal ranges had lower values, suggesting that very strong and very weak reflexions were not given enough weight relative to the others. A similar determination of average $w(|F_o| - |F_c|)^2$ in ranges of $\sin\theta/\lambda$ showed an analogous trend. Thus the weighting scheme was satisfactory for all reflexions but those with high $\sin\theta/\lambda$ and those with very high or very low intensities. A final difference Fourier map showed no peak heights larger than 0·5 e Å^{-3}. In view of the known charge delocalization in complex ions (Raymond, Meek & Ibers, 1968; Iwata & Saito, 1973), the scattering factor curve for Co^{2+} was used in the structure factor calculations. For Co^{2+} and Cl^- the scattering factors of Doyle & Turner (1968) were used. Values for O, N, C and S were obtained from *International Tables for X-ray Crystallography* (1968) and for H, the values of Stewart, Davidson & Simpson (1965) were used. The anomalous components $\Delta f'$ and $\Delta f''$ for Co (0·3, 1·0), Cl (0·1, 0·2) and S (0·1, 0·2) were acquired from *International Tables* (1968).

Zalkin's program *FORDAPB* for Fourier computations was used for structure solution. Program *FOURFLS*, a local modification of Busing, Martin & Levy's (1962) *ORFLS*, was used for the refinement. The derived structural parameters and their standard deviations were determined with program *ORFFE* (Busing, Martin & Levy, 1964). H atom coordinates were calculated with *PLANEH*, a modification of Blount's *PLANET*. This was also used for the determination of least-squares planes. Blount's *BLANDA* was used for periodical checks on structural geometry during the refinement. Perspective ellipsoid plots were achieved with Johnson's *ORTEPB*.

The atomic parameters are listed in Table 2 with their estimated standard deviations.*

Results and discussion

The crystal structure of $(-)_{589}$-[Co(*S*,*S*-ebm)]ClO_4 is shown in Fig. 2 as a projection down the **c*** direction. Both the $(-)_{589}$-[Co(*S*,*S*-ebm)]$^+$ cation and the perchlorate anion have rigorous C_2 symmetry and lie on separate crystallographic twofold axes parallel to **b**. The cation and anion interact through N—H···O hydrogen bonds to form chains parallel to **c**. There is only one independent interaction, the others being related by the crystal symmetry. This N(1)—H(8)···O(5) contact satisfies the distance

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32019 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. *Positional* (× 10^4; *for* H × 10^5) *and thermal* (× 10^5) *parameters*

The form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. The isotropic temperature factor for hydrogen is 3·0 Å^2.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Co	0	0	0	236 (7)	389 (18)	436 (13)	0	35 (7)	0
Cl	0	3571 (4)	5000	423 (19)	972 (43)	662 (28)	0	133 (19)	0
S(1)	397 (1)	−2036 (3)	1665 (2)	401 (11)	610 (28)	574 (19)	−1 (15)	−56 (12)	106 (24)
O(1)	1448 (3)	130 (8)	−425 (5)	275 (22)	852 (80)	694 (48)	23 (48)	44 (29)	206 (74)
N(1)	407 (5)	1731 (9)	1370 (8)	375 (34)	644 (99)	835 (77)	−32 (51)	14 (44)	−340 (79)
O(2)	3077 (4)	1138 (9)	387 (6)	318 (29)	1390 (107)	1133 (77)	−55 (47)	116 (42)	62 (85)
C(1)	−6 (5)	3379 (10)	807 (7)	469 (44)	681 (112)	729 (75)	141 (61)	75 (51)	130 (91)
C(2)	1629 (5)	1615 (10)	1767 (8)	326 (34)	725 (106)	689 (79)	−115 (59)	26 (47)	−134 (98)
C(3)	2114 (5)	953 (10)	484 (8)	308 (37)	670 (105)	746 (80)	15 (53)	63 (47)	19 (89)
C(4)	1874 (5)	375 (11)	3006 (7)	323 (34)	1213 (166)	629 (70)	−99 (61)	−74 (41)	−137 (100)
C(5)	1733 (6)	−1480 (13)	2592 (8)	420 (41)	1103 (133)	746 (82)	3 (70)	−138 (49)	73 (117)
C(6)	−475 (6)	−1671 (12)	3040 (8)	442 (43)	1181 (156)	688 (79)	−59 (69)	73 (49)	376 (107)
O(5)	−636 (6)	2539 (13)	3983 (8)	795 (49)	2856 (219)	1243 (91)	−458 (90)	107 (57)	−1015 (134)
O(6)	726 (7)	4567 (13)	4259 (9)	1113 (67)	2664 (252)	1815 (116)	− 658 (100)	122 (73)	1120 (149)

