

CRYSTAL AND MOLECULAR STRUCTURE
OF DINICKEL(II) (S,S)-ETHYLENEDIAMINE-N,N'-DISUCCINATE
HEPTAHYDRATE

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$[\text{Ni}_2(\text{S,S})\text{-EDDS}]\cdot 7\text{H}_2\text{O}$ structure has been solved by the heavy atom method and by the least squares method at $R = 0.058$; the substance crystallizes in orthorhombic system and space symmetry group $P2_12_12_1$ with the lattice parameters $a = 0.9904$ (5), $b = 1.2477$ (8), $c = 1.6036$ (17) nm. The crystal structure is composed of the binuclear units $\text{Ni}_2(\text{H}_2\text{O})_5[(\text{S,S})\text{-EDDS}]$ and molecules of crystal water. The anion $[(\text{S,S})\text{-EDDS}]^{4-}$ coordinates to Ni(II) as a stereospecific hexadentate ligand, the six-membered β -alanine rings being situated in equatorial plane of the coordination polyhedron, the glycine rings being axial. Absolute configuration of the complex anion is (OC-6-13-A).

From the structural viewpoint relatively little attention has been given so far to complexes of ethylenediamine-N,N'-disuccinic acid, $\text{HOCOCH}_2\text{CH}(\text{COOH})\text{NHCH}_2\cdot\text{CH}_2\text{NHCH}(\text{COOH})\text{CH}_2\text{COOH} = \text{H}_4\text{EDDS}$, which, according to absolute configuration of the chiral carbon atoms of the aspartate units, can exist in three stereoisomeric forms. Crystal structures of cobalt(III) complexes of the respective optically active form and *meso* form are known¹⁻³.

Infrared and ¹H-NMR spectra⁴ and kinetic measurements⁵ of nickel(II) complex of $[(\text{S,S})\text{-EDDS}]^{4-}$ in solution show that at pH 6–7 the ligand is coordinated by all its six donor groups. At lower pH values IR spectra indicate that one carboxylic group is partially non-coordinated and protonated to give the hydrated form² $\text{Ni}[(\text{S,S})\text{-EDDS}(\text{H}_2\text{O})]^{2-}$.

In the case of metal complexes of the isomeric EDTA Porai-Koshic pointed out⁶ diversity of coordination and crystal structure at the stoichiometric ratio $M : \text{EDTA} = 2 : 1$ depending on nature of the metal atom. Nickel(II) forms an anionic hydrated complex $[\text{Ni}(\text{H}_2\text{O})\text{HEDTA}]^-$ with this ligand, HEDTA^{3-} acting as a pentadentate ligand with the sixth coordination position of the octahedral complex occupied by a water molecule⁷.

The aim of this work is to study crystallo-chemical properties of the nickel(II) complex with $[(\text{S,S})\text{-EDDS}]^{4-}$ having the ratio $\text{Ni} : (\text{S,S})\text{-EDDS} = 2 : 1$ and de-

termine absolute configuration of the complex anion $[\text{Ni}(\text{S,S})\text{-EDDS}]^{2-}$ which can be either (*OC-6-13-A*) or (*OC-6-33-C*)^{3,8}.

EXPERIMENTAL

Preparation of $[\text{Ni}_2(\text{S,S})\text{-EDDS}] \cdot 7 \text{H}_2\text{O}$

0.03 mol (*S,S*)- $\text{H}_4\text{EDDS} \cdot 5 \text{H}_2\text{O}$ (synthesized by modified⁴ procedure of ref.⁹) and 0.06 mol fresh $\text{Ni}(\text{OH})_2 \cdot x \text{H}_2\text{O}$ were mixed in 100 ml H_2O . Slow evaporation of the formed solution gave grey-blue crystals of octahedral habit. For $\text{C}_{10}\text{H}_{26}\text{N}_2\text{Ni}_2\text{O}_{15}$ calculated: 22.59% C, 4.94% H, 5.27% N, 22.09% Ni; found: 22.9% C, 4.7% H, 5.1% N, 21.94% Ni.

