

Crystal Structures of 3-Phenylpropenal Thiosemicarbazone and Its Nickel and Zinc Chelates

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Abstract—3-Phenylpropenal thiosemicarbazone hydrate $C_6H_5-CH=CH-CH=N-NH-C(S)-NH_2 \cdot H_2O$ (**I** · H_2O , **I**) and two chelates $[Ni(L)_2] \cdot nCH_3OH$ (**II**) and $[Zn(L)_2]$ (**III**) are studied by X-ray diffraction. The crystals of **I** are orthorhombic: $a = 6.227(1)$ Å, $b = 7.763(2)$ Å, $c = 25.585(5)$ Å, $\beta = 90^\circ$, space group $P2_12_12_1$, $Z = 4$, $R = 0.0426$. A nonplanar molecule of **I** has an *E* conformation. The crystals of **II** are triclinic: $a = 6.551(2)$ Å, $b = 10.752(3)$ Å, $c = 10.885(3)$ Å, $\alpha = 64.751(5)^\circ$, $\beta = 82.753(5)^\circ$, $\gamma = 89.857(5)^\circ$, space group $P\bar{1}$, $Z = 1$, $R = 0.0661$. In a centrosymmetric molecule of **II**, the central atom coordinates two deprotonated ligands L through the imine nitrogen atom and thioamide sulfur atom at the vertices of a distorted square. The crystals of **III** are monoclinic: $a = 25.342(2)$ Å, $b = 9.150(2)$ Å, $c = 21.340(3)$ Å, $\alpha = 90^\circ$, $\beta = 111.84(2)^\circ$, $\gamma = 90^\circ$, space group $C2/c$, $Z = 8$, $R = 0.0556$. In a molecule of complex **III**, two deprotonated bidentate ligands L are coordinated by the zinc ion through the imine nitrogen atoms and thioamide sulfur atoms to form a distorted tetrahedron at the central atom. In both **II** and **III**, ligand L after coordination by the metal ion changes the *E* conformation with respect to the N(1)–C(2) bond for the *Z* conformation. In crystals **I–III**, molecules are packed to form infinite layers parallel to the planes (001) and (010).

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INTRODUCTION

Thiosemicarbazones are convenient starting substances for syntheses of coordination compounds. They make it possible to diversify the composition and geometry of the coordination sphere. A change in the composition of the aldehyde or ketone fragment in the thiocarbazide ligand substantially affects the physicochemical and biological properties of the corresponding coordination compounds of *d* elements. Transition metal complexes with thiosemicarbazones are thoroughly studied. However, since mainly aromatic aldehydes or ketones are used as the starting substances in their syntheses, it was of interest to establish the influence of the replacement of these ingredients by an aldehyde containing an unsaturated radical on the structure and properties of the complexes. Therefore, we synthesized 3-phenylpropenal thiosemicarbazone hydrate $C_6H_5-CH=CH-CH=N-NH-C(S)-NH_2 \cdot H_2O$ (**I** · H_2O , **I**) bis(4-methanol-phenylpropenalidene-thiosemicarbazido)nickel solvate $[Ni(L)_2] \cdot CH_3OH$ (**II**), and bis(4-phenylpropenalidene-thiosemicarbazido)zinc $[Zn(L)_2]$ (**III**) and determined their crystal structures by X-ray diffraction analysis.

EXPERIMENTAL

Synthesis of I. Azomethine was synthesized by the reaction of a hot (55–60°C) alcohol solution containing 3-phenylpropenal (10 mmol) in methanol (15 ml) with a solution containing thiosemicarbazide (10 mmol) in CH_3OH (35 ml). On cooling the reaction mixture, a light yellow precipitate was formed. It was filtered off on a glass filter, washed with a small amount of alcohol, and dried in air (65% yield). Thiosemicarbazone **I** is well soluble in dimethylformamide, dimethyl sulfoxide, and (on heating) alcohols.

