THE CRYSTAL AND MOLECULAR STRUCTURE OF CALCIUM (S,S)-ETHYLENEDIAMINE-N,N'-DISUCCINATOFERRATE OCTAHYDRATE

František PAVELČÍK and Viktor KETTMANN

Department of Analytical Chemistry,
Pharmaceutical Faculty, Comenius University, 832 32 Bratislava

Crystals of Ca[Fe((S,S)-EDDS)]$_2$.8 H$_2$O are monoclinic with lattice parameters of $a = 1.0284$ $b = 0.8403$, $c = 2.1273$ nm, $\beta = 116.04°$. The space group is Pc, $Z = 2$. The structure was solved by the heavy atom method and refined by the least squares method to give $R = 0.057$. The crystals consist of [Fe(III) ((S,S)-EDDS)]$^-$ anions, hydrated Ca^{2+} cations and molecules of water of crystallization. The iron atoms are coordinated by two nitrogen atoms and four oxygen atom of the carboxyl groups of the hexadentate ligand. The coordination polyhedron of the iron atom forms a deformed octahedron. The absolute configuration of the complex is (OC-6-13-A) for the (S,S) absolute ligand configuration.

Ethylenediamine-N,N'-disuccinic acid (H$_4$EDDS), HOOCCH$_2$CH(COOH)NHCH$_2$. .CH$_2$NHCH(COOH)CH$_2$COOH can exist in three stereoisomeric forms[1], depending on the absolute configuration of the aspartate units. [(S,S)-EDDS]$^{4-}$ exhibits marked diastereoselectivity in coordination of transition metals, which has been demonstrated in solution by CD and NMR spectroscopy[2-4] and in the solid phase by X-ray structural analysis[5-7].

Sometimes multidentate amino acids coordinate around Fe(III) to form a complex with a coordination number of 6 or with the rather unusual coordination number of 7 (ref.[8]). This work was carried out in order to determine the type of coordination of EDDS in complexes with a central ion with d^5 electron configuration and to increase knowledge of the stereospecific coordination of EDDS.

EXPERIMENTAL

Preparation of Ca[Fe((S,S)-EDDS)]$_2$.8 H$_2$O. 0.06 mol of (S,S)-H$_4$EDDS.5 H$_2$O (synthesized by procedure[1]) were mixed with 0.06 mol of freshly prepared precipitated Fe(OH)$_3$ and 0.03 mol CaCO$_3$ in 200 ml H$_2$O. After dissolution, the solution was filtered and concentrated on a water bath. Slow evaporation led to precipitation of yellow crystals that were recrystallized from water. For C$_{20}$H$_{40}$N$_4$O$_{24}$CaFe$_2$ (872.3) calculated: 27.54% C, 4.62% H, 12.88% Fe, 6.42% N; found: 27.61% C, 4.44% H, 12.91% Fe, 6.12% N.

The approximate dimensions of the unit cell and the crystal symmetry were found from oscillation and Weissenberg patterns. Systematic absences of $h0l$ with $l = 2n + 1$ type reflections indicated that space groups of Pc or $P2/c$ are possible. Space group $P2/c$ was later excluded on the

basis of Patterson synthesis. The lattice parameters were refined on a Syntex $P2_1$ diffractometer from the positional angles of 10 reflections using Mo K_α radiation. The crystal density was found by the flotation method in a bromoform–methanol mixture. The basic crystallographic data are as follows:

$$a = 1\cdot0284(4) \text{ nm} \qquad V = 1\cdot6517 \text{ nm}^3$$
$$b = 0\cdot8403(4) \text{ nm} \qquad Z = 2$$
$$c = 2\cdot1273(12) \text{ nm} \qquad D_0 = 1\cdot74(2) \text{ Mg m}^{-3}$$
$$\beta = 116\cdot04(4)° \qquad D_X = 1\cdot753 \text{ Mg m}^{-3}$$
$$\mu(\text{MoK}_\alpha) = 1\cdot16 \text{ mm}^{-1} \qquad \lambda(\text{MoK}_\alpha) = 0\cdot071069 \text{ nm}$$
monoclinic system   space group Pc

The crystal used for the intensity measurements was roughly prismatic in shape with dimensions of $0\cdot22 \times 0\cdot15 \times 0\cdot20$ mm. The integral intensities were measured on a Syntex P2$_1$ diffractometer using graphite monochromatized MoK$_\alpha$ radiation and the $\theta - 2\theta$ scanning technique in the interval $2\cdot9° < 2\theta < 50°$. The program controlling the intensity measurements automatically determined the scanning rate in the interval $2\cdot55 - 29\cdot3°$ min^{-1} on the basis of two-second prior intensity measurement. To include peak splitting resulting from the presence of Kα_1 and Kα_2 radiation, the scanning interval was 1° under the calculated 2θ value for Kα_1 and 1° above the calculated value for Kα_2. The background was measured at each end of the scanning range for period of time equal to one half of the reflection scanning time. The intensities of two control reflections measured after each 96 measurements did not change significantly during the experiment. Of the overall number of 2754 recorded reflections, 1940 reflections with $I > 1\cdot96\sigma(I)$ were considered observed. The intensities of all the reflections were corrected for the Lorentz and polarization factors. Corrections were not carried out for absorption and extinction.

Three-dimensional Patterson synthesis computed for all the observed reflections indicated the positions of both iron atoms. The positions of the other atoms (except the H atoms) were found by five subsequent Fourier syntheses of the electron density phased with a gradually increasing number of localized atoms. The positional and isotropic temperature factors were refined by the full matrix least squares method with relative weights $w = 1$ for all the observed reflections to give $R = 0\cdot15$. The coordinates of the hydrogen atoms for both EDDS ligands were calculated on the basis of concepts concerning sp^3 hybridization (bond lengths C—H and N—H were taken to equal $0\cdot109$ and $0\cdot100$ nm, respectively, and the valence angles equal to $109\cdot5°$).