	x	y	z		x	y	z
H(1)	2648	552	3487	H(5)	1934	2776	2072
H(2)	1337	618	3737	H(6)	−779	3574	1056
H(3)	2312	−1767	1947	H7)	493	4321	1280
H(4)	1875	−2197	3500	H(8)	24	1540	2250

criterion for hydrogen bonding suggested by Hamilton & Ibers (1968) if the calculated position for H(8) is approximately correct. The N···O distance of 3·00 (1) Å and N—H···O angle of 149° are well within the ranges 2·87 to 3·07 Å and 119 to 175° established by neutron diffraction for unbranched N—H···O hydrogen bonds. There are no close contacts in the crystal significantly less than their van der Waals radii sums. If the methyl group has an effective van der Waals radius of 2·0 Å (Bondi, 1964) as a free rotor, there are no evident close contacts restricting such rotation in the crystal.

The complex cation $(-)_{589}$-[Co(*S,S*-ebm)]$^+$ has the *Λ* absolute configuration and is shown in Fig. 3. The configuration about the asymmetric C is *S*, whereas both the N and S atoms are present in the *R* configurational arrangement. The six-membered S-containing rings are equatorially disposed with respect to the cobalt–diamine ring as is required by the *Λ* configuration of the complex with the *S* configuration at the asymmetric C. The geometry of the cation is given in Table 3. The Co—S distance of 2·267 (3) Å is the first to be reported for a Co^{III} to thioether group. It may be compared to those involving Co^{III} S_6 chromophores formed with the anionic ligands dithiocarbamate, 2·258 (3) Å (Merlino, 1968); ethylthioxanthate, 2·266 (1) Å (Ting-i & Lippard, 1974); dithiophosphate, 2·322 (3) Å (McConnell & Schwartz, 1972); and thiooxalate, 2·444 (5) Å (Butler & Snow, 1975). In the complexes [Co(ethylenediamine)$_2$B]$^{2+}$ where B is either $^-SCH_2COO^-$ or $^-SCH_2CH_2NH_2$ the Co—S distances are 2·243 (2) and 2·226 (2) Å respectively (Elder, Florian, Lake & Yacynych, 1973) and span those found for the Co to thioether bond. In these mercapto structures a lengthening of the Co—N bond *trans* to the S of approximately 0·04 Å to values of 2·005 (5) and 2·001 (5) Å was observed. No such extension is seen in the [Co(*S,S*-ebm)]$^+$ case where a substantial *contraction* of the Co—N bonds *trans* to the S to a value of 1·912 (7) Å occurs. This contraction should not be assigned to the presence of the *trans* S atoms nor to the concentrated attachment of the sexidentate ligand. Thus similar contracted values of 1·926 (5) and 1·902 (5) Å were observed in the bis-*S*-aspartato complex ions, *cis*(*N*)-*trans*(O_5)- and *cis*(*N*)-*trans*(O_6)-[Co(*S*-asp)$_2$]$^-$ (Oonishi, Shibata, Marumo & Saito, 1973) and in Na[Co(ethylenediamine)(malonato)$_2$], 1·925 (20) Å, by

Table 3. *Molecular geometry*

Symmetry notation: (i) $\bar{x},y,\bar{z}$; (ii) $\bar{x},y,\bar{z}+1$.