For $C_{10}H_{13}N_3OS$

anal. calcd. (%): C, 58.40; H, 5.30; N, 19.09; S, 14.18.

Found (%): C, 58.81; H, 5.83; N, 18.83; S, 14.35.

Synthesis of II. A solution containing thiosemicarbazone **I** (20 mmol) in alcohol (30 ml) was added to a methanol solution containing nickel diacetate tetrahydrate (10 mmol) in alcohol (20 ml) on continuous stirring with a magnetic stirrer and heating (45–50°C). Then, the reaction mixture was heated with a reflux condenser for 25–30 min. On cooling, dark brown crystals precipitated from the resulting solution. The crystals were filtered off on a glass filter, washed with small

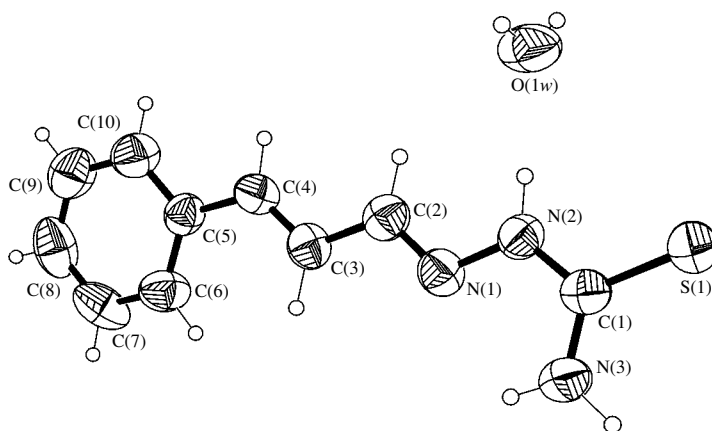


Fig. 1. Structure of molecule **I**.

amounts of alcohol and ether, and dried in air. Complex **II** is well soluble in dimethylformamide and dimethyl sulfoxide, weakly soluble in water and alcohols, and virtually insoluble in ether.

For $C_{21}H_{24}N_6NiOS_2$

anal. calcd. C, 50.50; H, 4.81; N, 16.83; Ni, 11.82; S, 12.83. (%)

Found (%): C, 50.39; H, 4.59; N, 16.75; Ni, 11.71; S, 12.70.

Synthesis of III. The complex was synthesized using a procedure similar to that described above, from zinc diacetate dihydrate and thiosemicarbazone **I** taken in a molar ratio of 1 : 2.

For $C_{20}H_{20}N_6S_2Zn$

anal. calcd. (%): C, 50.74; H, 4.23; N, 17.76; S, 13.53; Zn, 13.74.

Found (%): C, 50.62; H, 4.16; N, 17.54; S, 13.40; Zn, 13.60.

Single crystals of compounds **I–III** appropriate for X-ray diffraction analysis were prepared by the recrystallization of substances under study from a methanol solution.

X-ray diffraction analysis. The X-ray diffraction studies of compounds **I–III** were carried out on Philips PW1100 and Bruker Smart diffractometers with a CCD detector (MoK_{α} radiation, $\lambda = 0.71073 \text{ \AA}$). Absorption correction was applied for **II** and **III** using the SHELXTL-NT V. 5.1 programs [1]. The structures of compounds **I–III** were solved by the direct methods and refined by the least-squares method using the SHELX97 programs [2] in the anisotropic approximation for non-hydrogen atoms and in the isotropic approximation for hydrogen atoms. The positions of the latter were calculated geometrically. The main experimental parameters are presented in Table 1. The selected interatomic distances and bond angles are given in Table 2. The coordinates of basic atoms of the studied structures were deposited at the Cambridge Structure Database (CCDC 262822–262824). The geometric calculations were performed and figures were

plotted using the PLATON program [3]. The data from the Cambridge Structure Database (V. 5.25) were used for analysis of the obtained structures [4, 5].

