ISSN 1070-3284, Russian Journal of Coordination Chemistry, 2021, Vol. 47, No. 11, pp. 741–750. © Pleiades Publishing, Ltd., 2021.
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Complexes of 1-(4-Methoxyphenyl)-1,4-dihydro-5*H*-tetrazole-5-thione and 1-(2-Methoxyphenyl)-1,4-dihydro-5*H*-tetrazole-5-thione with Cadmium Chloride: Synthesis and Molecular and Crystal Structures

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Received March 21, 2021; revised April 16, 2021; accepted April 19, 2021

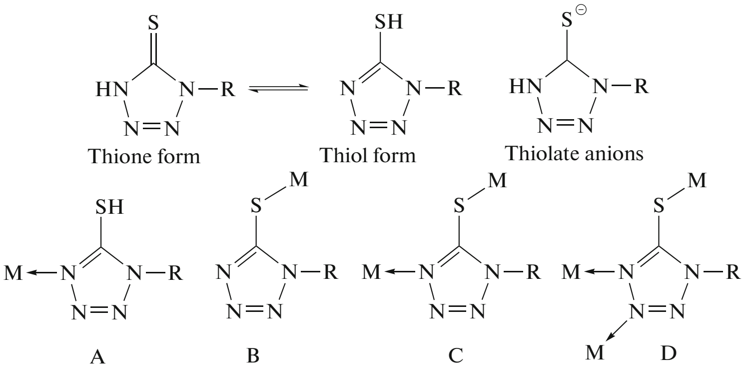
Abstract—New complex compounds $[Cd(\mu\text{-}L^1)_2]_n$ (**I**), $[Cd(\mu\text{-}L^2)(\mu\text{-}Cl)(\mu\text{-}DMSO)]_n$ (**III**), and $[Cd_2(\mu\text{-}L^2)(\mu\text{-}Cl)_3(\mu\text{-}DMSO)DMSO/EtOH]_n$ (**IV**) are synthesized by the reactions of 1-(4-methoxyphenyl)-1,4-dihydro-5*H*-tetrazole-5-thione (HL^1) and 1-(2-methoxyphenyl)-1,4-dihydro-5*H*-tetrazole-5-thione (HL^2) with cadmium chloride. The molecular and crystal structures of the complexes are determined by X-ray structure analysis (CIF files CCDC nos. 1993455 (**I**), 1869249 (**III**), and 1993497 (**IV**)). Complexes **I**, **III**, and **IV** have uniform polymeric structures. The O···H, Cl···H, and C···S contacts are observed between 1D polymeric chains in the crystal cells of complexes **I**, **III**, and **IV.** Complexes **III** and **IV** contain DMSO molecules. Under other equivalent conditions, the reaction of HL^1 or HL^2 with cadmium chloride in ethanol affords complex **I** or **II** of different compositions. Complex **II** contains the chlorine atom as found by scanning electron microscopy, whereas no chlorine is observed in complex **I** according to the X-ray structure analysis data.

Keywords: 1-(4-methoxyphenyl)-1,4-dihydro-5*H*-tetrazole-5-thione, 1-(2-methoxyphenyl)-1,4-dihydro-5*H*-tetrazole-5-thione, polymeric cadmium(II) complexes, crystal structure, X-ray structure analysis, scanning electron microscopy

DOI: 10.1134/S1070328421110014

INTRODUCTION

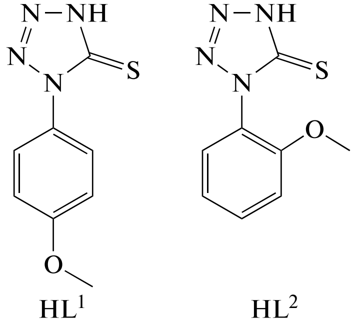
N-Substituted mercaptotetrazoles and other five-membered heterocyclic thiols containing the nitrogen atom near the C–SH group can exist in both thione and thiol forms due to tautomerism [1–4]. However, the thione form is considered to be more stable for mercaptotetrazoles and similar heterocyclic compounds [1]. In addition, they can form thiolate anions in the presence of bases. These forms of the reagents possess several electron-donating centers and, hence, can be used as polydentate ligands in complex formation with diverse metals for the synthesis of various complexes and supramolecular structures [5–13]. The forms of *N*-substituted mercaptotetrazoles and their coordination modes with metal atoms (A–D) are shown in Scheme 1.