Cation			
Co—S(1)	2·267 (3) Å	S(1)—Co—O(1^i)	90·92 (19)°
Co—N(1)	1·912 (7)	N(1)—Co—O(1)	86·12 (27)
Co—O(1)	1·884 (5)	N(1)—Co—O(1^i)	89·36 (26)
S(1)—C(6)	1·815 (8)	Co—S(1)—C(6)	106·82 (29)
S(1)—C(5)	1·818 (7)	Co—S(1)—C(5)	105·23 (32)
C(5)—C(4)	1·529 (12)	C(6)—S(1)—C(5)	101·50 (41)
C(4)—C(2)	1·531 (11)	S(1)—C(5)—C(4)	115·07 (54)
C(2)—N(1)	1·508 (9)	C(5)—C(4)—C(2)	114·79 (59)
N(1)—C(1)	1·479 (10)	C(4)—C(2)—N(1)	108·79 (62)
C(1)—C(1^i)	1·529 (14)	C(2)—N(1)—Co	106·91 (47)
O(1)—C(3)	1·288 (9)	Co—N(1)—C(1)	110·15 (50)
C(3)—O(2)	1·213 (8)	N(1)—C(1)—C(1^i)	108·21 (46)
C(3)—C(2)	1·515 (11)	N(1)—C(2)—C(3)	107·90 (57)
S(1)—Co—S(1^i)	88·96 (15)°	C(4)—C(2)—C(3)	109·35 (63)
N(1)—Co—N(1^i)	88·01 (46)	C(2)—N(1)—C(1)	115·50 (61)
O(1)—Co—O(1^i)	173·72 (40)	C(2)—C(3)—O(2)	120·73 (66)
S(1)—Co—N(1)	91·59 (25)	C(2)—C(3)—O(1)	115·32 (54)
S(1)—Co—N(1^i)	177·02 (22)	O(2)—C(3)—O(1)	123·86 (73)
S(1)—Co—O(1)	93·56 (18)	C(3)—O(1)—Co	115·16 (44)
Anion			
Cl—O(5)	1·420 (8) Å	O(5)—Cl—O(6^{ii})	108·82 (48)°
Cl—O(6)	1·443 (8)	O(5)—Cl—O(5^{ii})	109·49 (86)
O(5)—Cl—O(6)	108·06 (49)°	O(6)—Cl—O(6^{ii})	113·55 (91)

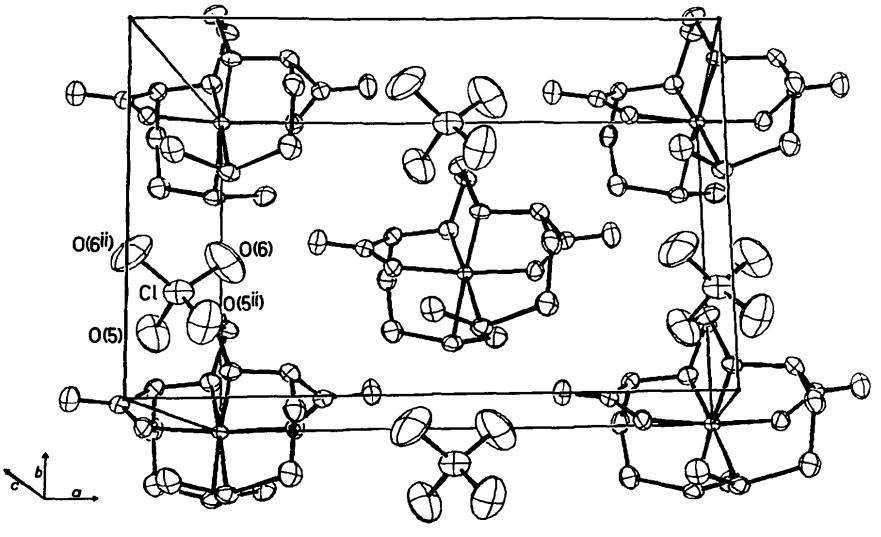


Fig. 2. The unit cell of $(-)_{589}$-[Co(ebm)]ClO_4 projected down **c***. The thermal ellipsoids enclose 50% probability.