RESULTS AND DISCUSSION

Azomethine molecule **I** (Fig. 1) is nonplanar, and the dihedral angle between the planes of the thiosemicarbazone chain (A) and phenyl ring is equal to 10.0° . Chain A in **I** has an *E* conformation relative to the C(1)–N(2) and N(1)–C(2) bonds. Dimeric layers parallel to the (001) plane are formed in crystal **I** due to hydrogen bonds (1–5, Fig. 2) that involve a molecule of water of crystallization. Thiosemicarbazone **I** contains an intramolecular hydrogen bond N(3)–H...N(1) (Table 3). The sulfur atom is involved in three hydrogen bonds, which results, most likely, in a considerable elongation of the S(1)–C(1) distance (to $1.754(4) \text{ \AA}$) as compared to the standard length of the S=C double bond. In similar compound 1-(4-*p*-tolyl-but-3-en-2-ylidene)thiosemicarbazide (**IV**) [6], this bond is shortened by 0.073 \AA as compared to that in **I**. The N(1)–N(2) ($1.431(4) \text{ \AA}$), C(2)–C(3) ($1.489(5) \text{ \AA}$), and C(4)–C(5) (1.513 \AA) bonds in **I** are shorter than those in **IV** (by 0.044 , 0.031 , and 0.045 \AA , respectively).

The structure of compound **II** is based on a tetracoordinated centrosymmetric monomeric complex $[Ni(L)_2]$ (Fig. 3). The central atom coordinates two deprotonated ligands L through the imine nitrogen atom N(1) and thioamide sulfur atom S(1) at the vertices of a distorted square. The N(1)Ni(1)S(1) angle is equal to $85.8(1)^\circ$. The Ni(1)–S(1) ($2.171(1) \text{ \AA}$) and Ni(1)–N(1) ($1.892(4) \text{ \AA}$) distances in **II** agree with those in square complexes of nickel(II) thiosemicarbazones (Ni–S 2.09 – 2.18 \AA and Ni–N 1.84 – 1.93 \AA) [7]. These bond lengths differ from the corresponding values in the octahedral nickel(II) thiosemicarbazone complexes (Ni–S 2.31 – 2.43 \AA and Ni–N 1.98 – 2.18 \AA) [7].

During coordination by the metal atom, ligand L in structure **II** changes the *E* conformation with respect to the N(1)–C(2) bond for the *Z* conformation. The S(1)–

Table 1. Crystallographic data and experimental details for structures **I–III**

Parameter	Value		
	I	II	III
<i>M</i>	223.29	531.33	473.95
Experimental temperature, K	293(2)	120(1)	293(2)
Crystal system	Orthorhombic	Triclinic	Monoclinic
Space group	<i>P</i> 2 ₁ 2 ₁ 2 ₁	<i>P</i> $\bar{1}$	<i>C</i> 2/ $\bar{1}$
Unit cell parameters			
<i>a</i> , Å	6.227(1)	6.551(2)	25.342(2)
<i>b</i> , Å	7.763(2)	10.752(3)	9.150(2)
<i>c</i> , Å	25.585(5)	10.885(3)	21.340(3)
α , deg	90	64.751(5)	90
β , deg	90	82.753(5)	111.84(2)
γ , deg	90	89.857(5)	90
<i>V</i> , Å ³	1236.8(4)	686.8(3)	4593.1(1)
<i>Z</i>	4	1	8
ρ (calcd), g/cm ³	1.199	1.285	1.371
μ_{aO} , mm ⁻¹	0.241	0.886	1.269
Crystal sizes, mm	0.4 × 0.2 × 0.2	0.2 × 0.1 × 0.05	0.5 × 0.3 × 0.1
θ range, deg	3.1–26.9	2.1–27.0	1.7–28.5
Number of measured reflections	1510		19185
Number of independent reflections	1510	2942 ($R_{\text{int}} = 0.0505$)	5127 ($R_{\text{int}} = 0.1017$)
Number of refined parameters	137	152	238
GOOF against F^2	0.81	0.980	0.856
Final <i>R</i> factor ($I > 2\sigma(I)$)	$R_1 = 0.0426$, $wR_2 = 0.0505$	$R_1 = 0.0661$, $wR_2 = 0.1309$	$R_1 = 0.0556$, $wR_2 = 0.1049$
<i>R</i> factor (over the whole array)	$R_1 = 0.066$, $wR_2 = 0.0649$	$R_1 = 0.1116$, $wR_2 = 0.1444$	$R_1 = 0.3227$, $wR_2 = 0.1621$
$\Delta\rho_{(\text{max})}$ and $\Delta\rho_{(\text{min})}$, e Å ⁻³	0.160 and –0.138	0.942 and –0.839	0.441 and –0.344