Crystallographical Data

Approximative dimensions of the unit cell and crystal symmetry were determined from the oscillation and the Weissenberg photographs. The lattice parameters were refined with the use of diffractometer $P2_1$ Syntex by the least squares method from 8 precisely centered reflections: $a = 0.9904$ (5), $b = 1.2477$ (8), $c = 1.6036$ (17) nm, $V = 1.9814$ nm³. Systematical extinction of the reflections of the type $h00$ for $h = 2n + 1$, $0k0$ for $k = 2n + 1$, and $00l$ for $l = 2n + 1$ indicated unambiguously the space group $P2_12_12_1$. Density of the crystals, $D_0 = 1.79$ gcm⁻³, was measured by the flotation method in bromoform-ethanol mixture. The calculated density for $Z = 4$ and m.wt. = 531.7 is $D_c = 1.78$ gcm⁻³. Linear absorption coefficient $\mu(\text{Mo}) = 10.1$ cm⁻¹.

Solution and Refinement Precising of Crystal Structure

The crystal used for the structural analysis had a shape of approximative octahedron with 0.15×0.15 mm² base and 0.25 mm height with well-developed faces of the type $\{101\}$ and $\{011\}$. The integral intensities were measured with the diffractometer Syntex $P2_1$ using graphite-mono-chromatized Mo $K\alpha$ ($\lambda = 0.071069$ nm) radiation and scan technique $2\theta - \theta$ within the interval $0 < 2\theta < 46^\circ$. The program controlling the intensity measurements determined automatically the scan speed within 4.88 to $29.3^\circ \text{min}^{-1}$ on the basis of preliminary two-second measurement of intensity. The scan interval was extended by 1.0° below and above the calculated positions $K\alpha_1$ and $K\alpha_2$, respectively, so that the peak splitting due to the presence of $K\alpha_1$ and $K\alpha_2$ radiation might be taken into account. The background was measured at each end of the scan for the half of the scan time of reflection. No significant fluctuations were observed in intensities of two standard reflections measured in an interval of 100 photographed reflections. From the whole of 1581 recorded reflections 936 with $I > 1.96\sigma(I)$ were considered to be observed. Intensities of all the reflections were corrected with respect to the Lorentz and polarization factors. No correction for absorption was carried out.

The three-dimensional Patterson synthesis calculated from all the observed reflections showed positions of the both nickel atoms. Positions of other non-hydrogen atoms were determined from successive Fourier syntheses of electron density phased with gradually increasing number of localized atoms. The position and isotropic temperature parameters of atoms were refined in two cycles by the least squares method using the full matrix and relative weights $w = 1$ for all reflections to $R = 0.094$, $E = \sum(|F_0| - |F_c|) / \sum|F_0|$. Further 6 cycles of anisotropic refinement in a 9×9 block-diagonal approximation and weight scheme $w = 1$ and $140/|F_0|$ for $|F_0| < 140$ and $|F_0| > 140$, respectively, gave the final value $R = 0.058$. The refinement and calculation of R factor did not involve the 37 observed reflections for which $|\Delta F|/|F_0| > 0.3$

(using all the reflections in calculation of R gave the value $R = 0.067$ and $R_w = 0.083$, $R_w = \sqrt{(\sum w|\Delta F|^2 / \sum w|F_0|^2)}$). In the both cases the functional $M = \sum w(|F_0| - |F_c|)^2$ was minimized. Distribution of values of the minimized function over the intervals $|F_0|$ and $\sin \theta/\lambda$ showed that the used weight scheme is satisfactory. For calculation of structural factors the known scattering curves¹⁰ were used. The maximum residual electron density in the difference synthesis was $800 \text{ e}^- \text{ nm}^{-3}$. The calculations were carried out with the XTL modul Syntex and computer Siemens 4004/150 using the published programs^{11,12}.