Scheme 1.

The reactions of 1-phenyl-1,4-dihydro-5*H*-tetrazole-5-thione and 1-(4-fluorophenyl)-1,4-dihydro-5*H*-tetrazole-5-thione with cadmium chloride were studied earlier, and the structures of the synthesized complexes were determined by X-ray structure analysis (XSA) [2, 5]. Both complexes are polymeric and have the chain structure. The structure of the reaction product of sodium 1-(2-methoxyphenyl)-1*H*-tetrazole-5-thiolate with cadmium chloride was presented [3].

In this work in continuation of our previous studies [2, 3], the cadmium(II) chloride complexes with 1-(4-methoxyphenyl)-1,4-dihydro-5*H*-tetrazole-5-thione (HL^1) and 1-(2-methoxyphenyl)-1,4-dihydro-5*H*-tetrazole-5-thione (HL^2) (Scheme 2) were synthesized under different conditions: $[Cd(\mu\text{-}L^1)_2]_n$ (**I**), $[Cd(\mu\text{-}L^2)(\mu\text{-}Cl)(\mu\text{-}DMSO)]_n$ (**III**), and $[Cd_2(\mu\text{-}L^2)(\mu\text{-}Cl)_3(\mu\text{-}DMSO)DMSO/EtOH]_n$ (**IV**). Their structures were studied by XSA.



Scheme 2.

We failed to study the structure of complex **II** by XSA but succeeded to find using scanning electron microscopy (SEM) combined with electron probe X-ray microanalysis (EPXMA) that complex **II** contained chlorine atoms in the ratio with sulfur and cadmium atoms Cl : S : Cd = 1 : 1 : 1.

EXPERIMENTAL

The starting reagents NaN_3, $CdCl_2$ (both not lower than reagent grade), and *p*-methoxyphenyl isothiocyanate (Acros Organics, Belgium) were used as received. Thione HL^2 was synthesized according to a described procedure [3].

Synthesis of HL^1 was carried out using a procedure similar to that for HL^2. The yield was (47%), white crystals, T_m = 154–155°C, T_{decomp} =160–1161°C. ^{1}H NMR (DMSO-d_6, 500 MHz, 298 K; δ, ppm): 7.70 (m, 2H, Ph), 7.12 (m, 2H, Ph), 3.82 (s, 3H, OCH_3).

For $C_8H_8N_4OS$

Anal. calcd., %	C, 46.15	H, 3.85	N, 26.92
Found, %	C, 46.25	H, 3.78	N, 26.83

Synthesis of complex I. A solution of anhydrous $CdCl_2$ (0.184 g, 1 mmol) in absolute ethanol (15 mL) was added to a solution of thione HL^1 (0.416 g, 2 mmol) in boiling absolute ethanol (25 mL). The reaction mixture was refluxed for 5 h and then cooled to 20°C. The formed precipitate was filtered off, washed with ethanol (50 mL), and dried at 353 K. The substance was recrystallized from ethanol for XSA. The yield of complex **I** was 0.205 g (39.7%), white powder, T_m = 238–240°C (with decomp.). ^{1}H NMR (DMSO-d_6, 500 MHz, 298 K; δ, ppm): 7.63 (d, 2H, *J* = 8.0 Hz, Ph), 7.08 (d, 2H, *J* = 8.0 Hz, Ph), 3.81 (s, 3H, OCH_3).

For $C_{16}H_{14}N_8O_2S_2Cd$

Anal. calcd., %	C, 36.50	H, 2.66	N, 21.29
Found, %	C, 36.38	H, 2.68	N, 21.44

Synthesis of complex II. A solution of anhydrous $CdCl_2$ (0.368 g, 2 mmol) in absolute ethanol (25 mL) was added to a solution of thione HL^2 (0.832 g, 4 mmol) in boiling absolute ethanol (50 mL). The reaction mixture was refluxed for 5 h and then cooled to 20°C. The formed precipitate was filtered off, washed with ethanol (50 mL), and dried at 353 K. The yield of complex **II** was 0.685 g, white powder, T_m = 224–225°C (with decomp.). ^{1}H NMR (DMSO-d_6, 500 MHz, 298 K; δ, ppm): 7.52 (m, 1H, Ph), 7.34 (dd, 1H, *J* = 8.0 Hz, 1.6 Hz, Ph), 7.24 (d, 1H, *J* = 8.5 Hz, Ph), 7.08 (m, 1H, Ph), 3.81 (s, 3H, OCH_3). Found, %: C, 28.40; H, 2.87; N, 15.42.