C(1) bond (1.739(5) Å) is shorter than 1.82 Å for the standard ordinary bond and longer than 1.56 Å for the S=C double bond [8], and coincides in length within 3σ with the C–S bond in free thiosemicarbazone of cinnaric aldehyde. The plane of the chelating fragment S(1)C(1)N(1)N(2) in **II** is unfolded relative to the planes of the C(2)C(3)C(4) chain and phenyl ring by 16.8° and 27.5°, respectively.

Dimeric layers parallel to the (001) plane are formed in crystal **II** due to hydrogen bonds 7–9 involving a methanol molecule of crystallization (Fig. 4). Crystal **II** also contains an intramolecular hydrogen bond C(2)–H(9A)⋯S(1) (Table 3), which closes the second five-membered metallocycle.

In compound **III**, two deprotonated bidentate ligands L are coordinated by the zinc ion through the

Table 2. Selected interatomic distances and bond angles for compounds **I–III**

Bond	I	II, M = Ni	III, M = Zn*	
			ligand 1	ligand 2
	<i>d</i> , Å			
Me–S(1)		2.171(1)	2.271(2)	2.259(2)
Me–N(1)		1.892(4)	2.047(5)	2.069(6)
S(1)–C(1)	1.754(4)	1.739(5)	1.784(7)	1.779(8)
N(3)–C(1)	1.332(5)	1.324(6)	1.363(7)	1.347(7)
N(2)–C(1)	1.356(4)	1.318(6)	1.272(7)	1.283(8)
N(2)–N(1)	1.431(4)	1.402(6)	1.362(6)	1.373(7)
N(1)–C(2)	1.289(6)	1.303(7)	1.281(7)	1.274(8)
C(2)–C(3)	1.489(5)	1.436(8)	1.424(8)	1.444(9)
C(3)–C(4)	1.343(5)	1.334(8)	1.329(8)	1.331(8)
C(4)–C(5)	1.513(5)	1.468(9)	1.464(7)	1.445(8)
O(1S)–C(1S)		1.473(12)		
	ω , deg			
N(11)MN(12)		180	114.7(2)	
N(11)MS(12)		94.2(1)	120.2(2)	
N(12)MS(12)		85.8(1)	87.3(2)	
N(11)MS(11)		85.8(1)	87.2(2)	
N(12)MS(11)		94.2(1)	119.5(2)	
S(12)MS(11)		180	130.67(9)	
C(2)N(1)M		126.4(3)	127.2(4)	127.7(5)
N(2)N(1)M		121.3(3)	116.9(5)	115.9(5)
C(1)S(1)M		96.20(16)	91.5(3)	92.4(3)
C(2)N(1)N(2)	116.1(3)	112.3(4)	115.9(6)	116.3(6)
C(1)N(2)N(1)	120.5(3)	111.8(4)	115.9(6)	116.2(6)
N(2)C(1)N(3)	115.0(3)	118.2(5)	119.4(6)	117.9(7)
N(2)C(1)S(1)	120.9(3)	122.2(4)	128.5(5)	128.0(6)
N(3)C(1)S(1)	124.1(3)	119.6(4)	112.2(6)	114.1(7)
N(1)C(2)C(3)	120.9(4)	126.8(5)	125.2(7)	126.3(7)
C(4)C(3)C(2)	122.5(4)	121.7(5)	123.2(7)	121.6(8)
C(3)C(4)C(5)	128.0(4)	126.3(6)	128.0(6)	128.8(8)
C(6)C(5)C(4)	120.3(4)	122.2(7)	118.5(6)	118.0(8)
C(10)C(5)C(4)	123.9(4)	119.1(6)	121.4(6)	122.0(8)

* Numbering of atoms for structure **III**: 1*n*–5*n* (*n* = 1, 2).

