CRYSTAL AND MOLECULAR STRUCTURE OF THE TETRADECAHYDRATE OF COBALT(II) (*R*,*S*)-ETHYLENEDIAMINE-N,N′-DISUCCINATO-COBALTATE(III)

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Crystals of $Co_3((R,S)\text{-EDDS})_2.14\,H_2O$ are monoclinic with lattice parameters $a = 1{\cdot}1393$, $b = 1{\cdot}1856$, $c = 1{\cdot}5267$ nm, $\beta = 114{\cdot}6°$. The space group is $P2_1/c$, $\bar{Z} = 2$. The structure was solved by the heavy atom method and refined by the least squares method to $R = 0{\cdot}082$. The crystals are composed of binuclear $[CO_2((R,S)\text{-EDDS})_2]^{2-}$ anions, $[Co(OH_2)_6]^{2+}$ cations and crystal water molecules. The cobalt atom in $[Co_2((R,S)\text{-EDDS})_2]^{2-}$ is coordinated octahedrally by two nitrogen atoms and three oxygen atoms from different carboxyl groups in a single $[(R,S)$--$\text{EDDS}]^{4-}$ molecule and one oxygen atom from a neighbouring $[(R,S)\text{-EDDS}]^{4-}$ molecule. The $[Co(OH_2)_6]^{2+}$ cation is coordinated octahedrally.

The dimeric unit $[Co_2((R, S)\text{-EDDS})_2]^{2-}$ (H_4EDDS is ethylenediamine-N,N′--disuccinic acid, $HOCOCH_2(HOOC)CHNHCH_2CH_2NHCH(COOH)CH_2COOH$) was found in the Li Co$(R, S)$-EDDS . 3 H_2O crystals[1]. This type of coordinating the central atom has not yet been observed in analogous compounds[2]; in $[Co(EDTA)]^-$ and $[Co((S, S)\text{-EDDS})]^-$, the central atoms are coordinated octahedrally by the hexadentate ligand[3,4]. The crystal structure analysis of $Co_3[(R, S)\text{-EDDS}]_2$. 14 H_2O was carried out to obtain further structural information on the coordination of $[(R, S)\text{-EDDS}]^{4-}$.

EXPERIMENTAL AND STRUCTURE DETERMINATION

Dissolution of $Li[Co((R,S)\text{-EDDS})].3\,H_2O$ (prepared according to the literature[1]) in hot water and slow evaporation of the solution at room temperature resulted in a redox process and red--purple prismatic $Co_3((R,S)\text{-EDDS})_2.14\,H_2O$ crystals precipitated from the solution. Calculated for $C_{20}H_{52}N_4Co_3O_{30}$ (m.w. 1005·4): 23·89% C, 5·21% H, 5·57% N, 17·58% Co; found: 23·80% C, 5·02% H, 5·69% N, 17·03% Co.

The approximate unit cell dimensions and the crystal symmetry were found from oscillation and Weissenberg photographs. The lattice parameters were refined on a Syntex $P2_1$ diffractometer by the least squares method from 8 precisely centred reflections: $a = 1{\cdot}1393(8)$, $b = 1{\cdot}1856(12)$, $c = 1{\cdot}5267(13)$ nm, $\beta = 114{\cdot}6(6)$, $V = 1{\cdot}8755\ \text{nm}^3$. Systematic extinction of reflections of the *h0l* type for $l = 2n + 1$ and *0k0* for $k = 2n + 1$ unambiguously proved the presence of space group $P2_1/c$. The crystal density $D_0 = 1{\cdot}75\ \text{Mg.m}^{-3}$ was measured by the flotation method in a bromoform–ethanol mixture. The calculated density for $Z = 2$ is $D_c = 1·78$ Mg.m^{-3}. The linear absorption coefficient μ(Mo) = 1·48 mm^{-1}. The crystal used for the structure analysis was prismatic in shape with approximate dimensions 0·30 × 0·15 × 0·15 mm. The integral intensities were measured on a Syntex $P2_1$ diffractometer using graphite monochromatized MoKα radiation ($\lambda = 0·071069$ nm) and a $\Theta - 2\Theta$ scanning technique in the interval $0 < 2\Theta < 46°$. The program controlling the measuring of the intensities automatically fixed the scanning rate in the range 2·92 to 29·3° min^{-1} in 2Θ. The scan interval was extended by 1·0° below and above the calculated K_{α_1} positions so that the peak splitting due to the presence of K_{α_1} and K_{α_2} radiation might be taken into account. The background was measured at each end of the scan