The differential electron density map contained a number of maxima corresponding to the hydrogen atoms in the water molecules. Unambiguous assignment of the hydrogen atoms for all the water molecules could not be carried out. Final refinement was made using the block-diagonal least squares method. The positional parameters for all the atoms, the isotropic temperature parameters for the hydrogen atoms and the anisotropic temperature parameters for the other atoms were refined. The function $M = \Sigma w(|F_0| - |F_c|)^2$ was minimized; the weighting scheme $w^{-1} = \sigma^2(F_0) + (C \cdot |F_0|)^2$ was used, where $\sigma(F_0)$ is found from counting statistics and $C = 0\cdot07$. The C value was optimized in order to obtain a constant value for $\Sigma w|F_0| - |F_c|)^2$ for various intervals of $|F_0|$. The final value of the R factor, $R = \Sigma |\Delta F| / \Sigma |F_0|$, was $0\cdot057$ for the observed reflections and $0\cdot085$ for all the reflections. The Hamilton factor R_w ($R_w = [\Sigma w|\Delta F|^2 / \Sigma w|F_0|^2]^{1/2}$) was $0\cdot058$ for the observed and $0\cdot061$ for all the reflections. Atom scattering curves for the neutral atoms[9] were used in the calculation. The maximal residual electron density in the zero synthesis was $1\,070$ e nm^{-3} in the vicinity of the Fe(2) atom. The refined coordinates of all the atoms (except the hydrogen atoms) are given in Table I and the corresponding anisotropic temperature parameter coefficients are given in Table II. The refined coordinates of the hydrogen atoms and their temperature coefficients are given in Table III. The values of the mea-

Table I

Final atomic coordinates (. 10^4) for nonhydrogen atoms. Estimated standard deviations are given in parentheses

Atom	x	y	z
Fe(1)	0(0)	1 654(2)	0(0)
C(1)	− 2 010(17)	− 354(19)	−1 034(7)
C(2)	− 378(19)	4 801(19)	357(8)
C(3)	−2 009(15)	− 875(19)	− 368(7)
C(4)	799(18)	4 856(19)	82(9)
C(5)	− 923(16)	−1 348(18)	−1 183(7)
C(6)	352(19)	4 553(19)	1 160(8)
C(7)	612(17)	− 732(17)	− 835(8)
C(8)	1 299(16)	3 060(18)	1 430(7)
C(9)	−3 000(17)	2 368(23)	−1 070(8)
C(10)	−2 472(19)	3 873(22)	− 688(9)
N(1)	−1 771(13)	1 293(15)	−1 008(6)
N(2)	−1 374(13)	3 533(15)	7(6)
O(1)	−1 177(12)	− 123(13)	187(5)
O(2)	924(13)	3 556(12)	− 199(6)
O(3)	−2 755(12)	−2 021(14)	− 323(6)
O(4)	1 482(16)	6 052(14)	122(8)
O(5)	1 052(10)	199(13)	− 309(5)
O(6)	1 195(11)	1 919(11)	1 008(4)
O(7)	1 489(13)	−1 278(12)	−1 048(6)
O(8)	2 085(12)	2 987(14)	2 054(5)
Fe(2)	7 430(2)	1 013(2)	1 663(1)
C(11)	4 707(14)	2 387(20)	750(7)
C(12)	8 505(16)	−2 147(17)	1 737(6)
C(13)	5 886(21)	3 066(23)	551 (9)
C(14)	8 209(15)	−1 856(14)	2 393(7)
C(15)	4 625(19)	3 505(24)	1 315(10)
C(16)	10 035(16)	−1 661(14)	1 933(7)
C(17)	5 987(19)	3 746(20)	1 975(10)
C(18)	10 483(18)	− 23(17)	2 278(8)
C(19)	4 903(19)	− 499(24)	493(9)
C(20)	5 934(18)	−1 867(22)	840(8)
N(11)	5 139(13)	788(14)	1 028(6)
N(12)	7 457(15)	−1 152(16)	1 173(6)
O(11)	7 123(11)	2 383(13)	849(5)
O(12)	7 452(11)	− 673(12)	2 362(5)
O(13)	5 569(14)	4 185(14)	135(7)
O(14)	8 828(15)	−2 721(13)	2 901(6)
O(15)	7 042(11)	2 815(13)	2 159(5)

TABLE I
(*Continued*)

Atom	x	y	z
O(16)	9 561(12)	1 095(12)	2 093(6)
O(17)	6 034(19)	4 925(24)	2 338(11)
O(18)	11 764(11)	226(13)	2 705(6)
Ca(1)	2 127(3)	2 949(3)	3 206(1)
W(1)	3 085(13)	4 077(16)	4 363(6)
W(2)	2 870(18)	5 564(15)	3 096(8)
W(3)	4 548(14)	2 136(25)	3 543(9)
W(4)	− 129(12)	4 275(12)	2 876(7)
W(5)	4 394(17)	404(19)	2 340(9)
W(6)	3 926(19)	6 903(19)	2 224(11)
W(7)	2 793(32)	7 965(25)	3 925(10)
W(8)	2 418(29)	8 465(35)	1 090(12)

sured and calculated structural factors can be obtained from the authors on request. The oxygen atoms of the water molecules are designated in the tables by the symbol *W*. The calculations were carried out on a Siemens 4004/150 computer at the Computing Centre Comenius University, Bratislava, using the NRC program system[10].