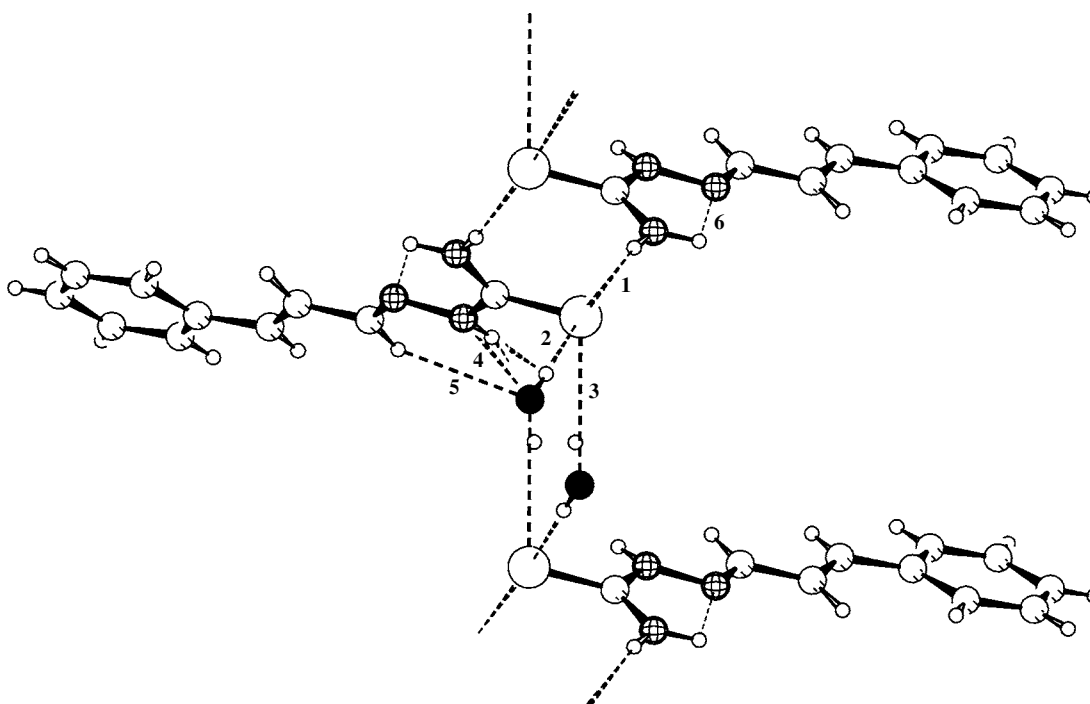


Fig. 2. Fragment of structural unit packing in crystal **I** (H bond nos. 1–6).

iminne nitrogen atoms and thioamide sulfur atoms at the vertices of the distorted tetrahedron (Fig. 5). The dihedral angle between the planes of the chelate cycles is equal to 87.9° . The NZnN angles range from

$87.2(2)^\circ$ to $120.2(2)^\circ$, and the S(12)Zn(1)S(11) and N(11)Zn(1)N(12) angles are $130.67(9)^\circ$ and $114.7(2)^\circ$, respectively. The Zn–S (2.271(2), 2.259(2) Å) and Zn–N (2.047(5), 2.069(6) Å) distances in **III** agree with