TABLE I

Final Atomic Coordinates for Nonhydrogen Atoms

Estimated standard deviations are given in parentheses (all 10^4).

Atom	*X*/*A*	*Y*/*B*	*Z*/*C*
CO (1)	656 (3)	519 (2)	3 570 (2)
N (1)	−666 (17)	−518 (14)	3 545 (11)
N (2)	1 592 (16)	−734 (12)	3 389 (10)
C (1)	−2 566 (19)	−310 (17)	4 536 (14)
C (2)	−2 907 (20)	−450 (19)	3 455 (13)
C (3)	−1 905 (20)	126 (15)	3 166 (12)
C (4)	−1 644 (25)	1 334 (15)	3 476 (12)
C (5)	−523 (20)	−1 566 (17)	3 084 (13)
C (6)	924 (22)	−1 815 (17)	3 414 (15)
C (7)	1 699 (21)	−400 (19)	2 462 (15)
C (8)	2 788 (21)	438 (17)	2 664 (16)
C (9)	2 654 (23)	1 502 (18)	3 159 (14)
C (10)	414 (20)	78 (19)	1 798 (13)
O (1)	−207 (14)	614 (12)	2 218 (9)
O (2)	85 (15)	61 (15)	915 (9)
O (3)	1 920 (14)	1 598 (11)	3 569 (8)
O (4)	3 425 (15)	2 246 (11)	3 210 (10)
O (5)	−1 404 (12)	−402 (11)	5 061 (9)
O (6)	−3 488 (12)	−127 (13)	4 790 (9)
O (7)	−2 445 (14)	1 944 (12)	3 520 (10)
O (8)	−435 (14)	1 679 (11)	3 689 (9)
W (1)	3 454 (15)	3 925 (13)	4 376 (11)
W (2)	3 724 (16)	6 343 (13)	4 408 (12)
W (3)	4 544 (13)	9 974 (12)	1 223 (9)
W (4)	4 973 (15)	1 961 (14)	2 251 (10)
W (5)	1 651 (18)	1 785 (14)	186 (11)
W (6)	4 442 (16)	8 332 (13)	3 990 (12)
W (7)	2 146 (15)	8 810 (13)	395 (11)
Co (2)	5 000 (0)	0 (0)	0 (0)

for half of the scan time of reflection. The intensity of two standard reflections measured in the interval of 98 recorded reflections showed no significant fluctuations. From the overall number of 2037 recorded symmetrically independent reflections, 943 with $I > 1\cdot96\sigma$ (I) were considered observed. The intensity of all the reflections was corrected for the Lorentz and polarization factors. Corrections were not made for absorption and extinction.

The three-dimensional Patterson synthesis calculated from all the observed reflections indicated the positions of both cobalt atoms (one heavy atom in a general and one in a special position).

TABLE II

Coefficients of Anisotropic Temperature Factors

Estimated standard deviations are given in parentheses (all 10^4). Temperature factor is of the form $T = \exp[-(B11 * H^2 + \ldots + B12 * HK + \ldots)]$.