Butler & Snow (1976). In the complex $[Co(penten)]^{3+}$, which has six nitrogen donors arranged as in $[Co(edta)]^-$, the secondary N—Co lengths average 1·964 (11) Å, typical of bis- and tris(ethylenediamine) complexes (1·97 ± 0·01 Å) (Muto, Marumo & Saito, 1970). In $[Co(edta)]^-$ (Weakliem & Hoard, 1959) the corresponding value is 1·925 (5) Å, but in $[Co(pdta)]^-$ where the diamine ring is six-membered the value is 1·966 (9) Å. Finally we note that the structure of the nitritoethylenediaminetriacetic acid complex (Bell & Blackmer, 1973) has values of 1·954 (4) (*trans* to carbonyl) and 1·965 (5) Å (*trans* to nitrito). The only conclusion permitted by these data is that a distinct contraction of Co—N distances occurs in CoN_2O_4 or $CoN_2O_2S_2$ chromophores, but six-membered rings and other substituents relieve the contraction. Thus no contractions are observed in $[Co(NH_3)_4(CO_3)]Br$ (Snow, 1972). In the $Co(ebm)^-$ complex the Co—O distance of 1·884 (5) Å is close to the mean distances of 1·885 (15), 1·861 (8) and 1·891 (4) Å found for the axial Co—O bonds in $[Co(edta)]^-$, $[Co(pdta)]^-$ and *cis*(*N*)-*trans*(O_5)-$[Co(S\text{-}asp)_2]^-$. The mean values of the ligand bonds S—C, 1·817 (5); C—C, 1·526 (6); and C—N, 1·494 (7) Å are all normal. The carboxyl C—O length of 1·288 (9) Å is significantly different from the carbonyl distance of 1·213 (8) Å, and the values are in

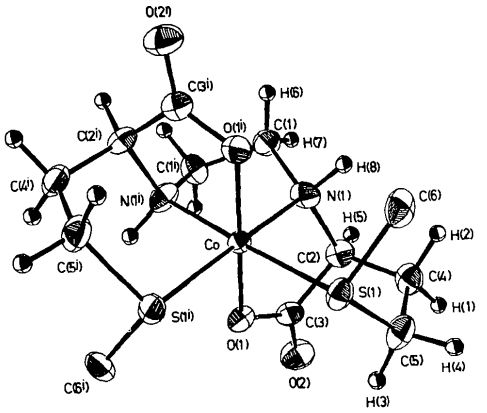


Fig. 3. The $(-)_{589}$-$[Co(ebm)]^+$ ion labelling scheme. Superscripts are defined in Table 3. Non-hydrogen thermal ellipsoids enclose 50% probability.

Table 4. *Least-squares planes*

Plane equations are in the form $LX + MY + NZ = P$. X,Y,Z are orthogonal coordinates (Å) referred to an orthonormal base system with axes parallel to a, b and c^*. The residuals were assigned unit weights. The mean isotropic e.s.d.'s for Co, S, N, O and C coordinates are 0, 2×10^{-3}, 7×10^{-3} and 8×10^{-3} Å respectively.

Plane	*L*	*M*	*N*	*P*	Symbol
S(1),Co,N(1)	0·9759	−0·0358	−0·2153	0·0	1
S(1),N(1),C(2),C(5)	0·4080	−0·1677	−0·8974	−1·1192	2
C(2),C(4),C(5)	0·9860	−0·0402	−0·1617	1·4477	3
O(1),C(3),C(2),O(2)	−0·1621	0·8547	−0·4932	−0·0071	4
N(1),Co,N(1^i)	0·9679	0·0	−0·2515	0·0	5
S(1),Co,S(1^i)	0·9837	0·0	−0·1796	0·0	6
N(1),N(1^i),S(1),S(1^i)	0·9779	0·0	−0·2093	0·0	7

Distances from the planes (Å)

	1	2	3		4		5	6	7
Co	0·0	1·119	−1·448	O(1)	−0·006	S(1)	−0·117	0·0	−0·048
S(1)	0·0	0·105	−1·354	C(3)	0·018	S(1^i)	0·117	0·0	0·048
N(1)	0·0	−0·129	−1·382	C(2)	−0·005	N(1)	0·0	0·098	0·058
C(2)	1·346	0·148	0·0	O(2)	−0·007	N(1^i)	0·0	−0·098	−0·058
C(4)	1·278	−0·669	0·0	N(1)	0·494	C(1)	−0·293		
C(5)	1·294	−0·124	0·0	Co	0·007	C(1^i)	0·293		