TABLE I

Coordinates ($\times 10^5 \text{ nm}$) of Atoms in Crystal Structure of $[\text{Ni}_2(\text{S,S})\text{-EDDS}]\cdot 7 \text{ H}_2\text{O}$ (the standard deviations are given in parentheses)

Atom	x/a	y/b	z/c
Ni(1)	1 348 (3)	— 459 (2)	5 642 (2)
Ni(2)	1 688 (3)	3 737 (2)	5 218 (2)
C (1)	2 492 (23)	— 2 318 (19)	6 464 (15)
C (2)	1 938 (21)	— 1 671 (16)	7 144 (13)
C (3)	2 523 (21)	— 2 244 (12)	4 906 (16)
C (4)	3 529 (17)	— 1 330 (16)	4 774 (13)
C (5)	1 600 (24)	— 2 243 (17)	4 100 (11)
C (6)	833 (21)	— 1 189 (22)	3 914 (13)
C (7)	894 (21)	178 (14)	7 344 (12)
C (8)	— 500 (23)	— 82 (15)	6 959 (11)
C (9)	1 254 (21)	1 397 (16)	7 209 (11)
C (10)	1 369 (23)	1 815 (15)	6 302 (13)
N (1)	1 752 (16)	— 2 100 (12)	5 711 (11)
N (2)	1 933 (18)	— 477 (14)	6 917 (9)
O (1)	567 (15)	— 527 (13)	4 447 (9)
O (2)	523 (19)	— 1 134 (15)	3 152 (8)
O (3)	1 367 (17)	1 161 (11)	5 664 (8)
O (4)	1 471 (19)	2 766 (10)	6 256 (10)
O (5)	3 289 (14)	— 450 (9)	5 133 (10)
O (6)	4 477 (14)	— 1 492 (10)	4 276 (9)
O (7)	— 544 (13)	— 460 (12)	6 224 (9)
O (8)	— 1 517 (18)	23 (16)	7 377 (9)
W(1)	3 778 (15)	3 744 (15)	5 455 (9)
W(2)	1 450 (16)	5 046 (11)	5 960 (8)
W(3)	1 866 (16)	4 853 (11)	4 257 (9)
W(4)	— 374 (14)	3 625 (12)	4 939 (9)
W(5)	1 977 (15)	2 445 (12)	4 417 (10)
W(6)	5 053 (17)	— 2 337 (16)	8 066 (10)
W(7)	5 748 (16)	— 469 (14)	7 318 (10)

The refined coordinates of the non-hydrogen atom and their standard deviations are given in Table I, the anisotropic coefficients of thermal vibrations are given in Table II, *W* denotes oxygen atom of water molecule in all the Tables. Values of bond lengths and bond angles are given in Table III. Fig. 1 shows numbering scheme of the atoms and the absolute configuration of the complex determined on the basis of the known absolute configuration of (*S*)-aspartic acid.

TABLE II

Anisotropic Temperature Coefficients ($\times 10^5$) in the Relation

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

The standard deviations are given in parentheses.