Atom	*B*11	*B*22	*B*33	*B*12	*B*13	*B*23
Co (1)	49 (4)	20 (2)	15 (1)	−7 (6)	28 (4)	−2 (4)
N (1)	74 (26)	41 (15)	28 (10)	87 (34)	72 (26)	−37 (22)
N (2)	35 (23)	20 (15)	15 (9)	14 (28)	−4 (23)	12 (18)
C (1)	6 (27)	47 (22)	28 (12)	23 (36)	15 (28)	21 (26)
C (2)	23 (28)	65 (21)	18 (12)	36 (41)	34 (28)	11 (28)
C (3)	60 (31)	41 (19)	12 (11)	122 (39)	47 (29)	54 (24)
C (4)	181 (40)	−1 (16)	−3 (11)	35 (41)	45 (34)	49 (20)
C (5)	22 (28)	43 (20)	5 (11)	36 (37)	−18 (26)	−16 (23)
C (6)	85 (37)	22 (19)	40 (15)	52 (40)	88 (38)	23 (27)
C (7)	26 (00)	66 (23)	43 (15)	70 (43)	31 (32)	3 (30)
C (8)	47 (31)	1 (16)	75 (18)	−49 (37)	90 (37)	−48 (28)
C (9)	77 (34)	51 (21)	20 (13)	−57 (43)	54 (34)	15 (26)
C (10)	33 (31)	69 (22)	20 (12)	−50 (42)	47 (30)	−30 (27)
O (1)	48 (20)	48 (13)	41 (10)	18 (28)	61 (22)	−7 (19)
O (2)	97 (23)	136 (20)	10 (8)	31 (36)	32 (21)	12 (21)
O (3)	70 (22)	35 (13)	33 (9)	−24 (25)	92 (23)	9 (17)
O (4)	80 (23)	19 (12)	61 (11)	−9 (26)	105 (26)	2 (19)
O (5)	−6 (17)	46 (12)	38 (9)	19 (24)	27 (19)	14 (18)
O (6)	−1 (18)	96 (17)	38 (10)	16 (28)	6 (20)	6 (21)
O (7)	14 (20)	58 (15)	58 (11)	11 (27)	35 (23)	−66 (21)
O (8)	40 (20)	39 (13)	28 (9)	−31 (24)	5 (21)	−23 (17)
W (1)	53 (23)	62 (15)	61 (12)	−86 (29)	−2 (26)	−60 (22)
W (2)	90 (24)	56 (16)	88 (13)	102 (31)	157 (30)	88 (23)
W (3)	60 (20)	54 (13)	25 (9)	30 (28)	44 (20)	7 (18)
W (4)	49 (21)	95 (18)	45 (12)	29 (31)	54 (26)	17 (22)
W (5)	139 (27)	82 (17)	51 (12)	52 (35)	104 (29)	18 (22)
W (6)	75 (23)	60 (16)	69 (13)	−29 (30)	44 (28)	24 (22)
W (7)	79 (24)	50 (14)	58 (11)	−58 (29)	85 (27)	−38 (21)
Co (2)	55 (6)	45 (4)	32 (3)	−9 (9)	49 (6)	3 (6)

The positions of the other non-hydrogen atoms were found from Fourier synthesis of the electron density. The positional and isotropic temperature parameters were refined by the least squares method using relative weights $w = 1$ to $R = 0{\cdot}102$. The positions of the hydrogen atoms in the (*R*,*S*)-EDDS ligand were calculated on the basis of assumed sp^3 hybridization (valence angles 109·5°, bond lengths CH 0·109 and N—H 0·100 nm). The coordinates of the hydrogen atoms were used in calculation of the structural factors ($B = 0{\cdot}04$ nm^2) but were not refined. The positional coordinates and the anisotropic thermal factors of the non-hydrogen atoms were refined in a 9 × 9 block diagonal approximation using all the observed reflections. The weight scheme $w^{-1} = \sigma^2(|F_0|) + (C|F_0|)^2$ was employed. Coefficient $C = 0{\cdot}05$ was adjusted so that the $w(|F_0| - |F_c|)^2$ values calculated for 17 intervals according to increasing $|F_0|$ were constant. Functional $M = \sum w(|F_0| - |F_c|)^2$ was minimized. The structure was refined to $R = 0{\cdot}082$ and $R_w = 0{\cdot}085$ for the observed reflections, where $R = \sum||F_0| - |F_c||/\sum|F_0|$ and $R_w = [\sum w|\Delta F|^2/\sum w|F_0|^2]^{1.2}$. Tabulated scattering curves[5] were used for calculation of the structural factors. The maximum residual electron density in the differential synthesis was 700 e$^-$/nm^3. The calculations were carried out on an XTL module from the firm Syntex and on a Siemens 4004/150 computer with NRC program system[6].

