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Synthesis of Optically Active Zn(II) Complexes with Thiosemicarbazones of (+)-Camphor (L) and (–)-Carvone (L^1). The Crystal Structures of L and $[Zn(L)_2Cl_2]$

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Abstract—The optically active complexes $[Zn(L)_2Cl_2]$ (**I**) and $[Zn(L^1)_2Cl_2]$ (**II**) (L and L^1 are thiosemicarbazones of (+)-camphor and (–)-carvone, respectively) were obtained. The crystal structures of L and complex **I** were determined by X-ray diffraction. The structure of L consists of hydrogen-bonded molecules united into chains. The crystal structure of complex **I** is built from mononuclear molecules. The coordination polyhedron of the Zn atom is a distorted tetrahedron Cl_2S_2. The molecule L functions as a monodentate ligand. According to data from IR spectroscopy, complex **II** is structurally similar to complex **I**.

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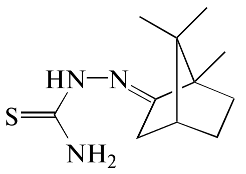
INTRODUCTION

Systematic investigations of transition metal complexes with thiosemicarbazones have been conducted for a prolonged period of time [1, 2]. However, the synthesis of such complexes, as well as the study of their structures and properties, remains of current interest for coordination and bioinorganic chemists because many of these complexes are biologically active [3]. For instance, transition metal complexes with thiosemicarbazones have been reported to exhibit antituberculosis, antibacterial, and antitumor activity [3–5]. Such are Zn(II) complexes, which take an important part in biological processes [4, 6–11]. For this reason, the synthesis and study of transition metal complexes with chiral thiosemicarbazones derived from natural terpenes are of increased interest. Chiral terpenes, specifically monoterpenes, widely occur among vegetable life and exhibit biological activity [12]. However, natural monoterpenes usually cannot be coordinated to metal ions. Functionalization of a natural monoterpene with electron-donating groups makes the resulting reagent capable for coordination [13]. The biological activity of the starting natural terpenes allows us to expect that thus modified reagents, as well as metal complexes with such chiral ligands, will be also biologically active.

The goal of this study was to obtain Zn(II) complexes with the chiral ligands (*E*)-2-((1*R*,4*R*)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-one) thiosemicarbazone (L) and (*R*,*E*)-2-(2-methyl-5-(prop-1-en-2-yl)cyclohex-2-en-1-one)thiosemicarbazone) (L^1), the derivatives of the monoterpenoids (+)-camphor and (–)-carvone, respectively, and examine their structures and properties.



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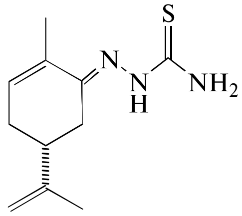

(L^1)

EXPERIMENTAL

Zinc(II) chloride (analytical grade), rectified ethanol, acetone (special purity grade), and *iso*-PrOH (special purity grade) were used.

Compound L ($[\alpha]_{589}^{25}$ –50, *c* 0.0036, $CHCl_3$; m.p. = 188°C from MeOH–$CHCl_3$ (9 : 1, v/v)) was prepared from (+)-camphor (Fluka, catalog no. 21300, $[\alpha]_{546}^{20}$ + 56, m.p. = 176–180°C from EtOH, ≥99% *ee* (enantioselective GLC)) as described in [14] (cf. m.p. = 192–193°C from aqueous EtOH [14]).

^{1}H NMR (500 MHz, δ, ppm): 0.71 (s, 3H, H(9)); 0.90 (s, 3H, H(8)); 0.96 (s, 3H, H(10)); 1.19 (ddd, 1H, *R*-H(5), *J* = 12.0 Hz, *J* = 9.2 Hz, *J* = 4.2 Hz); 1.34

(ddd, 1H, *S*-H(6), *J* = 12.7 Hz, *J* = 9.2 Hz, *J* = 4.4 Hz); 1.71 (ddd, 1H, *R*-H(6), *J* = 12.7 Hz, *J* = 12.0 Hz, *J* = 4.2 Hz, *J* = 0.7 Hz); 1.80–1.90 (m, 1H, *S*-H(5)); 1.88 (d, 1H, *S*-H(3), *J* = 16.9 Hz); 1.99 (dd, 1H, H(4), *J* = 4.2 Hz, *J* = 4.2 Hz); 2.38 (dd, 1H, *R*-H(3), *J* = 16.9 Hz, *J* = 4.2 Hz, *J* = 3.5 Hz, *J* = 0.7 Hz); 6.25 (br.s, 1H, NH); 7.17 (br.s, 1H, NH); 8.27 (br.s, 1H, NH).