DISCUSSION

The crystal structure of Ca[Fe((S,S)-EDDS)]$_2$.8 H$_2$O is composed of complex [Fe(1)(EDDS)]$^-$ anions (Fig. 1), and [Fe(2)(EDDS)]$^-$ (Fig. 2) anions, hydrated Ca^{2+} cations and water of crystallization. Both complex anions have the same absolute configuration, indicating that the crystals represent a racemic mixture. The structure was refined for (S,S) absolute configuration of the ligand. The structures of both complex anions are very similar. Differences result only from different positions in the crystal. The iron atom is octahedrally coordinated by two nitrogen atoms and four oxygen atoms from the carboxyl groups. EDDS has the maximum dentate number and forms 5 chelate rings. For [Fe(1)(EDDS)]$^-$ (and analogously for the other complex anion) was found: a pseudo-ethylenediamine ring (the *E*-ring) Fe(1)—N(1)—C(9)—C(10)—N(2)—, two six-membered β-alanine rings (*G*-rings) Fe(1)—O(5)—C(7)—C(5)—C(1)—N(1)— and Fe(1)—O(6)—C(8)—C(6)—C(2)——N(2)— and two glycine rings (*R*-rings) Fe(1)—O(1)—C(3)—C(1)—N(1)— and Fe(1)—O(2)—C(4)—C(2)—N(2)— (symbols *E*, *G* and *R* for the chelate rings are taken from the work of Weakliem and Hoard[11] and will be used as indices as general symbols for designation of the individual atoms). The complex anions have a pseudo-

TABLE II

Coefficients of anisotropic temperature factors (. 10^4) estimated standard deviations are given in parentheses. Temperature factor is of the form

$$T = \exp\left(-(B_{11}h^2 + \ldots + B_{12}hk + \ldots)\right)$$

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Fe(1)	85(2)	108(3)	13(0)	26(5)	29(2)	12(2)
C(1)	102(21)	126(25)	19(4)	− 55(37)	1(15)	4(17)
C(2)	138(23)	113(24)	24(5)	22(38)	60(17)	18(17)
C(3)	80(19)	165(27)	14(3)	54(36)	34(13)	− 6(16)
C(4)	111(21)	123(25)	32(5)	− 55(38)	63(17)	12(19)
C(5)	92(19)	173(26)	12(3)	120(36)	46(13)	9(15)
C(6)	154(26)	118(25)	27(5)	− 89(42)	62(19)	− 52(18)
C(7)	138(23)	99(22)	24(4)	81(35)	83(17)	− 21(15)
C(8)	91(19)	152(26)	19(4)	− 64(36)	57(13)	7(16)
C(9)	84(20)	204(32)	17(4)	− 1(41)	−18(14)	40(19)
C(10)	146(26)	196(32	30(5)	132(5)	105(20)	55(20)
N(1)	103(16)	142(20)	15(3)	35(29)	59(12)	− 11(12)
N(2)	73(15)	143(20)	23(4)	41(28)	54(12)	22(14)
O(1)	138(15)	154(18)	17(3)	−103(27)	65(11)	− 3(11)
O(2)	172(18)	104(16)	29(3)	− 58(27)	84(13)	− 8(12)
O(3)	110(16)	178(22)	31(4)	− 23(29)	54(12)	18(14)
O(4)	223(20)	134(20)	50(5)	−123(35)	138(19)	− 8(16)
O(5)	92(14)	161(19)	23(3)	30(26)	37(11)	− 38(12)
O(6)	144(15)	108(16)	11(2)	53(25)	39(9)	− 8(16)
O(7)	182(19)	97(16)	32(4)	11(27)	104(14)	− 11(12)
O(8)	130(15)	194(22)	17(3)	− 51(30)	37(10)	− 6(12)
Fe(2)	81(2)	71(2)	18(0)	13(4)	38(2)	8(2)
C(11)	30(15)	192(28)	19(4)	−107(36)	−12(12)	− 1(18)
C(12)	137(22)	105(21)	11(3)	10(35)	58(14)	− 17(13)
C(13)	170(29)	223(36)	28(5)	− 39(50)	107(20)	28(22)
C(14)	113(20)	44(17)	19(4)	28(29)	27(14)	24(13)
C(15)	105(23)	214(35)	40(7)	− 12(47)	80(21)	− 48(24)
C(16)	128(21)	32(16)	18(4)	34(29)	40(14)	11(13)
C(17)	134(26)	159(29)	40(6)	5(42)	120(22)	− 34(21)
C(18)	139(23)	86(20)	30(5)	40(36)	90(17)	36(17)
C(19)	118(25)	223(36)	32(6)	− 15(47)	72(20)	− 28(23)
C(20)	120(23)	223(36)	19(4)	−140(47)	36(16)	− 36(20)
N(11)	93(16)	113(19)	22(3)	− 13(28)	52(12)	− 13(13)
N(12)	150(20)	141(22)	22(4)	74(33)	91(14)	− 10(14)
O(11)	90(13)	172(19)	24(3)	107(26)	56(10)	64(13)
O(12)	101(16)	142(17)	19(3)	46(24)	59(10)	− 22(11)
O(13)	179(20)	151(20)	43(4)	115(31)	110(16)	93(16)
O(14)	235(22)	111(17)	35(4)	68(33)	112(16)	3(14)
O(15)	113(14)	99(15)	22(3)	38(23	28(10)	− 5(11)

TABLE II
(*Continued*)

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
O(16)	126(15)	110(16)	33(4)	− 7(26)	54(12)	− 17(13)
O(17)	221(31)	318(37)	84(10)	354(57)	− 4(27)	−115(33)
O(18)	80(13)	138(17)	28(3)	− 47(24)	30(10)	− 12(12)
Ca(1)	88(4)	99(4)	18(1)	23(7)	48(3)	− 4(3)
W(1)	137(16)	238(25)	25(3)	−183(33)	72(12)	− 61(15)
W(2)	311(31)	158(22)	43(5)	− 74(43)	150(21)	− 30(17)
W(3)	101(19)	504(51)	52(6)	33(47)	35(16)	−193(29)
W(4)	111(16)	91(17)	53(5)	58(26)	27(15)	− 16(15)
W(5)	202(24)	255(32)	59(7)	106(45)	127(21)	22(23)
W(6)	213(27)	246(32)	85(9)	141(47)	172(26)	26(27)
W(7)	557(63)	332(46)	46(7)	473(88)	55(33)	− 49(28)
W(8)	377(47)	605(73)	50(8)	186(97)	91(31)	127(38)

-two-fold axis of symmetry passing through the iron atom and through the middle of the N···N connecting line. This pseudo-axis connects the R and G rings in pairs. Idealized geometry of the $[\text{Fe(EDDS)}]^-$ complex results from averaging of four data sets.