Synthesis of complex III. The compound was prepared by the crystallization of complex **II** from DMSO. White crystals, T_m > 190°C (with decomp.). ^{1}H NMR (DMSO-d_6, 500 MHz, 298 K; δ, ppm): 7.52 (m, 1H, Ph), 7.34 (dd, 1H, *J* = 8.0 Hz, 1.6 Hz, Ph), 7.24 (d, 1H, *J* = 8.5 Hz, Ph), 7.08 (m, 1H, Ph), 3.81 (s, 3H, OCH_3).

Synthesis of complex IV. A solution of anhydrous $CdCl_2$ (0.184 g, 1 mmol) in absolute ethanol (15 mL) was added to a solution of thione HL^2 (0.416 g, 2 mmol) in a mixture of absolute ethanol (27 mL) and DMSO (3.85 mL) at 20°C. The reaction mixture was stored at 20°C for 168 h. The formed precipitate was filtered off, washed with ethanol (50 mL), and dried at 353 K. The substance was used for XSA without additional recrystallization. The yield of complex **IV** was 0.158 g (23.8%), white powder, T_m > 200°C (with decomp.). ^{1}H NMR (DMSO-d_6, 500 MHz, 298 K; δ, ppm): 7.52 (m, 1H, Ph), 7.34 (dd, 1H, *J* = 8.0 Hz, 1.6 Hz, Ph), 7.24 (d, 1H, *J* = 8.5 Hz, Ph), 7.08 (m, 1H, Ph), 3.81 (s, 3H, OCH_3).

For $C_{12}H_{19}N_4O_3S_2Cl_3Cd_2$

Anal. calcd., %	C, 21.74	H, 2.87	N, 8.45
Found, %	C, 21.83	H, 2.83	N, 8.36

Melting (decomposition) temperatures were determined in evacuated sealed capillaries and are presented without correction. ^{1}H NMR spectra were recorded on an Agilent DD2 400 spectrometer with the working frequency 400 MHz in the mode of internal stabilization of the 2H polar resonance line in $CdCl_3$ at 20°C. Chemical shifts are given in ppm relative to tetramethylsilane as the internal standard. The SEM images of samples of compound **II** were obtained on a JSM-IT300LV microscope (JEOL) at the electron beam diameter about 5 nm and the probe current lower than 0.5 nA. The topography of the sample surface was studied using low-energy secondary electrons and reflected electrons. The elemental compositions of the samples were studied by EPXMA on an X-Max^N 20 detector (Oxford Instruments). X-ray diffraction analyses (XRD) of compound **II** (powder) and $CdCl_2$ were carried out on a Shimadzu XRD-6100 diffractometer using the Ni filter (CuK_α, $\lambda = 1.5418$ Å) in a 2θ range of 10°–60° with a rate of 1 deg/min. Elemental analysis was carried out on a Vario EL cybe instrument.

XSA of compounds **I** and **III** were carried out on a Bruker Smart Apex diffractometer, and compound **IV** was studied on a Bruker D8 QUEST diffractometer (ω scan mode, MoK_α radiation, $\lambda = 0.71073$ Å). Experimental sets of reflection intensities were collected and integrated using the SMART [14] and SAINT [15] programs, respectively. The structures were solved by a direct method and refined by full-matrix least squares for F^2_{hkl} in the anisotropic approximation for non-hydrogen atoms. It was found that in the crystal of compound **IV** the DMSO molecule was disordered with the ethanol molecule in a population ratio of 0.78 : 0.22. The hydrogen atom of the solvate ethanol molecule in compound **IV** was localized from the electron density synthesis and refined in the isotropic approximation. The coordinates of other hydrogen atoms in compounds **I**, **III**, and **IV** were calculated from geometric concepts and refined with fixed positional (riding model) and thermal parameters ($1.5U_{iso}$(C) for methyl groups and $U_{iso}(H) = 1.2U_{iso}(C)$ for all other groups). The structures were refined and absorption corrections were applied using the SHELXTL [16] and SADABS [17] software. The crystallographic data and XSA parameters for compounds **I**, **III**, and **IV** are presented in Table 1. Selected bond lengths and bond angles are listed in Table 2.