RESULTS AND DISCUSSION

The refined coordinates of all the atoms (except hydrogen) and their standard deviations are given in Table I and the anisotropic coefficients of the thermal vibrations in Table II (some negative values of diagonal parameters *B*11, *B*22 and *B*33 are probably a result of neglecting the correction for absorption). The values of bond lengths, bonding angles and torsion angles are given in Table III. (The oxygen atom of the water molecule is designated by symbol *W* in the text and Tables.) Fig. 1 depicts the structure of the symmetrically independent part of the complex anion.

The crystal structure of $Co_3[(R, S)\text{-EDDS}]_2 \cdot 14\,H_2O$ consists of $[Co_2((R, S)\text{-EDDS})_2]^{2-}$ dimeric complex anions and $[Co(OH_2)_6]^{2+}$ cations and 8 molecules of crystal water. Half of the formula unit lies in the symmetrically independent part of the unit cell; thus, the complex cation and anion occupied the symmetry centres. Arrangement of the whole structure is depicted in Fig. 2. The cations and anions are bound in the crystal structure by ionic forces and a system of hydrogen bonds. Each co-ordinated water molecule in $Co(OH_2)_6^{2+}$ forms two hydrogen bonds. Except for the $W(1) \ldots O(4)$ contact, there is no direct interaction between anions and cations; interactions are through the crystal water molecules. The important hydrogen interactions are listed in Table IV. Complex anions take part in the hydrogen bond system through uncoordinated oxygen atoms of carboxyl groups.

The atoms of trivalent cobalt in $[Co_2((R, S)\text{-EDDS})_2]^{2-}$ are co-ordinated by two nitrogen atoms, three oxygen atoms of different carboxyl groups in a single molecule of (*R*, *S*)-EDDS and one oxygen atom from the carboxyl group of a neighbouring (*R*, *S*)-EDDS molecule, related by centre of symmetry. The length of the Co—N bonds, 0·191 and 0·193 nm, and Co—O bonds in the range 0·188–0·193 nm are somewhat shorter than in the analogous $[Co(Asp)_2]^-$ complex[7]. The C′—O bond in the carboxyl group is longer for the co-ordinated oxygen atom than for the unco-

TABLE III

The Interatomic Distances, Bonding Angles and Dihedral Angles in the $Co_3((R, S)\text{-EDDS})_2$. . 14 H_2O Complex

Interatomic distances, mm			
Co (1)—N (1)	0·193 (2)	O (5)—C (1)	0·124 (3)
Co (1)—N (2)	0·192 (2)	O (6)—C (1)	0·128 (3)
Co (1)—O (1)	0·188 (1)	O (7)—C (4)	0·119 (3)
Co (1)—O (3)	0·193 (2)	O (8)—C (4)	0·134 (3)
Co (1)—O (5)	0·191 (2)	C (1)—C (2)	0·154 (3)
Co (1)—O (8)	0·191 (2)	C (2)—C (3)	0·154 (3)
N (1)—C (5)	0·147 (3)	C (3)—C (4)	0·150 (3)
N (1)—C (3)	0·149 (3)	C (5)—C (6)	0·154 (4)
N (2)—C (6)	0·150 (3)	C (7)—C (8)	0·152 (3)
N (2)—C (7)	0·152 (3)	C (7)—C (10)	0·150 (3)
O (1)—C (10)	0·130 (3)	C (8)—C (9)	0·151 (3)
O (2)—C (10)	0·124 (2)	Co (2)—W (1)	0·206 (2)
O (3)—C (9)	0·124 (3)	Co (2)—W (2)	0·209 (2)
O (4)—C (9)	0·123 (3)	Co (2)—W (3)	0·124 (1)