The bond lengths, bond angles and torsion angles are listed in Table IV. The bond lengths in the organic ligand are normal. The mean length of the Fe—O_G bond,
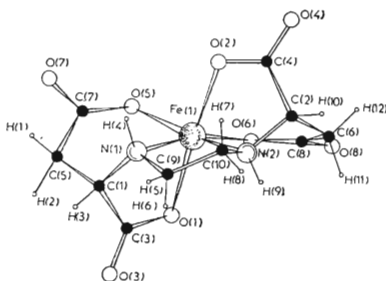

FIG. 1
Perspective projection of the structure of the complex anion, (OC-6-13-A) [Fe(1)((S,S)-EDS)]⁻

196 pm (interval of 193—198) is somewhat shorter than the mean Fe—O_R bond length, 200 pm (199—207), which is statistically significant at a standard deviation of 1 pm. This difference can be the result of different strain in the R and G rings (see below). The mean length of the Fe—N bond is 213 pm. All the coordination bonds are shorter than the analogous bonds in the hepta-coordinated ferric complexes of DCTA and EDTA (ref.[12,13] (the mean Fe—O and Fe—N bond lengths are 205 and 227 pm, (respectively). Lengthening of the Fe—N bond compared to the Fe—O bond, attributed to the unwillingness of Fe(III) to form bonds with amines[8], is not as marked in EDDS complexes as in the seven-coordinated EDTA complexes. Anomalous lengthening of the Fe—N bond length to 236 pm was found in the crystal structure[14] of the guanidine salt $(CN_3H_6)[Fe(H_2O)(EDTA)].2 H_2O$. The C—$O_c$ bond lengths in all the $[Fe(EDDS)]^-$ complexes are greater than the C—O_u bond length (O_c and O_u are the coordinated and uncoordinated oxygen atoms of the carboxyl groups respectively). The mean C—O_c length is 127·1 pm and C—O_u = 123·6 pm. These values are similar to the bond lengths in Ca[Fe(DCTA). .$(OH_2)]_2$.8 H_2O (ref.[12]) and indicate that the order of the C—O_c bond is less and for C—O_u greater than 1·5.

The bond angles in the coordination sphere are very different from a value of 90° for an ideal octahedron. The mean magnitude of the N—Fe—O_R angle in the chelate ring is 77·2° (interval of 76·3—78·0). N—Fe—N 81·4 (80·6—82·1°), N—Fe—O_G 88·9 (85·8—90·4°). The external angles between the rings are equal to 102·6 (99·7—105·6) for O_G—Fe—O_G and 170·8 (169·0—172·6) for O_R—Fe—O_R. These deviations result from the d^5 electron configuration of the central atom that does not lead to markedly directional orientation of the coordination bonds. The bond angles are then a compromise between the steric requirements of the ligand and repulsion between the donor
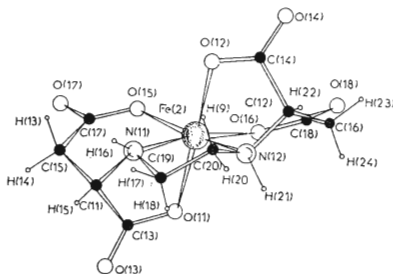

Fig. 2

Perspective projection of the structure of the complex anion, (OC-6-13-A) [Fe(2)((S,S)-EDDS)]⁻

atoms in the coordination sphere. The five-membered chelate rings have a tendency to decrease the bonding angles compared with the value of 90° for minimal repulsion in the octahedral complexes. The magnitude of the N—Fe—N angle is greater than

TABLE III

Final atomic coordinates ($. 10^4$) and isotropic temperature factors ($. 10^{20}$ m^2) for hydrogen atoms. Estimated standard deviations are given in parentheses

Atom	x	y	z	B
H(1)	−1 078(99)	−1 235(99)	−1 667(71)	0·4(28)
H(2)	−1 235(99)	−2 710(99)	−1 082(68)	−0·1(27)
H(3)	−2 849(99)	− 774(99)	−1 352(60)	−1·1(22)
H(4)	−1 504(99)	1 831(99)	−1 319(99)	13·1(99)
H(5)	−3 803(86)	2 332(97)	−1 471(40)	−3·4(14)
H(6)	−3 502(99)	1 780(99)	− 936(61)	−0·8(23)
H(7)	−2 164(99)	4 441(99)	− 884(52)	−1·7(19)
H(8)	−3 331(85)	4 367(93)	− 699(40)	−3·2(13)
H(9)	−2 134(99)	3 563(99)	66(99)	7·1(71)
H(10)	− 666(99)	5 843(99)	437(54)	−1·7(20)
H(11)	− 468(84)	4 393(92)	1 327(39)	−3·2(13)
H(12)	1 140(99)	5 281(99)	1 439(54)	−1·5(21)
H(13)	4 121(99)	3 005(99)	1 547(99)	7·3(73)
H(14)	4 209(99)	4 692(99)	1 153(79)	1·4(43)
H(15)	3 829(99)	2 177(99)	349(99)	5·1(58)
H(16)	4 495(99)	680(99)	1 011(82)	0·6(32)
H(17)	3 787(99)	− 932(99)	330(55)	−1·4(20)
H(18)	5 198(75)	29(82)	156(33)	−4·1(12)
H(19)	5 650(99)	−2 140(99)	1 144(79)	1·1(32)
H(20)	5 574(99)	−2 700(99)	431(52)	−1·6(19)
H(21)	7 627(97)	−1 283(99)	728(45)	−2·6(16)
H(22)	8 070(99)	−3 267(99)	1 541(46)	−2·3(17)
H(23)	10 617(99)	−2 636(99)	2 200(60)	−0·5(23)
H(24)	10 198(99)	−1 668(99)	1 570(48)	−2·3(16)
H(25)	4 192(99)	4 601(99)	4 632(61)	−0·9(24)
H(26)	2 950(99)	3 255(99)	430 7(84)	1·0(34)
H(27)	3 056(99)	6 830(99)	3 454(67)	−0·2(26)
H(28)	3 431(99)	5 859(99)	2 884(86)	1·4(35)
H(29)	5 715(99)	1 821(99)	3 887(53)	−1·8(19)
H(30)	− 355(99)	5 169(99)	2 793(81)	1·1(32)
H(31)	−1 249(99)	3 821(99)	2 882(84)	1·4(33)
H(32)	3 629(99)	27(99)	1 800(48)	−2·3(17)
H(33)	3 577(99)	695(99)	2 546(64)	−0·9(24)
H(34)	4 904(99)	6 683(99)	2 212(99)	2·9(49)
H(35)	3 127(99)	7 173(99)	1 702(84)	1·5(35)