The structures were deposited with the Cambridge Crystallographic Data Centre (CIF files CCDC nos. 1993455 (**I**), 1869249 (**III**), and 1993497 (**IV**); https://www.ccdc.cam.ac.uk/structures/).

RESULTS AND DISCUSSION

It has recently been shown that *N*-substituted mercaptotetrazoles with cadmium chloride form various 1D complexes with the chain structures [2–4].

In this work, we synthesized four new complexes **I**–**IV** by the reactions of HL^1 or HL^2 with cadmium chloride. The structures of synthesized compounds **I**, **III**, and **IV** were determined by the XSA method.

Compound **I** in crystal represents the 1D polymeric complex $[Cd(\mu\text{-}L^1)_2]_n$ (Fig. 1a), which is identical in structure to the previously synthesized ones [2, 5]. The structure forming unit of the polymeric complex is the cadmium complex $Cd(L^1)_2$ with two symmetric thione ligands L^1 (Fig. 1b) linked with each other by the axis of rotation C_2 passing through the Cd(1) atom. The polymeric chain in complex **I** is formed by the syndiotactic alternation of the cadmium complexes $Cd(L^1)_2$ Cd(1*A*), Cd(1), Cd(1*B*), Cd(1*D*), etc. along the crystallographic axis *c*. The coordination environment of the Cd(1) cadmium cation is a distorted tetrahedron the vertices of which contain two nitrogen atoms N(4) and N(4)' of two symmetric ligands L^1 and two sulfur atoms S(1*A*) and S(1*B*)' from two adjacent $Cd(L^1)_2$ complexes (**A** and **B**) in the chain. Thus, the bridging ligand L^1 in the polymeric chain is coordinated via the bidentate mode by the N(4) and S(1) atoms on two adjacent cadmium atoms. The Cd–S and Cd–N distances (2.506(11) and 2.233(3) Å, respectively) are close to analogous bond lengths in the earlier published complexes (2.497(11)–2.503(23) and 2.228(4)–2.245(70) Å [2–4]). The SCdS and NCdN angles in complex **I** are 100.01(5)° and 97.75(16)°, respectively.

The dihedral angle between the planes of the tetrazole and phenyl cycles in complex **I** is 50.14(16)°. The 1D chain in complex **I** contains the eight-membered cycle {–S–C=N→Cd–S–C=N→Cd} in the chair conformation (Fig. 1c). The distance between the metal atoms Cd···Cd in complex **I** is 4.196(8) Å. The methyl group in the *p*-methoxyphenyl fragment in compound **I** lies in the plane of the phenyl cycle (root-mean-square value (rms) is 0.0173 Å). The $MeOC^{Ph}C^{Ph}$ torsion angle is –2.4(6)°. The 1D chains in complex **I** in crystal are arranged along the *c* chain.

The polymeric chains of compound **I** parallel to the *c* axis are arranged as smooth (without breaks) rows along the *a* axis (Fig. 1b). The OH contacts (O(1)···H(3*A*) 2.656(4) Å) [18, 19] are observed between the neighboring rows of the polymeric chains.