^{13}C NMR (500 MHz, δ, ppm): 11.00 (C(10)); 18.55 (C(8)); 19.42 (C(8)); 27.14 (C(5)); 29.66 (C(7)); 32.47 (C(6)); 33.80 (C(3)); 43.96 (C(4)); 48.11 (C(1)); 168.75 (C(2)); 178.60 (C(11)).

Compound L^1 ($[\alpha]_{589}^{28}$ –142, *c* 0.013, $CHCl_3$; m.p. = 46–48°C from C_6H_6) was prepared from (–)-carvone (Acros Organics, catalog no. 154591000) as described in [15] (cf. for its racemate, m.p. = 172–174°C from aqueous EtOH [15]).

^{1}H NMR (500 MHz, δ, ppm): 1.75 (dd, 3H, H(9), *J* = 1.5 Hz, *J* = 0.9 Hz); 1.84 (ddd, 3H, H(10), *J* = 2.4 Hz, *J* = 1.3 Hz, *J* = 1.3 Hz); 2.11 (dd, 1H, *R*-H(3), *J* = 15.7 Hz, *J* = 12.7 Hz); 2.12 (dddp, 1H, *R*-H(5), *J* = 17.6 Hz, *J* = 11.2 Hz, *J* = 2.6 Hz, *J* = 2.4 Hz, *J* = 2.4 Hz, *J* = 2.4 Hz); 2.31 (ddddp, 1H, *S*-H(5), *J* = 17.6 Hz, *J* = 6.1 Hz, *J* = 4.7 Hz, *J* = 1.3 Hz, *J* = 1.3 Hz, *J* = 1.3 Hz, *J* = 1.3 Hz); 2.43 (dddd, 1H, H(4), *J* = 12.7 Hz, *J* = 11.2 Hz, *J* = 4.7 Hz, *J* = 4.2 Hz); 2.72 (ddd, 1H, *S*-H(3), *J* = 15.7 Hz, *J* = 4.2 Hz, *J* = 1.3 Hz); 4.77 (dp, 1H, *Z*-H(8), *J* = 1.5 Hz, *J* = 0.9 Hz, *J* = 0.9 Hz, *J* = 0.9 Hz); 4.82 (dt, 1H, *E*-H(8), *J* = 1.5 Hz, *J* = 1.5 Hz, *J* = 1.5 Hz, *J* = 1.5 Hz); 6.20 (ddp, 1H, H(6), *J* = 6.1 Hz, *J* = 2.6 Hz, *J* = 1.34 Hz, *J* = 1.34 Hz, *J* = 1.34 Hz); 6.66 (br.s, 1H, NH); 7.22 (br.s, 1H, NH); 8.84 (br.s, 1H, NH).

^{13}C NMR (500 MHz, δ, ppm): 17.95 (C(10)); 20.49 (C(9)); 29.20 (C(3)); 30.07 (C(5)); 40.59 (C(4)); 110.70 (C(8)); 131.98 (C(1)); 135.11 (C(6)); 146.77 (C(7)); 150.05 (C(2)); 178.90 (C(11)).

Synthesis of the complex [ZnL_2Cl_2] (I). A solution of compound L (0.045 g, 0.2 mmol) in ethanol–acetone (1 : 1, v/v; 4 mL) was slowly added to a stirred solution of $ZnCl_2$ (0.014 g, 0.1 mmol) in ethanol (2 mL). The resulting solution was kept at room temperature and concentrated to a minimum possible volume (1–2 mL). The white precipitate that formed was filtered off on a porous glass filter, washed with cooled *iso*-PrOH, and dried in a vacuum desiccator. The yield of complex **I** was 0.034 g (66%) ($[\alpha]_{580}^{25}$ –48, *c* 0.00488, $CHCl_3$).

For $C_{22}H_{38}N_6S_2Cl_2Zn$

anal. calcd., %:	C, 45.0;	H, 6.5;	N, 14.3;	S, 10.9.
Found, %:	C, 44.9;	H, 6.5;	N, 13.9;	S, 11.3.