Interplanar angles

Planes		Planes		Planes	
1,2	53·3°	1,5	3·0°	5,6	4·2 (3)°
1,3	3·1	1,6	2·9	5,7	2·5
2,3	56·3	1,7	2·1	6,7	1·7

Table 5. *Torsion angles in the chelate rings*

The angle is that between the planes i,j,k and j,k,l in the chain i–j–k–l. If the skew lines $i \rightarrow l$ and $j \rightarrow k$ define a right-handed helix, the angle is positive. It is negative for a left-handed helix.

Co—N(1)—C(1)—C(1^i)	−32·9 (8)°	C(4)—C(5)—S(1)—Co	+45·4 (6)°
N(1)—C(1)—C(1^i)—N(1)	+42·5 (10)	Co—N(1)—C(2)—C(3)	+30·3 (7)
Co—N(1)—C(2)—C(4)	−88·2 (6)	N(1)—C(2)—C(3)—O(1)	−22·2 (9)
N(1)—C(2)—C(4)—C(5)	+75·4 (8)	C(2)—C(3)—O(1)—Co	+2·4 (9)
C(2)—C(4)—C(5)—S(1)	−55·3 (8)		

agreement with those [1·276 (7) and 1·219 (7) Å] for the averaged lengths of the equivalent bonds in *cis*(*N*)-*trans*(O_5)-[Co(*S*-asp)$_2$]$^-$.

The angular geometry of the cobalt–ethylenediamine ring is similar to that found in [Co(edta)]$^-$ and that observed in the equivalent Co–en ring of [Co(penten)]$^{3+}$. The cobalt–glycinato ring has angular parameters closely matching those seen for the equivalent rings in *cis*(*N*)-*trans*(O_5)-[Co(*S*-asp)$_2$], and is broadly similar to the axial rings of [Co(edta)]$^-$ and [Co(pdta)]$^-$. Angular distortion of the coordination sphere from octahedral geometry is not marked except for the O(1)–Co–O(1^i) angle of 173·7 (4)° and the N(1)–Co–O(1) angle of 86·1 (3)° in the cobalt–glycinato ring. The equivalent angles in the similar aspartato complex have the values 176·7 (2) and 85·5 (2)°. In the N,N,S,S equatorial plane, the N(1)–Co–N(1^i), N(1)–Co–S(1) and S(1)–Co–S(1^i) angles of 88·0 (5), 91·6 (3) and 89·0 (2)° approach octahedral values as closely as do the appropriate N–Co–N, N–Co–O and O–Co–O angles of 93·9 (2), 89·7 (2) and 87·0 (2)° in *cis*(*N*)-*trans*(O_5)-[Co(*S*-asp)$_2$]$^-$. The equivalent angles N–Co–O and O–Co–O in the strained equatorial geometry of [Co(edta)]$^-$ have the mean values 83·2 (4) and 104·0 (7)° and indicate a much larger distortion than that observed here in [Co(*S*,*S*-ebm)]$^+$. These distortions would contribute to the strain associated with equatorially disposed cobalt–glycinato rings and provide an *a fortiori* reason for the equatorial coordination of the S atoms in [Co(*S*,*S*-ebm)]$^+$. The N,N,S,S donor set in [Co(*S*,*S*-ebm)]$^+$ is very closely planar as is revealed by the short distances of these atoms from their least-squares plane (Table 4) and the small dihedral angles between the N,N,S,S, the N,Co,N and the S,Co,S planes.

The six-membered rings assume the chair conformation as seen in Fig. 3. A distortion is evident, but this is probably due to differences in the covalent radii of S and N, and the least-squares plane through N(1), C(2), C(5), S(1) makes similar angles with the closely coplanar S(1), Co, N(1) and C(2), C(4), C(5) planes (Table 4). A conclusive indication of the chair conformation and its distortion is obtained from the relative magnitudes and signs of the torsion angles of the six-membered ring (Table 5).