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Ni(1)	49 (3)	29 (1)	16 (1)	14 (5)	-14 (3)	6 (3)
Ni(2)	45 (2)	31 (2)	22 (1)	7 (5)	2 (4)	-4 (3)
C (1)	45 (26)	57 (19)	33 (13)	17 (40)	-56 (32)	19 (27)
C (2)	42 (25)	25 (14)	12 (9)	11 (31)	34 (27)	20 (17)
C (3)	75 (28)	0 (11)	49 (11)	32 (14)	-60 (28)	16 (22)
C (4)	18 (20)	31 (13)	29 (9)	-22 (34)	-51 (29)	0 (24)
C (5)	94 (30)	48 (16)	7 (8)	-85 (41)	-74 (28)	-41 (20)
C (6)	53 (25)	80 (20)	17 (10)	32 (44)	75 (28)	-5 (30)
C (7)	76 (28)	8 (15)	13 (9)	29 (31)	42 (26)	2 (19)
C (8)	90 (29)	23 (14)	4 (8)	-25 (36)	-54 (28)	9 (19)
C (9)	70 (26)	43 (16)	5 (8)	62 (40)	-25 (25)	66 (21)
C (10)	53 (27)	17 (13)	24 (11)	67 (34)	-33 (30)	12 (20)
N (1)	34 (19)	20 (11)	28 (8)	43 (25)	48 (26)	-4 (17)
N (2)	94 (24)	35 (12)	7 (6)	20 (35)	11 (22)	7 (18)
O (1)	77 (18)	69 (13)	18 (6)	48 (31)	-12 (19)	-42 (18)
O (2)	137 (25)	85 (15)	8 (6)	13 (38)	-4 (21)	-13 (20)
O (3)	152 (24)	27 (9)	14 (5)	66 (31)	20 (23)	-18 (16)
O (4)	141 (25)	8 (9)	39 (8)	-14 (30)	-1 (27)	8 (15)
O (5)	62 (16)	10 (8)	55 (8)	-20 (25)	58 (22)	-28 (17)
O (6)	56 (17)	22 (10)	30 (8)	-12 (22)	7 (21)	5 (16)
O (7)	25 (15)	52 (11)	29 (7)	34 (27)	-32 (17)	3 (19)
O (8)	97 (22)	136 (19)	20 (7)	-5 (36)	75 (24)	-17 (20)
W(1)	63 (18)	97 (15)	33 (8)	3 (34)	2 (21)	5 (21)
W(2)	80 (20)	42 (10)	21 (7)	18 (26)	-37 (21)	-16 (14)
W(3)	92 (20)	36 (11)	21 (7)	-36 (24)	16 (22)	-3 (15)
W(4)	49 (16)	63 (12)	28 (8)	-25 (28)	4 (18)	7 (19)
W(5)	73 (19)	47 (11)	33 (7)	10 (25)	40 (22)	-26 (17)
W(6)	81 (23)	131 (20)	22 (8)	-52 (38)	-42 (23)	-50 (22)
W(7)	83 (20)	76 (14)	38 (8)	50 (35)	34 (23)	7 (22)

TABLE III

Interatomic Distances and Angles in Complex
 $\{\text{Ni}(\text{H}_2\text{O})_5[\text{Ni}(\text{S,S})\text{-EDDS}]\}$ with Standard Deviations in Parentheses.

Interatomic distances, nm

Ni(1)—N (1)	2.09 (1)	N (1) — C (3)	1.51 (3)
Ni(1)—N (2)	2.12 (2)	C (3) — C (4)	1.53 (3)
Ni(1)—O (5)	2.09 (1)	C (4) — O (5)	1.26 (2)
Ni(1)—O (7)	2.09 (1)	C (4) — O (6)	1.25 (2)
Ni(1)—O (1)	2.07 (1)	N (2) — C (7)	1.48 (2)
Ni(1)—O (3)	2.02 (1)	C (7) — C (8)	1.55 (3)
Ni(2)—O (4)	2.07 (1)	C (8) — O (7)	1.27 (2)
Ni(2)—W(1)	2.10 (1)	C (8) — O (8)	1.22 (3)
Ni(2)—W(2)	2.03 (1)	O (1) — C (6)	1.22 (3)
Ni(2)—W(3)	2.08 (1)	C (6) — C (5)	1.55 (3)
Ni(2)—W(4)	2.09 (1)	C (5) — C (3)	1.58 (3)
Ni(2)—W(5)	2.08 (1)	C (6) — O (2)	1.26 (2)
N (1)—C (1)	1.45 (3)	O (3) — C (10)	1.31 (2)
N (2)—C (2)	1.47 (3)	C (10)—C (9)	1.55 (3)
C (1)—C (2)	1.53 (3)	C (9) — C (7)	1.58 (3)
		C (10)—O (4)	1.19 (2)