Synthesis of the complex $ZnL_2^1Cl_2$ (II). A solution of $ZnCl_2$ (0.014 g, 0.1 mmol) in ethanol (2 mL) was added to a solution of compound L^1 (0.045 g, 0.2 mmol) in ethanol–acetone (1 : 1, v/v; 4 mL). The resulting solution was treated as described for the synthesis of complex **I**. The yield of complex **II** was 0.037 g (64%) ($[\alpha]_{580}^{25}$ –133, *c* 0.00366, $CHCl_3$).

For $C_{22}H_{34}N_6S_2Cl_2Zn$

anal. calcd., %:	C, 45.3;	H, 5.8;	N, 14.4;	S, 10.9.
Found, %:	C, 46.0;	H, 6.1;	N, 14.3;	S, 10.9.

Microanalysis for C, H, and N was carried out on a Euro EA 3000 analyzer. IR spectra were recorded for KBr and polyethylene pellets on Scimitar FTS 2000 and Vertex 80 FTIR spectrometers in the 4000–200 cm^{-1} range. Optical rotation was measured on a PolAAr 3005 polarimeter. NMR spectra were recorded on a Bruker DRX-500 instrument (500.13 (^{1}H) and 125.75 MHz (^{13}C)) for solutions in $CDCl_3$ (*C* = 5 mg/mL). The signals of the solvent (δ_H 7.27, δ_C 77.00) were used as the internal standards.

The crystals of compound L obtained as described in [14] are suitable for X-ray diffraction. To grow single crystals of complex **I**, solutions of the starting reagents were mixed as in the synthesis of this complex and the resulting solution was slowly evaporated.

X-ray diffraction study. Experimental data were collected on an X8 APEX automated diffractometer at 150 K according to a standard procedure. Structures L and **I** were solved by the direct methods and refined anisotropically (for non-hydrogen atoms) by the full-matrix least-squares method with the SHELXL-97 program package [16]. Crystallographic parameters and the data collection and refinement statistics for structures L and **I** are summarized in Table 1. Selected bond lengths and bond angles in these structures are listed in Table 2. Comprehensive tables of the atomic coordinates, bond lengths, and bond angles have been deposited with the Cambridge Crystallographic Data Centre (nos. 904724 (L) and 904723 (**I**); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/data_request/cif) or can be made available from the authors upon request.

RESULTS AND DISCUSSION

Reactions of $ZnCl_2$ with levorotatory compounds L and L^1 in ethanol–acetone gave optically active levorotatory complexes **I** and **II**, respectively, with a molar Zn : ligand ratio of 1 : 2.

Structure L, with all its atoms in general positions, is shown in Fig. 1. We found that the fragment S(1)N(1)N(2)N(3)C(1)C(10)C(11)C(13)C(14) is

Table 1. Crystallographic parameters and the data collection and refinement statistics for free ligand L and complex **I**

Parameter	Value	
Compound	L	**I**
Empirical formula	$C_{11}H_{19}N_3S$	$C_{22}H_{38}N_6S_2Cl_2Zn$
M	225.35	586.97
Crystal system	Orthorhombic	Orthorhombic
Space group	$P2_12_12_1$	$P2_12_12_1$
a, Å	7.6062(2)	11.3488(3)
b, Å	11.3138(3)	15.9516(5)
c, Å	14.3572(4)	16.0217(3)
V, Å^3	1235.51(6)	2900.4(1)
Z; ρ_{calcd}, mg/cm^3	4; 1.212	4; 1.344
μ, mm^{-1}	0.236	1.196
Crystal dimensions, mm	0.33 × 0.16 × 0.13	0.45 × 0.15 × 0.12
θ scan range, deg	2.29–30.58	2.20–32.79
Number of measured reflections	11588	39163
Number of independent reflections	3784	10608
R_{int}	0.0254	0.0435
Number of reflections with $I > 2\sigma(I)$	3784	10608
Number of parameters refined	212	305
GOOF on F^2	1.032	1.076
R factor, $I > 2\sigma(I)$	$R_1 = 0.0298$ $wR_2 = 0.0675$	$R_1 = 0.0312$ $wR_2 = 0.0493$
R factor (for all I_{hkl})	$R_1 = 0.0352$ $wR_2 = 0.0703$	$R_1 = 0.0425$ $wR_2 = 0.0519$
Residual electron density (max/min), e/Å^3	0.264/–0.169	0.242/–0.246