Bonding angles, °			
N (1)—Co (1)—N (2)	88·8 (7)	O (5)—C (1)—O (6)	128 (2)
N (1)—Co (1)—O (1)	88·2 (7)	O (5)—C (1)—C (2)	114 (2)
N (1)—Co (1)—O (3)	177 (1)	O (6)—C (1)—C (2)	118 (2)
N (1)—Co (1)—O (5)	88·0 (7)	C (1)—C (2)—C (3)	112 (2)
N (1)—Co (1)—O (8)	85·9 (7)	C (2)—C (3)—C (4)	114 (2)
N (2)—Co (1)—O (1)	87·5 (7)	N (1)—C (3)—C (2)	111 (2)
N (2)—Co (1)—O (3)	93·1 (7)	N (1)—C (3)—C (4)	110 (2)
N (2)—Co (1)—O (5)	94·6 (6)	O (7)—C (4)—C (3)	123 (2)
N (2)—Co (1)—O (8)	174 (1)	O (7)—C (4)—O (8)	122 (2)
O (1)—Co (1)—O (5)	176 (1)	O (8)—C (4)—C (3)	115 (2)
O (1)—Co (1)—O (3)	90·6 (6)	N (1)—C (5)—C (6)	109 (2)
O (1)—Co (1)—O (8)	89·9 (6)	N (2)—C (6)—C (5)	108 (2)
O (3)—Co (1)—O (5)	93·2 (6)	N (2)—C (7)—C (8)	111 (2)
O (3)—Co (1)—O (8)	92·2 (6)	N (2)—C (7)—C (10)	107 (2)
O (5)—Co (1)—O (8)	87·7 (6)	C (8)—C (7)—C (10)	112 (2)
Co (1)—N (1)—C (3)	107 (1)	C (7)—C (8)—C (9)	114 (2)
Co (1)—N (1)—C (5)	108 (1)	O (3)—C (9)—O (4)	121 (2)
C (3)—N (1)—C (5)	121 (2)	O (3)—C (9)—C (8)	124 (2)
Co (1)—N (2)—C (6)	110 (1)	O (4)—C (9)—C (8)	114 (2)
Co (1)—N (2)—C (7)	101 (1)	O (1)—C (10)—O (2)	124 (2)
C (6)—N (2)—C (7)	119 (2)	O (1)—C (10)—C (7)	115 (2)
Co (1)—O (1)—C (10)	112 (1)	O (2)—C (10)—C (7)	120 (2)
Co (1)—O (3)—C (9)	127 (1)	W (1)—Co (2)—W (2)	88·0 (7)
Co (1)—O (5)—C (1)	126 (1)	W (1)—Co (2)—W (3)	86·6 (6)
Co (1)—O (8)—C (4)	114 (1)	W (2)—Co (2)—W (3)	89·3 (6)

TABLE III
(*Continued*)

Dihedral angles, °			
Co (1)—N (1)—C (3)—C (4)	−32·6	O (5^i)—Co (1)—N (1)—C (3)	114·1
N (1)—C (3)—C (4)—O (8)	23·1	Co (1)—N (1)—C (3)—C (2)	−159·2
C (3)—C (4)—O (8)—Co (1)	−1·4	N (1)—C (3)—C (2)—C (1)	72·0
C (4)—O (8)—Co (1)—N (1)	−14·8	C (3)—C (2)—C (1)—O (5)	−40·0
O (8)—Co (1)—N (1)—C (3)	26·2	C (2)—C (1)—O (5)—Co (1^i)	−169·3
Co (1)—N (1)—C (5)—C (6)	38·7	C (1)—O (5)—Co (1^i)—N (1^i)	−137·3
N (1)—C (5)—C (6)—N (2)	−43·5	C (3)—N (1)—C (5)—C (6)	162·0
C (5)—C (6)—N (2)—Co (1)	27·3	C (4)—C (3)—N (1)—C (5)	−156·4
C (6)—N (2)—Co (1)—N (1)	−5·1	C (2)—C (3)—N (1)—C (5)	76·9
N (2)—Co (1)—N (1)—C (5)	−19·3	C (4)—C (3)—C (2)—C (1)	−52·1
		C (5)—C (6)—N (2)—C (7)	−88·7
Co (1)—N (2)—C (7)—C (8)	80·6	C (6)—N (2)—C (7)—C (8)	−158·9
N (2)—C (7)—C (8)—C (9)	−57·8	C (6)—N (2)—C (7)—C (10)	78·6
C (7)—C (8)—C (9)—O (3)	16·2	C (8)—C (7)—C (10)—O (1)	−89·0
C (8)—C (9)—O (3)—Co (1)	−7·1	C (10)—C (7)—C (8)—C (9)	61·7
C (9)—O (3)—Co (1)—N (2)	27·4	C (2)—C (3)—C (4)—O (8)	147·9
O (3)—Co (1)—N (2)—C (7)	−57·0		
Co (1)—N (2)—C (7)—C (10)	−41·9		
N (2)—C (7)—C (10)—O (1)	32·7		
C (7)—C (10)—O (1)—Co (1)	−4·8		
C (10)—O (1)—Co (1)—N (2)	−18·0		
O (1)—Co (1)—N (2)—C (7)	33·0		