Bond angles, °

N (1)—Ni(1)—N (2)	83.5 (6)	N (1)—C (1) — C (2)	109 (2)
N (1)—Ni(1)—O (5)	81.4 (6)	N (2)—C (2) — C (1)	111 (2)
N (2)—Ni(1)—O (7)	79.4 (6)	N (1)—C (3) — C (5)	114 (1)
N (1)—Ni(1)—O (1)	94.6 (6)	C (3)—C (5) — C (6)	116 (2)
N (2)—Ni(1)—O (3)	89.5 (6)	C (5)—C (6) — O (1)	123 (2)
O (1)—Ni(1)—O (3)	93.5 (6)	Ni(1)—O (1) — C (6)	127 (1)
N (2)—Ni(1)—O (5)	97.2 (6)	O (1)—C (6) — O (2)	126 (2)
O (1)—Ni(1)—O (5)	89.0 (6)	N (2)—C (7) — C (9)	108 (1)
O (3)—Ni(1)—O (5)	89.6 (6)	C (9)—C (10)—O (3)	122 (2)
N (1)—Ni(1)—O (7)	98.5 (6)	C (9)—C (10)—O (4)	114 (2)
O (1)—Ni(1)—O (7)	94.5 (6)	N (1)—C (3) — C (4)	111 (1)
O (3)—Ni(1)—O (7)	90.0 (6)	Ni(1)—O (5) — C (4)	110 (1)
O (4)—Ni(2)—W(1)	87.7 (6)	O (5)—C (4) — O (6)	125 (2)
O (4)—Ni(2)—W(5)	93.3 (6)	Ni(1)—O (7) — C (8)	112 (1)
O (4)—Ni(2)—W(2)	89.3 (6)	C (7)—C (8) — O (8)	120 (2)
O (4)—Ni(2)—W(4)	91.8 (6)	C (2)—N (2) — C (7)	115 (1)
W(1)—Ni(2)—W(2)	90.3 (6)	C (4)—C (3) — C (5)	105 (1)
W(1)—Ni(2)—W(3)	92.6 (6)	C (5)—C (6) — O (2)	111 (2)
W(1)—Ni(2)—W(5)	88.9 (6)	C (7)—C (9) — C (10)	118 (1)
W(2)—Ni(2)—W(3)	84.6 (6)	Ni(1)—O (3) — C (10)	130 (1)
W(2)—Ni(2)—W(4)	93.8 (6)	O (3)—C (10)—O (4)	125 (2)

TABLE III

(Continued)

W(3)–Ni(2)–W(4)	88.3 (6)	C (3)–C (4) –O (5)	118 (2)
W(3)–Ni(2)–W(5)	92.8 (6)	C (3)–C (4) –O (6)	117 (2)
W(4)–Ni(2)–W(5)	87.6 (6)	N (2)–C (7) –C (8)	109 (1)
Ni(1)–N (1)–C (1)	109 (1)	C (7)–C (8) –O (7)	119 (2)
Ni(1)–N (1)–C (3)	100 (1)	O (7)–C (8) –O (8)	121 (2)
Ni(1)–N (2)–C (2)	104 (1)	C (1)–N (1) –C (3)	115 (2)
Ni(1)–N (2)–C (7)	104 (1)	C (8)–C (7) –C (9)	110 (1)

RESULTS AND DISCUSSION

The crystal structure of $[\text{Ni}_2(\text{S,S})\text{-EDDS}]\cdot 7\text{H}_2\text{O}$ consists of the complex anions $[\text{Ni}(\text{S,S})\text{-EDDS}]^{2-}$ (*Ia*) and pentahydrated cations $[\text{Ni}(\text{H}_2\text{O})_5]^{2+}$ (*Ib*) mutually connected by acetate group of six-membered chelate ring to form a discrete binuclear unit (Fig. 1) and crystal water molecules. Such structural type has not yet been observed, not even with metal complexes involving the isomeric ligand EDTA and having the stoichiometric ratio $\text{M} : \text{EDTA} = 2 : 1$ (ref.⁶).

The coordination polyhedrons of the both Ni atoms are distorted octahedrons. In the anionic part (*Ia*) of the complex the six-membered chelate rings (*G* – rings) are situated in the equatorial plane, *i.e.* the plane defined by Ni and two N atoms.