TABLE IV

Interatomic distances, bonding angles and torsion angles in Ca[Fe(S,S)-EDDS)]$_2$.8 H$_2$O with standard deviations in parentheses

Interatomic distances, pm

Fe(1)—O(1)	206·7(12)	Fe(2)—O(11)	198·5(11)
Fe(1)—O(2)	199·7(12)	Fe(2)—O(12)	204·8(10)
Fe(1)—O(5)	192·9(11)	Fe(2)—O(15)	198·4(11)
Fe(1)—O(6)	196·1(9)	Fe(2)—O(16)	197·1(14)
Fe(1)—N(1)	214·0(11)	Fe(2)—N(11)	214·9(14)
Fe(2)—N(2)	212·4(14)	Fe(2)—N(12)	210·3(13)
C(1)—C(3)	148(2)	C(11)—C(13)	156(3)
C(1)—C(5)	154(2)	C(11)—C(15)	156(3)
C(1)—N(1)	140(2)	C(11)—N(11)	146(2)
C(2)—C(4)	156(3)	C(12)—C(14)	157(2)
C(2)—C(6)	155(2)	C(12)—C(16)	150(2)
C(2)—N(2)	144(2)	C(12)—N(12)	147(2)
C(3)—O(1)	128(2)	C(13)—O(11)	128(2)
C(3)—O(3)	126(2)	C(13)—O(13)	123(2)
C(4)—O(2)	128(2)	C(14)—O(12)	125(2)
C(4)—O(4)	121(2)	C(14)—O(14)	122(2)
C(5)—C(7)	151(2)	C(15)—C(17)	150(3)
C(6)—C(8)	154(2)	C(16)—C(18)	153(2)
C(7)—O(5)	127(2)	C(17)—O(15)	125(2)
C(7)—O(7)	126(2)	C(17)—O(17)	124(3)
C(8)—O(6)	129(2)	C(18)—O(16)	127(2)
C(8)—O(8)	121(2)	C(18)—O(18)	125(2)
C(9)—C(10)	147(2)	C(19)—C(20)	152(3)
C(9)—N(1)	151(2)	C(19)—N(11)	151(2)
C(10)—N(2)	144(2)	C(20)—N(12)	153(3)
Ca—O(7^{vii})	241·4(12)	Ca—O(8)	243·3(11)
Ca—O(18^{ii})	248·3(11)	Ca—W(1)	240·8(12)
Ca—W(2)	237·2(14)	Ca—W(3)	236·9(17)
Ca—W(4)	238·4(14)		

Bonding angles, °

O(1)—Fe(1)—O(2)	172·6(5)	O(11)—Fe(2)—O(12)	169·0(4)
O(1)—Fe(1)—O(5)	94·1(4)	O(11)—Fe(2)—O(15)	91·7(5)
O(1)—Fe(1)—O(6)	90·6(4)	O(11)—Fe(2)—O(16)	96·0(5)
O(1)—Fe(1)—N(1)	77·1(5)	O(11)—Fe(2)—N(11)	78·0(5)
O(1)—Fe(1)—N(2)	95·0(5)	O(11)—Fe(2)—N(12)	95·8(5)
O(2)—Fe(1)—O(5)	92·6(5)	O(12)—Fe(2)—O(15)	94·7(4)
O(2)—Fe(1)—O(6)	90·7(5)	O(12)—Fe(2)—O(16)	91·8(5)

TABLE IV
(Continued)