ordinated oxygen. This type of bonding has also been found for the other cobalt(III) complexes of amino acids, *e.g.* $[\mathrm{Co(EDTA)}]^-$, $[\mathrm{Co}((S,S)\text{-EDDS})]^-$, $[\mathrm{Co(Asp_2}]^-$ (ref.[3,4,7]) and appears to be typical for carboxyl group co-ordination.

One (*R*, *S*)-EDDS molecule coordinates the cobalt atom through one aspartate residue, which forms five-, six- and seven-membered chelate rings. This aspartate unit is connected through a five-membered ethylenenediamine ring with the second aspartate unit, which forms a five-membered glycine chelate ring with the cobalt atom. The β-alanine branch does not form a six-membered ring, but is co-ordinated to the neighbouring cobalt atom. As there is a centrosymmetric analogue to this branch, a twelve-membered ring is formed containing two cobalt atoms connecting two $[\mathrm{Co}((R,\,S)\text{-EDDS})]^-$ units in a binuclear complex.

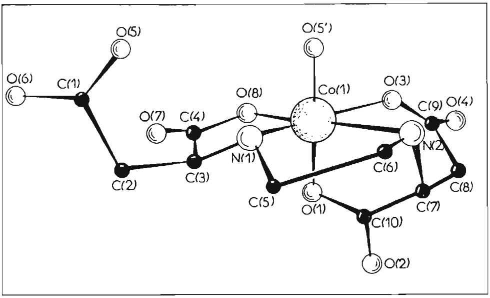

FIG. 1

Perspective Projection of the $[Co((R,S)\text{-}EDDS)]^-$ Complex with Atom Numbering

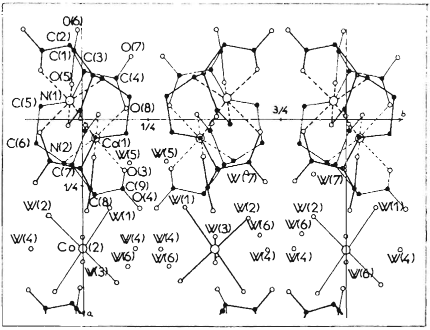

FIG. 2

Projection of the Crystal Structure of $Co_3 . [(R,S)\text{-}EDDS]_2 . 14\ H_2O$ Along the c-Axis

Two different (R,S)-EDDS molecules in a single binuclear unit are distinguished by the line thickness. Coordination bonds are dotted. The Co(1) and N(1) atoms overlap in the projection.