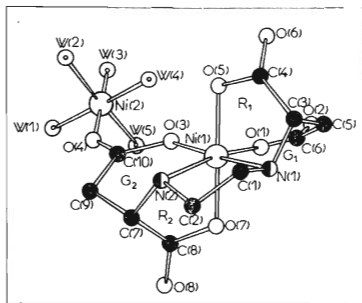


FIG. 1

Crystal Structure of $[\text{Ni}_2(\text{S,S})\text{-EDDS}]\cdot 7\text{H}_2\text{O}$

Oxygen atoms of the carboxylic groups of the five-membered chelate ring (R - rings) occupy axial positions of the coordination octahedron ($trans$ - O_5 coordination^{3,4}). $[(S,S)\text{-EDDS}]^{4-}$ acts as a stereospecific ligand in coordination with Ni(II) and gives the complex with absolute configuration⁸ (OC -6-13- A). This configuration is probably preferred due to energetically more advantageous arrangement of the system 6-5-6 chelate rings in the equatorial plane as compared with the system 5-5-5, the reason being lower distortion of bond angles. The analogous complex anion $[\text{Ni}(\text{HEDTA})(\text{H}_2\text{O})]^-$ (II) present⁷ in the crystal structure of $\text{Ni}_3(\text{HEDTA})_3 \cdot 10 \text{H}_2\text{O}$ undergoes (due to the abovementioned strain) opening of one chelate ring, the liberated coordination place being occupied by a water molecule. Comparison of the structures Ia and II shows that the greatest differences in coordination angles can be observed in the equatorial plane - the angles $\text{N}-\text{Ni}-\text{O}_G$ are 94.6 and 76° in Ia and II , respectively, the angles $\text{O}_G-\text{Ni}-\text{O}_G$ are 93.5 and 100° in Ia and II , respectively (one atom O_G from H_2O molecule). Smaller distortion of the octahedral geometry in Ia as compared with II follows from the fact that the six-membered rings formed by $(S,S)\text{-EDDS}^{4-}$ locate the oxygen atoms in equatorial plane considerably closer to the corners of ideal square than the five-membered rings EDTA do.

The distances $\text{Ni}-\text{O}_R$ in the both five-membered rings and the $\text{Ni}-\text{O}_G$ bond in G_1 ring are equivalent (average length 0.209 nm) and fall within the interval which is usually observed in octahedral complexes of Ni(II) (0.205 to 0.210 nm). The second $\text{Ni}-\text{O}_G$ bond (in the G_2 ring), in which the donor oxygen atom comes from that acetate group whose carbonyl oxygen atom complements the sixth octahedral position of the penta-coordinated nickel atom in the cationic part Ib of the complex, is significantly shorter (by 0.007 nm).

The ethylenediamine ring has usual symmetrical gauche conformation (deviations of the carbon atoms from the $\text{N}-\text{Ni}-\text{N}$ plane are -0.033 and $+0.035$ nm for $C(1)$ and $C(2)$, respectively).

The mutually corresponding interatomic distances in the both glycine and β -alanine rings are practically the same with average values $\text{N}-\text{C}$ 0.149 and $\text{C}-\text{C}$ 0.156 nm. A difference can be only observed in the bond lengths $\text{C}-\text{O}_c$ and $\text{C}-\text{O}_u$ (where O_c and O_u are the coordinated and uncoordinated oxygen atoms of the carboxylate group, respectively, the coordination concerning the Ni atom in the anionic part of the complex) in different rings. The rings exhibiting approximately the same length of the coordination bond $\text{Ni}-\text{O}_c$ (the both R rings and the G_1 ring) have the distances $\text{C}-\text{O}_c$ and $\text{C}-\text{O}_u$ balanced, too. A significant difference in the lengths of these bonds is in the group COO^- from the β -alanine G_2 ring in which the oxygen atom O_c is coordinated at the shortest distance to the Ni atom of the anionic part of the complex. Although the equivalence of the bonds $\text{C}-\text{O}_c$ and $\text{C}-\text{O}_u$ is characterized for the dissociated carboxylic group COO^- , it is likely that the three bonds $\text{Ni}-\text{O}$

of approximately the same length have a considerable ionic contribution, whereas Ni—O(3) is predominantly covalent.