Bonding angles. °

O(2)—Fe(1)—N(1)	100·2(5)	O(12)—Fe(2)—N(11)	93·1(5)
O(2)—Fe(1)—N(2)	77·7(5)	O(12)—Fe(2)—N(12)	76·3(5)
O(5)—Fe(1)—O(6)	105·6(4)	O(15)—Fe(2)—O(16)	99·7(5)
O(5)—Fe(1)—N(1)	85·8(5)	O(15)—Fe(2)—N(11)	88·8(5)
O(5)—Fe(1)—N(2)	161·5(5)	O(15)—Fe(2)—N(12)	166·8(5)
O(6)—Fe(1)—N(1)	164·0(5)	O(16)—Fe(2)—N(11)	169·8(5)
O(6)—Fe(1)—N(2)	90·4(5)	O(16)—Fe(2)—N(12)	90·4(5)
N(1)—Fe(1)—N(2)	80·6(5)	N(11)—Fe(2)—B(12)	82·1(5)
C(3)—C(1)—C(5)	110·0(13)	C(13)—C(11)—C(15)	107·5(14)
C(3)—C(1)—N(1)	109·1(13)	C(13)—C(11)—N(11)	108·2(13)
C(5)—C(1)—N(1)	114·5(13)	C(15)—C(11)—N(11)	110·7(13)
C(4)—C(2)—C(6)	109·7(14)	C(14)—C(12)—C(16)	107·5(12)
C(4)—C(2)—N(2)	108·8(14)	C(14)—C(12)—N(12)	106·1(12)
C(6)—C(2)—N(2)	111·1(14)	C(16)—C(12)—N(12)	112·1(12)
C(1)—C(3)—O(1)	117·1(13)	C(11)—C(13)—O(11)	115·1(16)
C(1)—C(3)—O(3)	123·5(14)	C(11)—C(13)—O(13)	118·8(17)
O(1)—C(3)—O(3)	119·4(14)	O(11)—C(13)—O(13)	126·1(18)
C(2)—C(4)—O(2)	113·8(15)	C(12)—C(14)—O(12)	116·0(12)
C(2)—C(4)—O(4)	121·4(16)	C(12)—C(14)—O(14)	117·5(13)
O(2)—C(4)—O(4)	124·7(17)	O(12)—C(14)—O(14)	126·2(14)
C(1)—C(5)—C(7)	114·2(13)	C(11)—C(15)—C(17)	117·4(16)
C(2)—C(6)—C(8)	116·4(14)	C(12)—C(16)—C(18)	115·9(12)
C(5)—C(7)—O(5)	122·2(14)	C(15)—C(17)—O(15)	122·2(17)
C(5)—C(7)—O(7)	117·2(14)	C(15)—C(17)—O(17)	117·0(18)
O(5)—C(7)—O(7)	120·4(14)	O(15)—C(17)—O(17)	120·8(19)
C(6)—C(8)—O(6)	120·2(14)	C(16)—C(18)—O(16)	119·3(14)
C(6)—C(8)—O(8)	117·3(14)	C(16)—C(18)—O(18)	119·9(14)
O(6)—C(8)—O(8)	122·5(15)	O(16)—C(18)—O(18)	120·6(15)
C(10)—C(9)—N(1)	111·9(14)	C(20)—C(19)—N(11)	109·2(15)
C(9)—C(10)—N(2)	109·2(15)	C(19)—C(20)—N(12)	106·4(14)
C(1)—N(1)—C(9)	117·5(13)	C(11)—N(11)—C(19)	115·7(13)
C(2)—N(2)—C(10)	116·3(14)	C(12)—N(12)—C(20)	112·8(13)
Fe(1)—O(1)—C(3)	113·0(10)	Fe(2)—O(11)—C(13)	115·7(11)
Fe(1)—O(2)—C(4)	115·5(11)	Fe(2)—O(12)—C(14)	113·4(9)
Fe(1)—O(5)—C(7)	130·7(10)	Fe(2)—O(15)—C(17)	131·3(11)
Fe(1)—O(6)—C(8)	132·0(10)	Fe(2)—O(16)—C(18)	130·2(11)
Fe(1)—N(1)—C(1)	103·7(10)	Fe(2)—N(11)—C(11)	103·2(9)
Fe(1)—N(1)—C(9)	108·3(9)	Fe(2)—N(11)—C(19)	107·8(10)
Fe(1)—N(2)—C(2)	103·3(10)	Fe(2)—N(12)—C(12)	104·6(9)
Fe(1)—N(2)—C(10)	111·4(10)	Fe(2)—N(12)—C(20)	109·6(10)

TABLE IV
(*Continued*)

Bonding angles, °

O(7^{vii})---Ca---O(8)	141·2(4)	O(18^{ii})---Ca---W(1)	136·0(4)
O(7^{vii})—Ca—O(18^{ii})	73·4(4)	O(18^{ii})—Ca—W(2)	143·7(5)
O(7^{vii})—Ca—W(1)	70·4(4)	O(18^{ii})—Ca—W(3)	78·7(5)
O(7^{vii})—Ca—W(2)	142·7(5)	O(18^{ii})—Ca—W(4)	111·2(4)
O(7^{vii})—Ca—W(3)	100·7(5)	W(1)—Ca—W(3)	74·4(5)
O(7^{vii})—Ca—W(4)	87·5(4)	W(1)—Ca—W(3)	84·3(5)
O(8)—Ca—O(18^{ii})	69·3(4)	W(1)—Ca—W(4)	91·5(4)
O(8)—Ca—W(1)	147·5(4)	W(2)—Ca—W(3)	87·5(6)
O(8)—Ca—W(2)	75·7(5)	W(2)—Ca—W(4)	81·5(5)
O(8)—Ca—W(3)	82·0(5)	W(3)—Ca—W(4)	168·9(6)
O(8)—Ca—W(4)	96·5(4)	Ca—O(18)—C(18)	112·3(10)
Ca—O(7)---C(7)	153·1(11)	Ca—O(8)—C(8)	144·1(11)