Table 3. Geometric parameters of hydrogen bonds for compounds **I–III**

H bond no.	Bond D–H...A	Distance, Å			Angle DHA, deg	Coordinates of atom A
		D...A	H...A	D–H		
I						
1	N(1)–H(4)...S(1)	3.483(4)	2.54	0.96	167	$1/2 + x, 3/2 - y, -z$
2	O(1w)–H(11)...S(1)	3.326(3)	2.53	0.82	167	$-1 + x, y, z$
3	O(1w)–H(17)...S(1)	3.289(3)	2.47	0.84	168	$-1/2 + x, 1/2 - y, -z$
4	N(2)–H(14)...O(1w)	2.850(4)	1.95	0.93	163	x, y, z
5	C(2)–H(5)...O(1w)	3.511(5)	2.73	0.98	137	x, y, z
6	N(1)–H(13)...N(3)	2.644(5)	2.24	0.94	105	x, y, z
II						
7	O(1S)–H(10)...N(2)	2.755(5)	1.93	0.85	165	x, y, z
8	N(3)–H(3A)...O(1S)	2.911(6)	2.04	0.88	173	$2 - x, -y, -1 - z$
9	N(3)–H(3B)...O(1S)	2.929(5)	2.09	0.88	160	x, y, z
10	C(2)–H(9A)...S(1)	3.071(6)	2.47	0.95	121	$2 - x, -y, -z$
III						
11	N(31)–H(13A)...N(21)	3.033(8)	2.19	0.86	167	$1/2 - x, -1/2 - y, 1 - z$
12	N(32)–H(23A)...N(22)	3.013(1)	2.17	0.86	167	$-x, 1 - y, 1 - z$

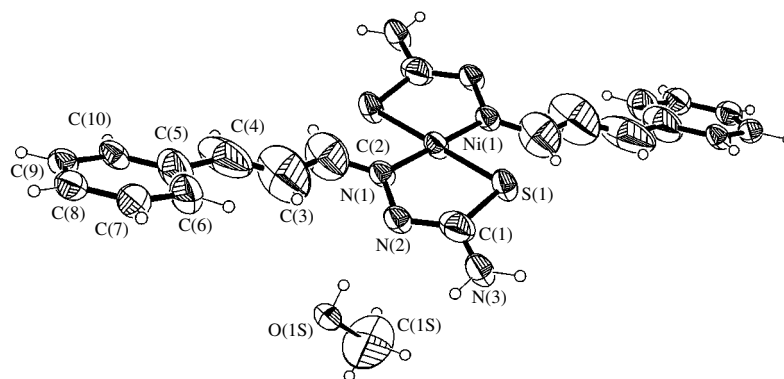


Fig. 3. Structure of compound **II**.