The five-membered cobalt–ethylenediamine and cobalt-glycinato rings have the δ and λ conformations respectively. Alternatively, for a skew-boat six-membered ring conformation, the envelope conformation of the cobalt–glycinato ring is favoured. This combination was found in *cis*(*N*)-*trans*(O_5)-[Co(*S*-asp)$_2$]$^-$ and further supports the Dreiding model predictions. The δ and λ conformations found here for the above mentioned chelate rings are clearly indicated by the signed values of the torsion angles about the C–C bonds (Table 5). The Co–O(1)–C(3)–C(2) torsion angle of +2·4 (9)° is not significantly different from zero and the Co, O(1), C(3), C(2) set is essentially planar. The values of Table 4 also indicate the accurately planar nature of the atoms Co, O(1), O(2), C(3), C(2) in the cobalt–glycinato linkage.

The anion geometry is approximately tetrahedral. The mean Cl–O bond distance of 1·432 (6) Å lies within the range 1·41–1·48 (6) Å established for Cl–O distances in ClO_4^- (*International Tables*, 1968). The O–Cl–O angles range from 108·1 (5) to 113·5 (9)°, the latter value being the only one significantly different from the tetrahedral value of 109·47°.

The authors acknowledge the financial support of the Australian Research Grants Committee.

References

BELL, J. D. & BLACKMER, G. L. (1973). *Inorg. Chem.* **12**, 836–840.

BONDI, A. (1964). *J. Phys. Chem.* **68**, 441–451.

BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). *ORFLS*. Oak Ridge National Laboratory Report ORNL-TM-305.

BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1964). *ORFFE*. Oak Ridge National Laboratory Report ORNL-TM-306.

BUTLER, K. R. & SNOW, M. R. (1975). *Acta Cryst.* B**31**, 354–358.

BUTLER, K. R. & SNOW, M. R. (1976). *J. Chem. Soc. Dalton*, pp. 259–262.

DOYLE, P. A. & TURNER, P. S. (1968). *Acta Cryst.* A**24**, 390–397.

ELDER, R. C., FLORIAN, L. R., LAKE, R. E. & YACYNYCH, A. M. (1973). *Inorg. Chem.* **12**, 2690–2699.

FREEMAN, H. C. & GOLOMB, M. L. (1970). *Chem. Commun.* pp. 1523–1525.

HAMILTON, W. C. & IBERS, J. A. (1968). *Hydrogen Bonding in Solids*, pp. 260–265. New York: Benjamin.

International Tables for X-ray Crystallography (1968). Vol. III. Birmingham: Kynoch Press.

IUPAC Information Bulletin (1968). No. 33, p. 68. *Inorg. Chem.* (1970), **9**, 1.

IWATA, M. & SAITO, Y. (1973). *Acta Cryst.* B**29**, 822–832.

MCCONNELL, J. F. & SCHWARTZ, A. (1972). *Acta Cryst.* B**28**, 1546–1550.

MAGEE, R. J., MAZUREK, W., O'CONNOR, M. J. & PHILLIP, A. T. (1974). *Aust. J. Chem.* **27**, 1629–1637.

MERLINO, S. (1968). *Acta Cryst.* B**24**, 1441–1447.

MUTO, A., MARUMO, F. & SAITO, Y. (1970). *Acta Cryst.* B**26**, 226–233.

NAGAO, R., MARUMO, F. & SAITO, Y. (1972). *Acta Cryst.* B**28**, 1852–1856.

NEAL, J. A. & ROSE, N. J. (1968). *Inorg. Chem.* **7**, 2405–2412.

NEAL, J. A. & ROSE, N. J. (1973). *Inorg. Chem.* **12**, 1226–1232.

OONISHI, I., SHIBATA, M., MARUMO, F. & SAITO, Y. (1973). *Acta Cryst.* B**29**, 2448–2455.

RAE, A. D. (1965). *Acta Cryst.* **19**, 683–684.