nearly planar: the deviation of its constituent atoms from the mean-square plane is 0.022(1) Å. The dihedral angle between the planes C(10)C(11)C(13)C(14) and C(11)C(13)C(15)C(16) is 70.1(1)°. The projection of the crystal structure of L onto the plane (010) is shown in Fig. 2a. Weak H-bonds S···H–C and S···H–N (S(1)···C(14), 3.359(1) Å; S(1)···N(1), 3.374(1) Å; S(1)···N(2), 3.463(1) Å; the sums of the van der Waals radii of S + N and S + C are 3.45 and 3.55 Å, respectively [17]) unite the molecules of L multiplied by the axis 2_1 into zigzag chains along the axis *x*. A fragment of one chain is shown in Fig. 2b.

According to X-ray diffraction data, complex **I** is mononuclear (Fig. 3). The Zn atom is coordinated to the S atoms of two monodentate ligands L and two Cl atoms. The coordination polyhedron Cl_2S_2 is a distorted tetrahedron. The Zn–S and Zn–Cl bond lengths differ insignificantly (Table 2). The structure contains two six-membered H-rings ZnSCNHCl formed by the intramolecular H-bond N–H···Cl (N(12)···Cl(1) 3.322(2), N(22)···Cl(2) 3.276(2) Å). The angles N(12)H(12)Cl(1) and N(22)H(22)Cl(2) are 157° and 165°, respectively. Both the rings exist in an envelope conformation: the Zn atom deviates from the mean-square plane of the other five atoms by 1.131 and 0.717 Å.

The coordination polyhedron of the Zn atom in complex **I** is similar to that in $Zn(4PhTSCAc)_2Cl_2$ (**III**), in which acetone 4-phenylthiosemicarbazone (4PhTSCAc) also functions as a monodentate ligand [18]. The bond lengths and bond angles in complex **I** are close to those in complex **III**. In contrast, acetone thiosemicarbazone (TSCAc) in the complex $Zn(TSCAc)Cl_2$ (**IV**) acts as a bidentate ligand [19]. The Zn atom in complex **IV** shows a tetrahedral coordination involving the S and N atoms of the bidentate ligand and two Cl atoms. Apparently, the presence of such bulky substituents as the phenyl group or the terpene fragment can be responsible for the monodentate coordination of the ligands 4PhTSCAc (in **III**) and L (in **I**) to the Zn atom, in contrast to other thiosemicarbazones capable of acting as bi- and tridentate ligands [18].

A fragment of the molecular packing of complex **I** projected onto the plane (100) is shown in Fig. 4. In this structure, the molecules are multiplied by twofold helical axes 2_1 and united into zigzag chains involving the NH_2 groups and the S and Cl atoms. Along the axis *y*, the molecules of the complex are linked by weak H-bonds (the sum of the van der Waals radii of N + Cl is 3.40 Å) between the N atoms and the Cl atoms only (N(11)···Cl(1)' 3.293(2), N(11)···Cl(2)' 3.436(2) Å). Along the axis *z*, the N atoms show contacts with both the Cl and S atoms (N(21)···Cl(2)'' 3.341(2), N(21)···S(1)'' 3.497(2) Å).