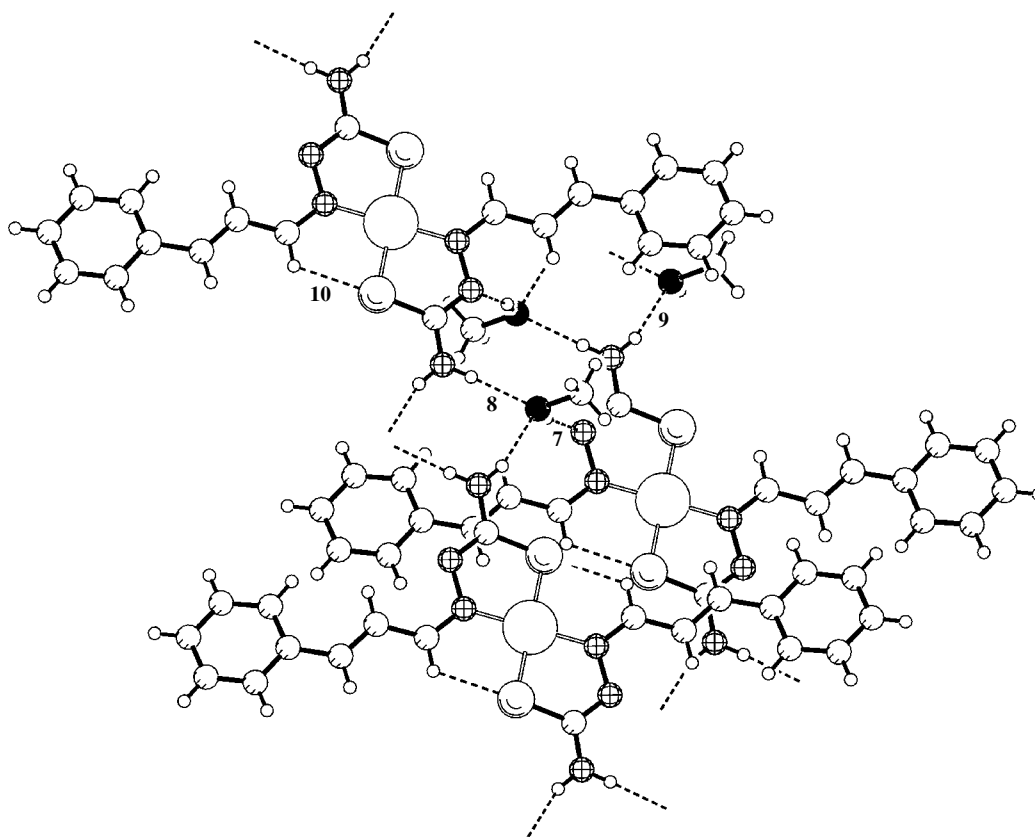


Fig. 4. Fragment of structural unit packing in crystal **II** (H bond nos. 7–10).

those in eight zinc complexes with anionic thiosemicarbazone ligands (2.255(3)–2.408(3) and 1.989(6)–2.177(3) Å, respectively [9–11]). The C–S distances (1.784(7) Å and 1.779(8) Å) in compound **III**, as well as in complex **II**, are intermediate between the standard C–S and C=S bond lengths. Their values in **III** exceed the values of similar bonds in [9–11] (1.705(16)–1.759(8) Å). The N(2)=C(1) (1.272(7) and 1.283(8) Å) and N(1)=C(2) (1.281(7) and 1.274(8) Å) double bonds in complex **III** are shortened as compared to those in compound **II** (1.318(6) and 1.303(7) Å), respectively).

In both structures **III** and **II**, ligand L has a *Z* conformation with respect to the N(1)–C(2) bond. In coordination compound **III**, the plane of the chelating fragment S(11)C(11)N(11)N(21) is rotated about the C(21)C(3)C(41) chain and phenyl cycle through 7.6° and 23.0°, respectively. For the second ligand L, analogous angles are 4.6° and 12.6°. Dimeric layers parallel to the (010) plane are formed in crystal **III** due to hydrogen bonds 11 and 12 (Fig. 6).

Thus, after coordination by nickel(II) and zinc(II) ions, deprotonated ligand L changes its *E* conformation

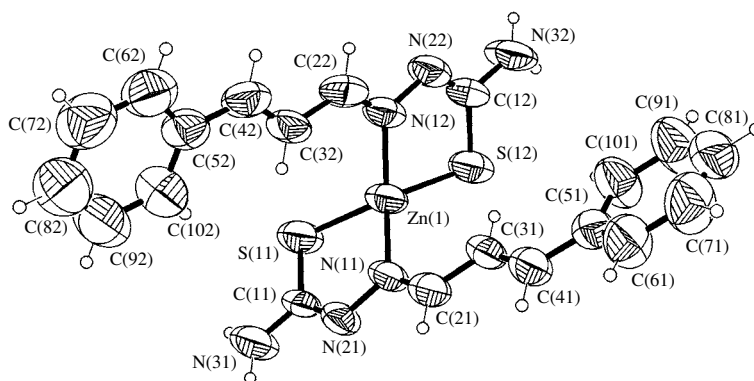


Fig. 5. Structure of complex molecule **III**.