Unlike complex **I**, we failed to determine the structure of compound **II** (reaction product of HL^2 with cadmium chloride) by the XSA method. Therefore, to determine the elemental composition, we studied compound **II** by the SEM method combined with EPXMA. It turned out that, unlike complex **I** and the earlier synthesized complexes [2, 5], compound **II** contained chlorine atoms. The SEM study showed that the obtained powder represented particles about 200 nm in size, which is insufficient for the XSA method. However, the element distribution maps indicate that elements S, Cl, and Cd are arranged uni-

Table 1. Selected crystallographic data and structure refinement parameters for compounds **I**, **III**, and **IV**

Parameters	Value		
	I	**III**	**IV**
Empirical formula	$C_{16}H_{14}N_8O_2S_2Cd$	$C_{10}H_{13}N_4O_2S_2ClCd$	$C_{12}H_{19}N_4O_3S_{2.22}Cl_3Cd_2$
FW	526.87	433.21	669.47
Temperature, K	296(2)	296(2)	100(2)
Crystal sizes, mm^3	0.270 × 0.173 × 0.095	0.130 × 0.100 × 0.070	0.200 × 0.080 × 0.080
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$C2/c$	$P2_1$	$P2_1/n$
a, Å	23.549(5)	8.4924(4)	12.3628(4)
b, Å	11.342(3)	7.5183(3)	12.9467(5)
c, Å	7.5391(18)	11.9066(5)	14.2464(5)
α, deg	90	90	90
β, deg	106.592(4)	90.2446(7)	105.2140(10)
γ, deg	90	90	90
V, Å^3	1929.8(8)	760.21(6)	2200.32(14)
Z	4	2	4
ρ_{calc}, g/cm^3	1.813	1.893	2.021
μ, mm^{-1}	1.380	1.891	2.527
$F(000)$	1048	428	1302
Range of data collection over θ, deg	28	30	30
Measured reflections	9176	8627	35817
Independent reflections	2313	4230	6433
Number of refined parameters	132	184	281
R_1 ($I > 2\sigma(I)$)	0.0419	0.0227	0.0234
wR_2 (all data)	0.0814	0.0409	0.0494
GOOF	1.001	1.001	1.036
T_{min}; T_{max}	0.6061; 0.7461	0.6837; 0.7461	0.652; 0.802
Residual electron density (ρ_{min}/ρ_{max}), e Å^{-3}	–0.747/1.268	–0.371/0.491	–0.670/0.788

formly over the sample. In addition, the study of the individual particles showed that their compositions coincided.

The results of determination of the composition of compound **II** ignoring carbon are presented in Table 3. It is shown that the ratio of the chlorine, cadmium, and sulfur is approximately Cl : S : Cd = 1 : 1 : 1 (measurement inaccuracy 0.1 at %).

No impurities of cadmium chloride were found in compound **II** (powder) by the XRD method (Fig. 2). The absence on the XRD pattern of reflections corresponding to cadmium chloride and homogeneity of the elemental composition indicate that the obtained phase of compound **II** is individual. The NMR spectrum of compound **II** exhibits no signals of the initial HL^2 ligands, which also indicates that substance **II** is an individual compound.

The XSA results for complex **III**, which was obtained by the recrystallization of compound **II** in DMSO, are consistent with the SEM data for complex **II**. Complex **III** also contains chlorine, cadmium, and sulfur atoms in a ratio of 1 : 1 : 1. In addition, the XSA method shows that complex **III** contains DMSO molecules.

Compound **III** has the 1D chain structure of the composition $[Cd(\mu\text{-}L^2)(\mu\text{-}Cl)(\mu\text{-}DMSO)]_n$. The coordination environment of the cadmium cation is a distorted octahedron, the base of which is formed of two O(2) and O(2*C*) atoms of two DMSO molecules and chlorine atoms Cl(1) and Cl(1*C*). The axial positions are occupied by the N(4) and S(1*C*) atoms of two L^2 ligands. The N(4)Cd(1)S(1*C*) angle is 159.39(7)°. The Cd(1)–S(1*C*) and Cd(1)–N(4) distances are 2.574(9) and 2.34(2) Å, respectively. The sum of bond angles between the equatorial substituents is 360°. The

Table 2. Selected bond lengths (d) and bond angles (ω) in compounds **I**, **III**, and **IV**