Torsion angles, °

Fe(1)---O(5)—C(7)—D(5)	−24(2)	Fe(2)—O(15)—C(17)—C(15)	8(3)
O(5)—C(7)---C(5)—C(1)	20(2)	O(15)—C(17)—C(15)—C(11)	−18(3)
C(7)—C(5)—C(1)—N(1)	38(2)	C(17)—C(15)—C(11)—N(11)	60(2)
C(5)—C(1)—N(1)—Fe(1)	−78(1)	C(15)—C(11)—N(11)—Fe(2)	−77(1)
C(1)—N(1)—Fe(1)—O(5)	58(1)	C(11)—N(11)—Fe(2)—O(15)	53(1)
N(1)---Fe(1)—O(5)—C(7)	−13(2)	N(11)—Fe(2)—O(15)—C(17)	−24(2)
Fe(1)—N(1)—C(9)—C(10)	33(2)	Fe(2)—N(11)—C(19)—C(20)	41(2)
N(1)—C(9)—C(10)—N(2)	−49(2)	N(11)—C(19)—C(20) N(12)	−55(2)
C(9)—C(10)—N(2)—Fe(1)	40(2)	C(19)—C(20)—N(12)—Fe(2)	42(1)
C(10)—N(2)—Fe(1)—N(1)	−17(1)	C(20)—N(12)—Fe(2)—N(11)	−16(1)
N(2)—Fe(1)---N(1)—C(9)	−9(1)	N(12)—Fe(2)—N(11)—C(19)	−13(1)
Fe(1)—N(2)—C(2)—C(6)	−79(2)	Fe(2)—N(12)—C(12)—C(16)	−75(1)
N(2)—C(2)—C(6)—C(8)	63(2)	N(12)—C(12)—C(16)—C(18)	67(2)
C(2)—C(6)—C(8)—O(6)	−16(3)	C(12)—C(16)—C(18)—O(16)	−34(2)
C(6)—C(8)—O(6)—Fe(1)	1(3)	C(16)—C(18)—O(16)—Fe(2)	24(2)
C(8)—O(6)—Fe(1)—N(2)	−17(2)	C(18)—O(16)—Fe(2)—N(12)	−30(1)
O(6)—Fe(1)—N(2)—C(2)	51(1)	O(16)—Fe(2)—N(12)—C(12)	50(1)
Fe(1)—N(1)—C(1)—C(3)	46(2)	Fe(2)—N(11)—C(11)—C(13)	41(1)
N(1)—C(1)—C(3)—O(1)	−33(2)	N(11)—C(11)—C(13)—O(11)	−20(2)
C(1)—C(3)—O(1)—Fe(1)	−1(2)	C(11)—C(13)—O(11)—Fe(2)	−15(2)
C(3)—O(1)—Fe(1)—N(1)	21(1)	C(13)—O(11)—Fe(2)—N(11)	31(1)
O(1)—Fe(1)—N(1)—C(1)	−37(1)	O(11)—Fe(2)—N(11)—C(11)	−39(1)

TABLE IV

(*Continued*)

Torsion angles, °

Fe(1)—N(2)—C(2)—C(4)	42(1)	Fe(2)—N(12)—C(12)—C(14)	42(1)
N(2)—C(2)—C(4)—O(2)	−21(2)	N(12)—C(12)—C(14)—O(12)	−15(2)
C(2)—C(4)—O(2)—Fe(1)	−15(2)	C(12)—C(14)—O(12)—Fe(2)	−22(2)
C(4)—O(2)—Fe(1)—N(2)	32(1)	C(14)—O(12)—Fe(2)—N(12)	37(1)
O(2)—Fe(1)—N(2)—C(2)	−40(1)	O(12)—Fe(2)—N(12)—C(12)	−42(1)
C(7)—C(5)—C(1)—C(3)	−85(2)	C(17)—C(15)—C(11)—C(13)	−58(2)
C(5)—C(1)—N(1)—C(9)	163(1)	C(15)—C(11)—N(11)—C(19)	165(2)
C(3)—C(1)—N(1)—C(9)	−73(2)	C(13)—C(11)—N(11)—C(19)	−77(2)
C(5)—C(1)—C(3)—O(1)	94(2)	C(15)—C(11)—C(13)—O(11)	99(2)
C(1)—N(1)—C(9)—C(10)	150(1)	C(11)—N(11)—C(19)—C(20)	156(2)
C(9)—C(10)—N(2)—C(2)	158(2)	C(19)—C(20)—N(12)—C(12)	159(1)
C(10)—N(2)—C(2)—C(6)	159(2)	C(20)—N(12)—C(12)—C(16)	166(1)
C(10)—N(2)—C(2)—C(4)	−80(2)	C(20)—N(12)—C(12)—C(14)	−77(2)
C(4)—C(2)—C(6)—C(8)	−57(2)	C(14)—C(12)—C(16)—C(18)	−49(2)
O(2)—C(4)—C(2)—C(6)	101(2)	O(12)—C(14)—C(12)—C(16)	105(2)

the analogous values 76·5 and 74·2° for $[\text{Fe}(H_2O)(\text{DCTA})]^-$ and $[\text{Fe}(H_2O) \cdot (\text{EDTA})]^-$ (ref.[12] and [13]), which can be explained by a change in the coordination number. The mean magnitude of the N—Fe—O$_R$ angle, 77·2°, is comparable with the values 75·7 and 79·9° for the *R*-ring but much larger than the values 71·8 and 70·8° for the *G*-ring in the given compounds[12,13]. The overall sum of the bonding angles in the *R*-rings in $[\text{Fe}(\text{EDDS})]^-$, 520·0, 520·2, 519·1 and 516·4° (mean 518·9°) is closer to the values[12,13] for the *G*-rings (518·2 and 524°) than for the *R*-rings (529·2 and 534°). The overall sum of the angles, which is a measure of the strain in the chelate rings, indicates that the *R*-ring in $[\text{Fe}(\text{EDDS})]^-$ is under considerable strain, differing from the character of strain in EDTA complexes.

The conformations of the individual chelate rings in the $[\text{Fe}((S,S)\text{-EDDS})]^-$ anions are the same as the conformations found in other EDDS complexes[5−7]: the *E* rings have asymmetric gauche conformation, the *R* rings have asymmetric envelope conformation with a C* atom (IUPAC-IUB nomenclature[15]) bent out of the plane of the other atoms and the *G* rings have the conformation of an asymmetric half-rotated boat, as is apparent from the torsion angles given in Table IV.

Comparison of the $[\text{Fe(III)}((S,S)\text{-EDDS})]^-$ and $[\text{Co(III)}((S,S)\text{-EDDS})]^-$ complexes[3] indicates that there is a relatively small difference between the mean values of the bonding and torsion angles of the ligand. There are, however, large differences in the rigidity of the whole complex units that can be characterized by the scatter

of the values of the pseudosymmetrically dependent torsion angles that are locally deformed most by the lattice forces in the crystal. In Co(III) complexes, the scatter lies in the interval $0-3°$ except for the $N-C^{\alpha}-C^{\beta}-C^{\gamma}$, $C^{\alpha}-C^{\beta}-C^{\gamma}-O$, $C^{\beta}-C^{\gamma}-$ $-O-M$ and $C^{\gamma}-O-M-N$ torsion angles, where the scatter attains values of 8, 14, 14 and 6°, respectively. In Fe(III) complexes, the scatter of the pseudosymmetric torsion angles is in the range $5-9°$ and the given torsion angles equal 29, 54, 48 and 17°, respectively. The differences between the average values of the torsion angles for Fe(III) and Co(III) are always less than the differences for the Fe(III) complexes. The large deformation of the torsion angles in the G-rings indicate a certain structural flexibility of this ring in octahedral complexes.