Table 2. Selected bond lengths and bond angles in structures L and **I**

Bond	*d*, Å	Bond	*d*, Å
		L	
S(1)–C(1)	1.690(1)	N(2)–N(3)	1.392(1)
N(1)–C(1)	1.332(2)	N(3)–C(10)	1.276(2)
N(2)–C(1)	1.346(2)		
		I	
Zn(1)–Cl(2)	2.2622(4)	N(12)–C(1)	1.333(2)
Zn(1)–Cl(1)	2.2650(4)	N(12)–N(13)	1.400(2)
Zn(1)–S(1)	2.3464(4)	N(13)–C(10)	1.278(2)
Zn(1)–S(2)	2.3559(4)	N(21)–C(2)	1.338(2)
S(1)–C(1)	1.723(1)	N(22)–C(2)	1.328(2)
S(2)–C(2)	1.704(2)	N(22)–N(23)	1.398(2)
N(11)–C(1)	1.314(2)	N(23)–C(20)	1.273(2)
Angle	**ω, deg**	**Angle**	**ω, deg**
		L	
C(1)N(2)N(3)	118.5(1)	N(2)C(1)S(1)	120.3(1)
C(10)N(3)N(2)	116.7(1)	N(3)C(10)C(11)	122.8(1)
N(1)C(1)N(2)	117.4(1)	N(3)C(10)C(14)	129.7(1)
N(1)C(1)S(1)	122.3(1)		
		I	
Cl(2)Zn(1)Cl(1)	112.32(2)	C(2)N(22)N(23)	116.9(1)
Cl(2)Zn(1)S(1)	105.74(1)	C(20)N(23)N(22)	115.6(1)
Cl(1)Zn(1)S(1)	109.93(2)	N(11)C(1)N(12)	119.2(1)
Cl(2)Zn(1)S(2)	112.49(2)	N(11)C(1)S(1)	119.5(1)
Cl(1)Zn(1)S(2)	108.87(2)	N(12)C(1)S(1)	121.3(1)
S(1)Zn(1)S(2)	107.33(2)	N(22)C(2)N(21)	117.7(1)
C(1)S(1)Zn(1)	105.01(5)	N(22)C(2)S(2)	122.2(1)
C(2)S(2)Zn(1)	107.93(5)	N(21)C(2)S(2)	120.0(1)
C(1)N(12)N(13)	118.4(1)	N(13)C(10)C(11)	123.2(1)
C(10)N(13)N(12)	115.0(1)	N(13)C(10)C(14)	129.0(1)

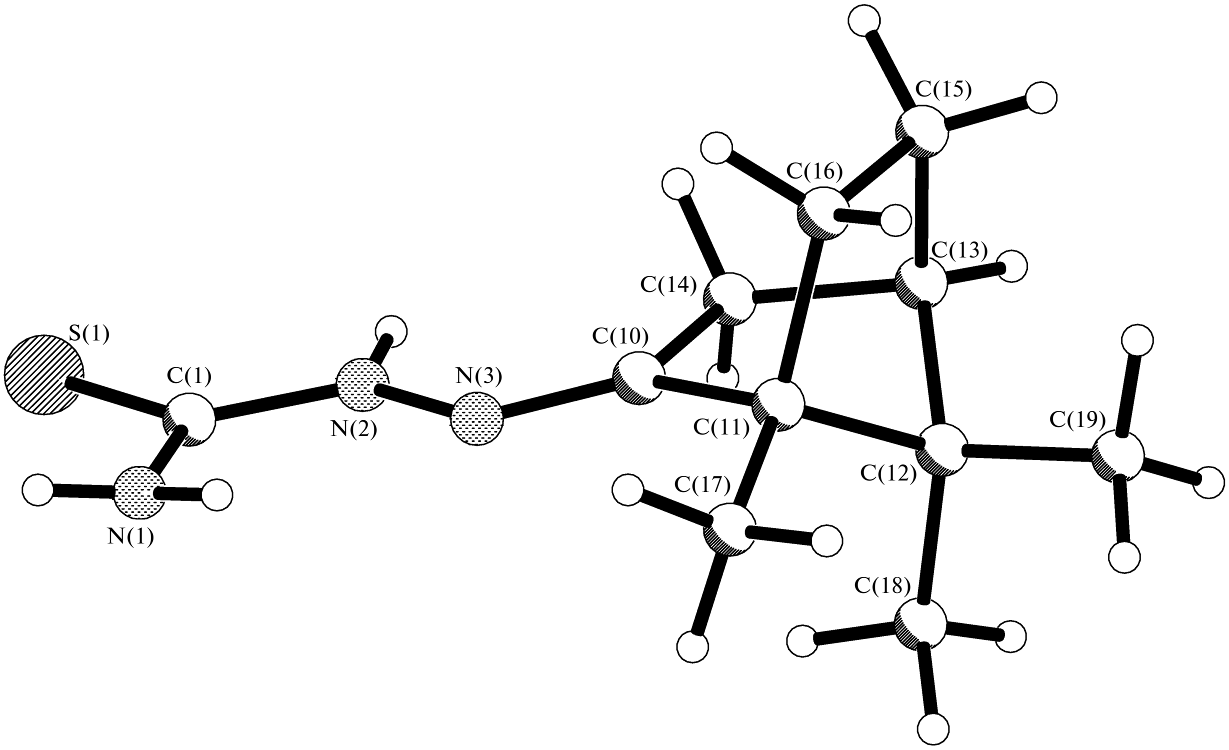

Fig. 1. Structure L with numbering of the non-hydrogen atoms.