The conformation of the aspartate part of the ligand, which is bonded to the central atom by three donor atoms, is the same as in the $[Co(Asp)_2]^-$ or $[Co((S, S)$-$EDDS)]^-$ complex[4,7]. The bond lengths and angles are similar. The five-membered glycine chelate ring has a markedly asymmetric envelope conformation and the six-membered β-alanine ring has the conformation of an asymmetric half-twisted boat. The conformations of the individual chelate rings are apparent from Table V, which lists the deviations of the atoms from important planes passing through the

TABLE IV

Interatomic Distances Characterizing Hydrogen Bonds in the $Co_3((R, S)$-$EDDS)_2 . 14 H_2O$ Crystal Structure of Less Than 0·3 nm

Symmetric codes: (i) $-x, -y, 1 - z$; (ii) $x, 1/2 - y, z + 1/2$; (iii) $-x, y - 1/2, 1/2 - z$.

N (1) ... O (5)	0·278 (2)	N (2) ... O (6^i)	0·291 (2)
	Intermolecular distances, nm		
O (2) ... W (5^i)[a]	0·296 (2)	W (1) ... W (5^{ii})	0·293 (3)
O (2) ... W (7^i)[a]	0·283 (2)	W (2) ... W (6)	0·266 (2)
O (4) ... W (1)	0·266 (2)	W (2) ... W (7^{ii})[a]	0·279 (3)
O (4) ... W (4)	0·274 (2)	W (3) ... W (4)[a]	0·276 (2)
O (6) ... W (6)[a]	0·283 (2)	W (3) ... W (7)	0·284 (2)
O (7) ... W (4)[a]	0·277 (2)	W (4) ... W(6^{iii})[a]	0·278 (2)
O (7) ... W (7^{iii})	0·270 (2)		

[a] Atoms from neighbouring cells.

TABLE V

Deviations of the Atoms of the Chelate Rings from the Planes Passing through the Cobalt Atoms and Two Donor Atoms of the Given Chelate Ring

Atoms defining the plane	Other atoms and their deviations nm					
Co (1) N (1) O (8)	C (3)	0·0633	C (4)	0·0314		
Co (1) N (1) N (2)	C (5)	0·0463	C (6)	−0·0124		
Co (1) N (2) O (1)	C (7)	0·0821	C (10)	0·0374		
Co (1) N (2) O (3)	C (7)	0·1252	C (8)	0·0973	C (9)	0·0456

chelate rings. The central ethylenediamine chelate ring lies in the energetically unfavourable, very asymmetric gauche conformation close to the envelope conformation. Carbon atom C(5) lies 0·046 nm outside the N(1)—Co—N(2) plane and atom C(6) lies 0·012 nm out of the other side of the plane. The marked strain resulted from anelation of the chelate rings appears in deformation of the inter-ring bonding angles C(6)—N(2)—C(7) and C(3)—N(1)—C(5) with values of 119° and 121°, which are significantly different from the value 109·5° for an ideal tetrahedron. The N(1)—Co—N(2) angle is practically undeformed (88·8°). The dihedral angle N(1)—C(5)—C(6)—N(2) value of 43·5° lies at the lower boundary for normal values for ethylenediamine complexes. The almost eclipting conformation of the N(2)—C(6) bond with dihedral angle Co—N(2)—C(6)—C(5) equal to 27·3° is energetically unfavourable. An important consequence of the almost envelope conformation on the ethylenediamine ring is that both the N—H bonds are directed toward one side of the N(1)—Co—N(2) plane, enabling formation of strong intramolecular hydrogen bonds N(1)—H ... O(5) and N(2)—H ... O(6) with N(1) ... O(5) and N(2) ... O(6) distances of 0·287 and 0·291 nm. The energy gained in the formation of these hydrogen bonds probably compensates for the energy loss connected with formation of the deformed gauche conformatinn of the ethylenediamine ring. The glycine ring of the second aspartate unit has the conformation of a symmetrical envelope, in which atom C(3) lies 0·063 nm outside the plane defined by atoms N(1)—Co—O(8). This deviation from planarity enables the ring to avoid energetically unfavourable eclipting conformation of the N(1)—C(3) bond. No marked deformation of the bond lengths or angles was found in the twelve-membered chelate ring. The magnitude of the dihedral angles also approached the values of idealized angles except that the dihedral angle Co—N(1)—C(3)—C(2) had a value of 159·2° (ideal 180°); however, the N(1)—C(3) bond is also part of the glycine chelate cycle.

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