Ca^{2+} is coordinated by three oxygen atoms of the carboxyl groups and by four water molecules. Two basic types of polyhedra can exist in the hepta-coordinated complexes: pentagonal bipyramid (PB) and trigonal prism with an additional apex (MTP). The CaO_7 polyhedron in the crystal structure is very deformed and unambiguous assignment is not possible. If CaO_7 is idealized as MTP, then atoms $W(1)$, $W(3)$, $O(8)$ and $W(4)$ form a square base, molecule $W(2)$ corresponds to the additional apex and atoms $O(7)$ and $O(18)$ form the edge of the prism. MTP in the $Ca[Fe(DCTA)]_2.$ $.8 H_2O$ crystal structure[12] is known as the Hoard polyhedron. Comparison indicates

TABLE V

Interatomic distances less than 0.3 nm in the crystal structure of $Ca[(Fe(S,S)-EDDS)]_2.8 H_2O$

Atoms	Distance, nm	Atoms	Distance, nm
$N(1)\ldots O(14^{i})$	0·291(2)	$O(15)\ldots W(4^{v})$	0·290(2)
$N(2)\ldots O(11^{ii})$	0·299(2)	$O(17)\ldots W(6)$	0·266(3)
$O(3)\ldots W(3^{i})$	0·277(2)	$W(2)\ldots W(6)$	0·277(3)
$O(4)\ldots W(8)$	0·275(3)	$W(2)\ldots W(7)$	0·270(3)
$O(4)\ldots W(1^{iii})$	0·277(2)	$W(3)\ldots W(5)$	0·289(2)
$O(13)\ldots W(1^{iii})$	0·277(2)	$W(5)\ldots W(6^{vi})$	0·297(2)
$O(14)\ldots W(4^{iv})$	0·275(2)	$W(6)\ldots W(8)$	0·258(3)

Symmetric codes used

(i) $x-1,\ -y,\ z-1/2$
(ii) $x-1,\ y,\ z$
(iii) $x,\ 1-y,\ z-1/2$
(iv) $x+1,\ y-1,\ z$
(v) $x+1,\ y,\ z$
(vi) $x,\ y-1,\ z$
(vii) $x,\ -y,\ z+1/2$

that the greatest difference between the two polyhedra is in the $W(1)$—Ca—O(8) angle, which has a value of 148° in the studied structure and a value of 162° in the Hoard polyhedron. It has been found that PB is a somewhat better approximation to the CaO_7 polyhedron. The pentagonal base is then formed by the $W(1)$, $(W2)$, $O(8)$, $O(18)$, $O(7)$ atoms and the axial positions are occupied by the $W(3)$ and $W(4)$ atoms. The Ca—$W(3)$ and Ca—$W(4)$ bond lengths are shorter than those in the pentagonal base. The $W(3)$—Ca—$W(4)$ angle, 169°, deviates from the ideal value, 180°, by 11°. The angles in the pentagonal base vary in the interval $69 - 76°$ and are close to the value of 72° for an ideal pentagon.

In addition to ionic forces, the crystal structure is stabililized by the coordination bond of the Ca^{2+} ion with the $O(7)$ and $O(8)$ atoms, connecting the $[Fe(1)(EDDS)]^-$ anions in an infinite chain in the structure, in which the $[Fe(2)(EDDS)]^-$ anions are connected by a further Ca—O(18) coordination bond. Hydrogen bonds are formed between the oxygen atoms of the carboxyl groups and the protons of the imino groups and water molecules, as well as between water molecules. The system of hydrogen bonds can be derived from the data in Table V. Although all the hydrogen atoms could not localized, it was found that each water molecule forms two hydrogen bonds in which it acts as a proton donor (coordination activation). The shortest hydrogen bond, 258 pm, was found between the $W(6)$ and $W(8)$ molecules.

REFERENCES

1. Pavelčik F., Majer J.: Chem. Zvesti *32*, 37 (1978).
2. Neal J. A., Rose N. J.: Inorg. Chem. *7*, 2405 (1968).
3. Neal J. A., Rose N. J.: Inorg. Chem. *12*, 1226 (1973).
4. Radanovic D. J., Gailey K. D., Djuran M. I., Douglas B. F.: J. Coord. Chem. *10*, 115 (1980).
5. Pavelčik F., Majer J.: Acta Crystallogr. *B34*, 3582 (1978).
6. Pavelčik F., Kettmann V., Majer J.: This Journal *44*, 1070 (1979).
7. Soldánová J., Pavelčik F., Majer J.: Acta Crystallogr. *B37*, 921 (1981).
8. Porai-Koshits M. A.: *Proceedings of the* IVth *Conference on Coordination Chemistry*, p. 76. Smolenice 1973.
9. *International Tables for X-ray Crystallography*, Vol. IV. 1974. Birmingham. The Kynoch Press.
10. Ahmed F. R. in the book: *Crystallographic Computing* (F. R. Ahmed, Ed.), p. 55. Copenhagen, Munksgaard 1970).
11. Weakliem H. A., Hoard J. L.: J. Amer. Chem. Soc. *81*, 549 (1959).
12. Cohen G. H., Hoard J. L.: J. Amer. Chem. Soc. *88*, 3228 (1966).
13. Novozhilova N. V., Polynova T. N., Porai-Koshits M. A.: Zh. Struct. Khim. *16*, 865 (1975).
14. Nesterova J. M., Polynova T. N., Porai-Koshits M. A.: Koord. Khim. *1*, 966 (1975).
15. *IUPAC-IUB Commission on Biochemical Nomenclature*, Biochemistry 9, 3471 (1970).

Translated by M. Štulíková.