Comparison of the bond lengths and bond angles in structures L and **I** revealed no appreciable effect of the coordination to the Zn atom (Table 2). For instance, the C=S bonds in complex **I** are longer than that in compound L only by 0.014 and 0.033 Å. In addition, the planar fragment S(1)N(1)N(2)N(3)C(1)C(10)C(11)C(13)C(14) in L (Δ = 0.022(1) Å) undergo slight distortions in complex **I** (Δ = 0.069(1) and 0.085(1) Å), probably because of the presence of intramolecular H-bonds Cl···H–N in the latter structure.

Note that either structure shows chains in its molecular packing. However, free ligands L are united into chains through S···H–N bonds alone, while the chains in complex **I** are formed by both S···H–N and Cl···H–N bonds.

Since complexes **I** and **II** have similar compositions, one can assume that complex **II** also contains the tetrahedral environment Cl_2S_2 around the Zn atom and that L^1 functions as a monodentate ligand coordinated through the S atom. To verify this assumption, we analyzed the IR spectra of compounds L and L^1 and complexes **I** and **II** and identified the ν(NH), δ(NH), and ν(C=N) bands (Table 3) [4]. Weak ν(CS) bands were difficult to identify. Small shifts of the ν(NH), δ(NH), and ν(CN) bands in the IR spectra of the complexes from their positions in the spectra of the free ligands suggest a changed atomic environment and H-bonding through the NH groups. The IR spectra of complexes **I** and **II** exhibit new intense bands in the low-frequency range (Table 3). Based on X-ray diffraction data for **I** and having analyzed the data in [20], we assigned these bands to the Zn–Cl and Zn–S vibrations.

To sum up, we were the first to demonstrate that optically active Zn(II) complexes can be obtained from chiral thiosemicarbazones derived from natural terpenes. This offers scope for the synthesis of com-

Table 3. Selected vibrational frequencies (cm^{-1}) in the IR spectra of free ligands L and L^1 and complexes **I** and **II**

L	**I**	L^1	**II**	Assignment
3417, 3212, 3125	3428, 3300, 3214, 3050	3423, 3245, 3164	3404, 3294, 3261, 3218, 3172	ν(NH)
1665, 1583, 1513	1664, 1595, 1536	1642, 1590, 1498	1638, 1606, 1587, 1523	δ(NH), ν(C=N)
	297		292	ν(Zn–Cl)
	280		270	ν(Zn–S)