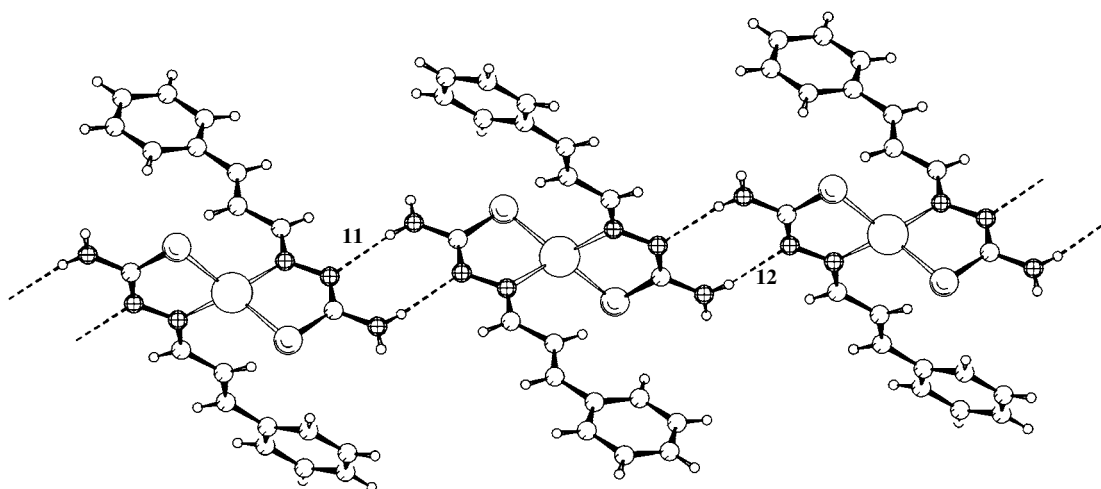


Fig. 6. Fragment of structural unit packing in crystal **III** (H bond nos. 11, 12).

(in an HL molecule (structure **I**)) with respect to the N(1)–C(2) bond for the *Z* conformation. This is accompanied by a considerable elongation of the S–C distance in the organic anion L[−] as compared to a standard value of the S=C double bond. The coordination polyhedra of the nickel (in **II**) and zinc (in **III**) atoms are distorted square and tetrahedron, respectively. In crystals **I–III**, molecules are packed into infinite layers parallel to the planes (001) and (010).

REFERENCES

1. Bruker, Axs Inc., 6300 Enterprise Lane, Msdison (WI, USA).
2. Sheldrick, G.M., *SHELX97. Program for the Refinement of Crystal Structure*, Göttingen (Germany): Univ. of Göttingen, 1997.
3. Spek, A.L., *J. Appl. Crystallogr.*, 2003, vol. 36, no. 1, p. 7.
4. Bruno, I.J., Cole, J.C., Edginton, P.R., *et al.*, *Acta Crystallogr., Sect. B: Struct. Sci.*, 2002, vol. 58, p. 389.
5. Allen, F.H., *Acta Crystallogr., Sect. B: Struct. Sci.*, 2002, vol. 58, p. 380.
6. Dimmock, J.R., Jonnalagadda, S.S., Hussein, S., *et al.*, *Eur. J. Med. Chem.*, 1990, vol. 25, no. 7, p. 581.
7. Garcia-Tojal, J., Pizarro, J.L., and Garcia-Orad, A., *J. Inorg. Biochem.*, 2001, vol. 86, nos. 2–3, p. 627.
8. Ali, M.A. and Mirza, A.H., *Transition Met. Chem. (London)*, 2000, vol. 25, no. 4, p. 430.
9. Castineiras, A. and West, D.X., *J. Mol. Struct.*, 2002, vol. 604, nos. 2–3, p. 113.
10. Fang Chen-jie, Duan Chun-jie, He Cheng, *et al.*, *New J. Chem.*, 2000, vol. 24, no. 6, p. 697.
11. Casas, J.S., Casatsno, M.V., and Castellano, E.E., *Inorg. Chem.*, 2002, vol. 41, no. 6, p. 1550.