RAYMOND, K. N., MEEK, D. W. & IBERS, J. A. (1968). *Inorg. Chem.* **1**, 1111–1117.
SNOW, M. R. (1970). *J. Amer. Chem. Soc.* **92**, 3610–3617.
SNOW, M. R. (1972). *Aust. J. Chem.* **25**, 1307–1309.
STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.
TING-I, L. & LIPPARD, S. J. (1974). *Inorg. Chem.* **13**, 1791–1792.
WEAKLIEM, H. A. & HOARD, J. L. (1959). *J. Amer. Chem. Soc.* **81**, 549–555.
WOODWARD, L. M. (1970). MS Thesis, Univ. of Washington Seattle, Washington, USA.

Acta Cryst. (1977). B**33**, 76–80

The Crystal and Molecular Structure of 6,9-Diaza-5,10-dioxotricyclo[7.3.0.0^{1,6}]dodecane, a Molecule Designed to Contain Non-planar Amide Bonds

BY S. E. EALICK AND DICK VAN DER HELM*

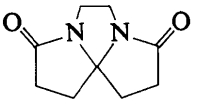
Department of Chemistry, University of Oklahoma, Norman, Oklahoma 73069, *USA*

(*Received* 24 *February* 1976; *accepted* 23 *June* 1976)

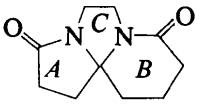
The crystal structure of 6,9-diaza-5,10-dioxotricyclo[7.3.0.0^{1,6}]dodecane, $C_{10}H_{14}N_2O_2.H_2O$, a molecule designed to contain non-planar amide bonds, has been determined and refined with three-dimensional least-squares techniques. The molecule crystallizes in space group $P2_1/c$ with unit-cell dimensions $a = 13{\cdot}4455$ (7), $b = 7{\cdot}3448$ (4), $c = 10{\cdot}7919$ (5) Å and $\beta = 99{\cdot}410$ (3)°. The crystal form is a monohydrate with the water molecule bridging the carbonyl groups of symmetry-related amide functions. The constraints of the tricyclic system result in highly non-planar amide groups, less so in the six-membered ring ($\chi_N = -16{\cdot}7$, $\tau' = 17{\cdot}8°$) than in the five-membered ring ($\chi_N = -41{\cdot}2$, $\tau' = 20{\cdot}8°$). The final R value for all 2160 reflections is 0·058 with standard deviations in non-hydrogen atomic parameters ranging from 0·0012 to 0·0024 Å.

Introduction

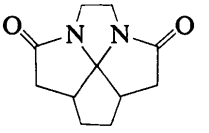
The structure of 6,9-diaza-5,10-dioxotricyclo-[7.3.0.0^{1,6}]dodecane was determined as the fourth compound in a series of polycyclic spirodilactams. The results of three of the structures (I, III, IV) have been published (Ealick & van der Helm, 1975; Ealick, Washecheck & van der Helm, 1976), while a preliminary report of this structure (II) has also been reported (van der Helm, Ealick & Washecheck, 1975). In addition, the synthesis and IR spectra of this series of molecules have been published (Smolíková, Koblicová & Bláha, 1973). This group of molecules is interesting structurally because the restrictions of the polycyclic system determine the conformation of the amide group. By changes of the ring sizes in the molecule a large variety of conformations is possible. A study to determine conformations of amide groups in medium-ring compounds has also been published (Dunitz & Winkler, 1975). Systematic studies of non-planar amides and peptides are important in light of the increasing number of examples of such groups in biological systems.



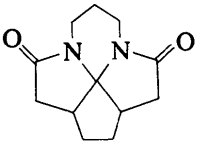
$C_9H_{12}N_2O_2$
(I)



$C_{10}H_{14}N_2O_2$
(II)



$C_{11}H_{14}N_2O_2$
(III)



$C_{12}H_{16}N_2O_2$
(IV)

Experimental

A crystalline sample of (II) was kindly provided by Professor K. Bláha, Institute of Organic Chemistry and Biochemistry, Czechoslovak Academy of Sciences, Prague. Large colorless crystals suitable for a diffraction experiment were obtained by adding water dropwise to an ethanolic solution of the compound. A plate-like crystal with approximate dimensions

* Supported by NIH Development Award K4-GM-42572.