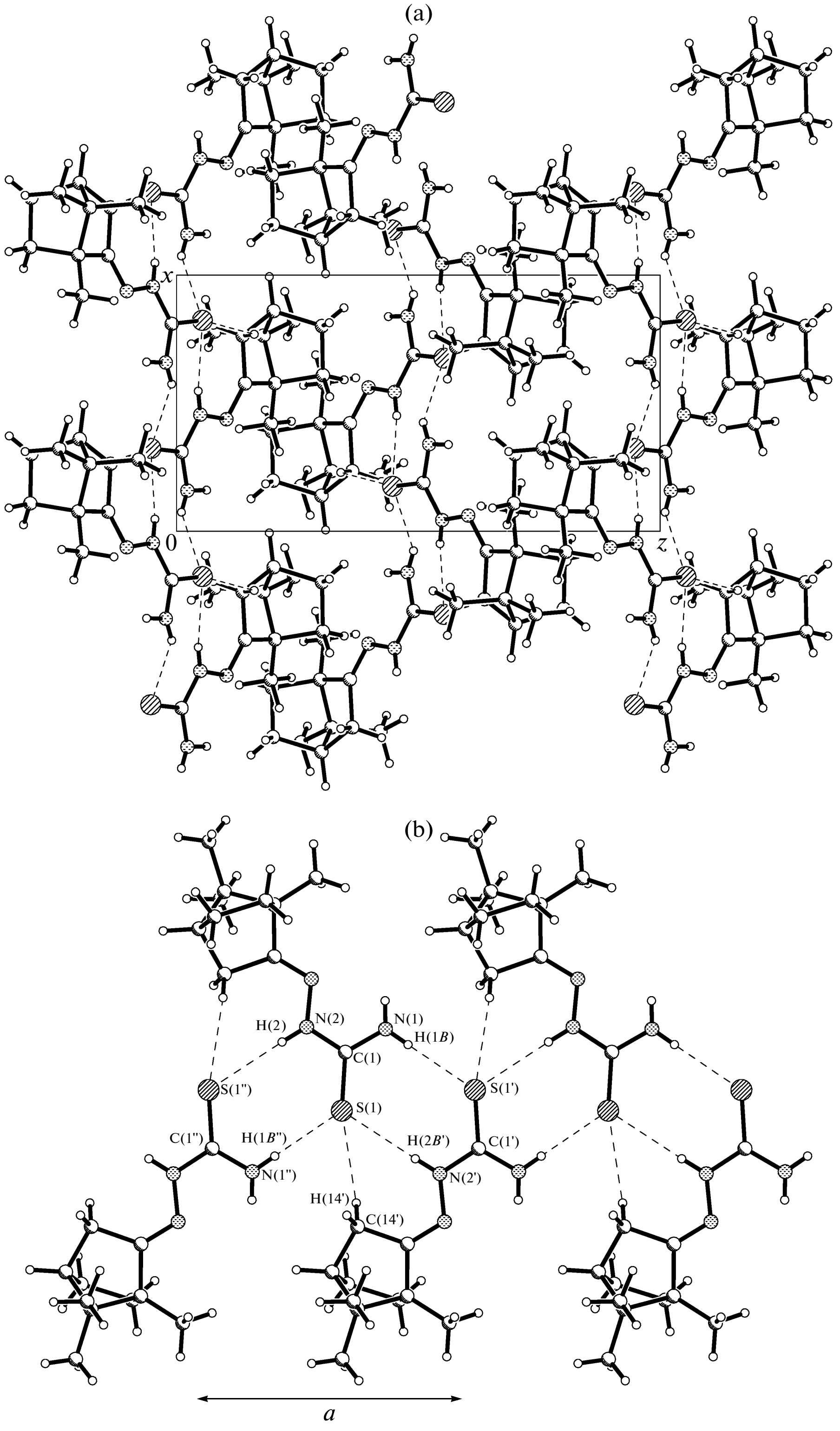

Fig. 2. (a) Projection of the crystal structure of L onto the plane (010) (H-bonds are indicated with dashed lines); (b) a fragment of a chain formed by H-bonds between adjacent molecules of L along the axis *x*.

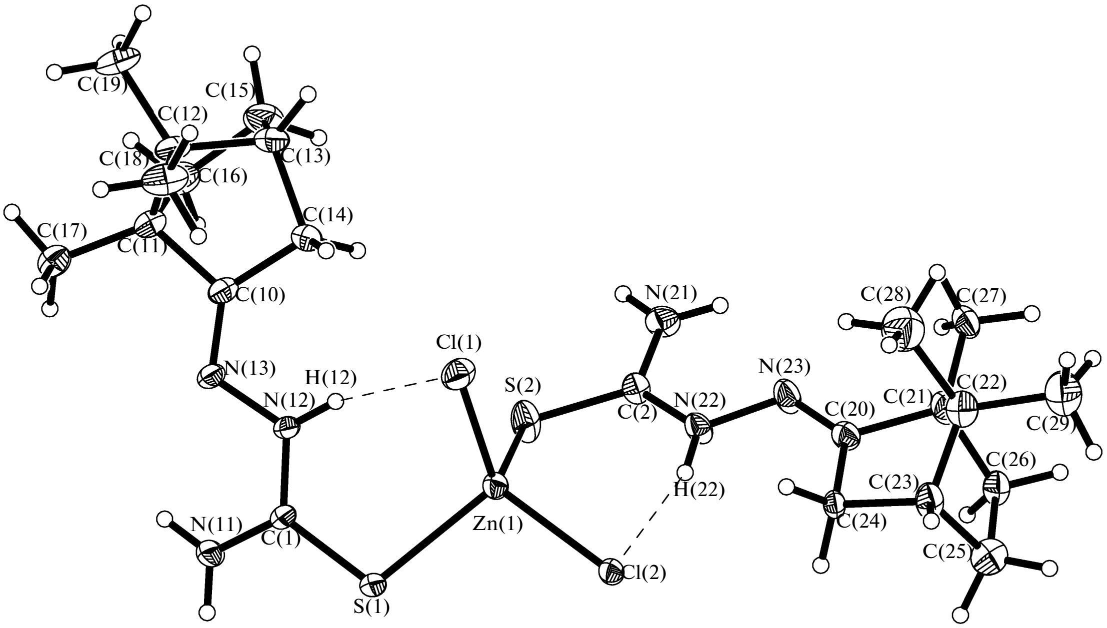

Fig. 3. Structure **I** with numbering of the non-hydrogen atoms.