Comparison of stereochemistry of the complex ions $[\text{Ni}(\text{S,S})\text{-EDDS}]^{2-}$ and $[\text{Co}(\text{S,S})\text{-EDDS}]^-$ (refs^{3,13}) reveals a larger ionic radius and lower degree of covalence of the coordination bonds of Ni(II) as compared with those of Co(III). This difference will make itself felt in greater distortion of the coordination polyhedron

TABLE IV

Deviations (nm) of Atoms of Individual Chelate Rings from the Planes Defined by Ni Atom and Two Donor Atoms of the Chelate Ring

<i>E</i> :	C(1)	-0.33	C(2)	0.35		
<i>R</i> ₁ :	C(3)	0.89	C(4)	0.57		
<i>R</i> ₂ :	C(7)	0.82	C(8)	0.49		
<i>G</i> ₁ :	C(3)	1.15	C(5)	0.80,	C(6)	0.43
<i>G</i> ₂ :	C(7)	1.18	C(9)	0.80,	C(10)	0.29

TABLE V

Intermolecular Interactions below 0.3 nm in Crystal Structure $[\text{Ni}_2(\text{S,S})\text{-EDDS}] \cdot 7 \text{H}_2\text{O}$

Atoms	Distance nm	Atoms	Distance nm
N(1)—O(6 ⁱ)	2.85	W(4)—O(5 ⁱⁱⁱ)	2.63
W(1)—O(1 ⁱⁱ)	2.85	W(5)—W(6 ^{iv})	2.96
W(1)—W(6 ^v)	2.96	O(2)—W(6 ⁱ)	2.77
W(2)—O(6 ⁱⁱⁱ)	2.68	O(2)—W(7 ^{iv})	2.71
W(3)—O(7 ⁱⁱ)	2.77	O(8)—W(7)	2.78
W(3)—W(7 ⁱⁱ)	2.86	O(3)—W(5)	2.63 ^a

The used symmetrical codes

(i)	$-1/2 + x,$	$-1/2 - y,$	$1 - z$
(ii)	$1/2 + x,$	$1/2 - y,$	$1 - z$
(iii)	$-1/2 + x,$	$1/2 - y,$	$1 - z$
(iv)	$1/2 - x,$	$-y,$	$-1/2 + z$
(v)	$1 - x,$	$1/2 + y,$	$3/2 - z$

^a Intramolecular hydrogen bond.

and greater strain of the Ni(II) complex. The angles N—M—N are 83.5 and 89.0° the angles O_G —M— O_G are 93.5 and 86.5° for the Ni(II) and Co(III) complexes, respectively. Average values of C_G —N— C_E angles between the *E* and *G* rings are 115.5 and 112.3° for the Ni(II) and Co(III) complexes, respectively. In $[\text{Ni}_2(\text{S,S})\text{-EDDS}]^{2-}$ there are greater differences between the angles related to the pseudo-twofold axis than those in the Co(III) complex. This fact is due to different coordination of carboxylic groups in *G* rings and less symmetrical lattice forces in the crystal $[\text{Ni}_2(\text{S,S})\text{-EDDS}]\cdot 7\text{H}_2\text{O}$.

Table IV gives deviations of atoms of the individual chelate rings from the planes crossing the central atom and the donor atoms of the chelate ring. From the data it is obvious that the chelate rings are non-planar. The *R* rings have asymmetrical envelope conformation, the *G* rings have asymmetrical twist-boat conformation.

The binuclear unit is stabilized, besides the coordination bond Ni(2)—O(4), by significant intramolecular hydrogen bond O(3)...H—W(5), the distance between the oxygen atoms being 0.263 nm. The whole crystal structure is held together by ionic forces and a system of hydrogen bonds involving the oxygen atoms of the carboxylic groups and the hydrogen atoms of the coordinated and crystal water molecules. Table V gives a survey of the potential hydrogen bonds. In contrast to the crystal structures of Co(III) complexes with ED DS (refs^{2,3}) in which the hydrogen bonds N—H...O are very significant, the crystal structure $[\text{Ni}_2(\text{S,S})\text{-EDDS}]\cdot 7\text{H}_2\text{O}$ contains only one bond of the mentioned type. The crystal water molecules W(6) and W(7) are important for stabilization of the structure, since each of them forms three hydrogen bonds.

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