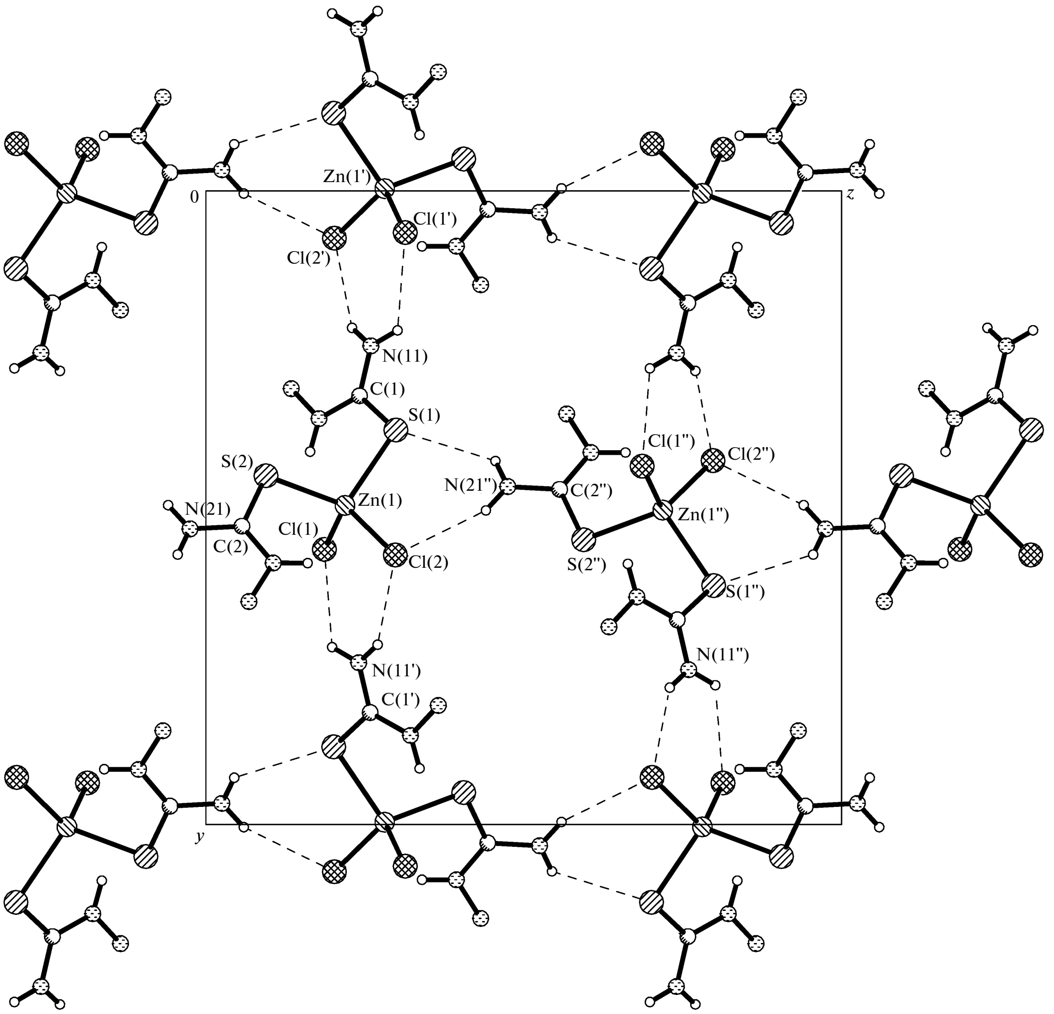

Fig. 4. Fragment of the molecular packing of complex **I** viewed in a projection onto the plane (100). The chains stretch along the axes *y* and *z*.

plexes of L and L^1 with other metal ions as well as for further investigations of their structures and properties, including biological activity.

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