I			
Bond	d, Å	Bond	d, Å
Cd(1)–N(4)	2.233(3)	S(1)–C(1)	1.725(4)
Cd(1)–S(1*A*)	2.506(11)	N(4)–C(1)	1.336(5)
Angle	ω, deg	Angle	ω, deg
N(4)Cd(1)N(4)'	97.75(16)	N(4)Cd(1)S(1*B*)'	117.19(9)
N(4)Cd(1)S(1*A*)	112.86(9)	S(1A)Cd(1)S(1*B*)'	100.01(5)
III			
Bond	d, Å	Bond	d, Å
Cd(1)–S(1*C*)	2.574(9)	Cd(1)–Cl(1*C*)	2.718(9)
Cd(1)–N(4)	2.34(2)	Cd(1)–O(2)	2.369(3)
Cd(1)–Cl(1)	2.604(9)	Cd(1)–O(2*C*)	2.413(3)
Angle	ω, deg	Angle	ω, deg
N(4)Cd(1)O(2)	90.07(9)	O(2*C*)Cd(1)Cl(1*C*)	80.46(6)
N(4)Cd(1)O(2*C*)	87.56(9)	S(1*C*)Cd(1)Cl(1)	102.23(3)
O(2)Cd(1)O(2*C*)	173.99(5)	N(4)Cd(1)Cl(1*C*)	94.96(7)
N(4)Cd(1)S(1*C*)	159.40(7)	O(2)Cd(1)Cl(1*C*)	94.24(6)
O(2)Cd(1)S(1*C*)	99.79(6)	O(2*C*)Cd(1)Cl(1)	106.11(6)
O(2*C*)Cd(1)S(1*C*)	84.21(6)	S(1*C*)Cd(1)Cl(1*C*)	83.85(3)
N(4)Cd(1)Cl(1)	80.34(7)	Cl(1)Cd(1)Cl(1*C*)	171.61(3)
O(2)Cd(1)Cl(1)	78.90(6)		
IV			
Bond	d, Å	Bond	d, Å
Cd(1)–O(2)	2.373(15)	Cd(2)–Cl(1)	2.560(6)
Cd(1)–N(3*A*)	2.459(18)	Cd(2)–O(3)	2.323(9)
Cd(1)–S(1)	2.569(6)	Cd(2)–O(2)	2.334(15)
Cd(1)–Cl(1)	2.579(6)	Cd(2)–Cl(2)	2.562(6)
Cd(1)–Cl(2*A*)	2.598(5)	Cd(2)–Cl(3)	2.564(6)
Cd(1)–Cl(3*A*)	2.646(6)	Cd(2)–N(4)	2.398(17)
Angle	ω, deg	Angle	ω, deg
O(2)Cd(1)N(3*A*)	78.89(6)	O(3)Cd(2)O(2)	82.3(3)
O(2)Cd(1)S(1)	100.22(4)	O(3)Cd(2)N(4)	164.7(2)
N(3*A*)Cd(1)S(1)	175.49(5)	O(2)Cd(2)N(4)	88.66(6)
O(2)Cd(1)Cl(1)	81.76(4)	O(2)Cd(2)Cl(1)	82.92(4)
N(3*A*)Cd(1)Cl(1)	86.12(4)	N(4)Cd(2)Cl(1)	88.53(4)
S(1)Cd(1)Cl(1)	98.156(19)	O(3)Cd(2)Cl(2)	83.3(3)
O(2)Cd(1)Cl(2*A*)	159.81(4)	O(2)Cd(2)Cl(2)	91.61(4)
N(3*A*)Cd(1)Cl(2*A*)	81.34(4)	N(4)Cd(2)Cl(2)	84.67(4)
S(1)Cd(1)Cl(2*A*)	99.81(2)	Cl(1)Cd(2)Cl(2)	171.38(19)
Cl(1)Cd(1)Cl(2*A*)	92.87(2)	O(3)Cd(2)Cl(3)	98.1(3)
O(2)Cd(1)Cl(3*A*)	96.23(4)	O(2)Cd(2)Cl(3)	179.45(4)
N(3*A*)Cd(1)Cl(3*A*)	85.58(4)	N(4)Cd(2)Cl(3)	90.97(5)
S(1)Cd(1)Cl(3*A*)	90.13(2)	Cl(1)Cd(2)Cl(3)	96.663(19)
Cl(1)Cd(1)Cl(3*A*)	171.69(2)	Cl(2)Cd(2)Cl(3)	88.759(19)
Cl(2*A*)Cd(1)Cl(3*A*)	86.28(2)		

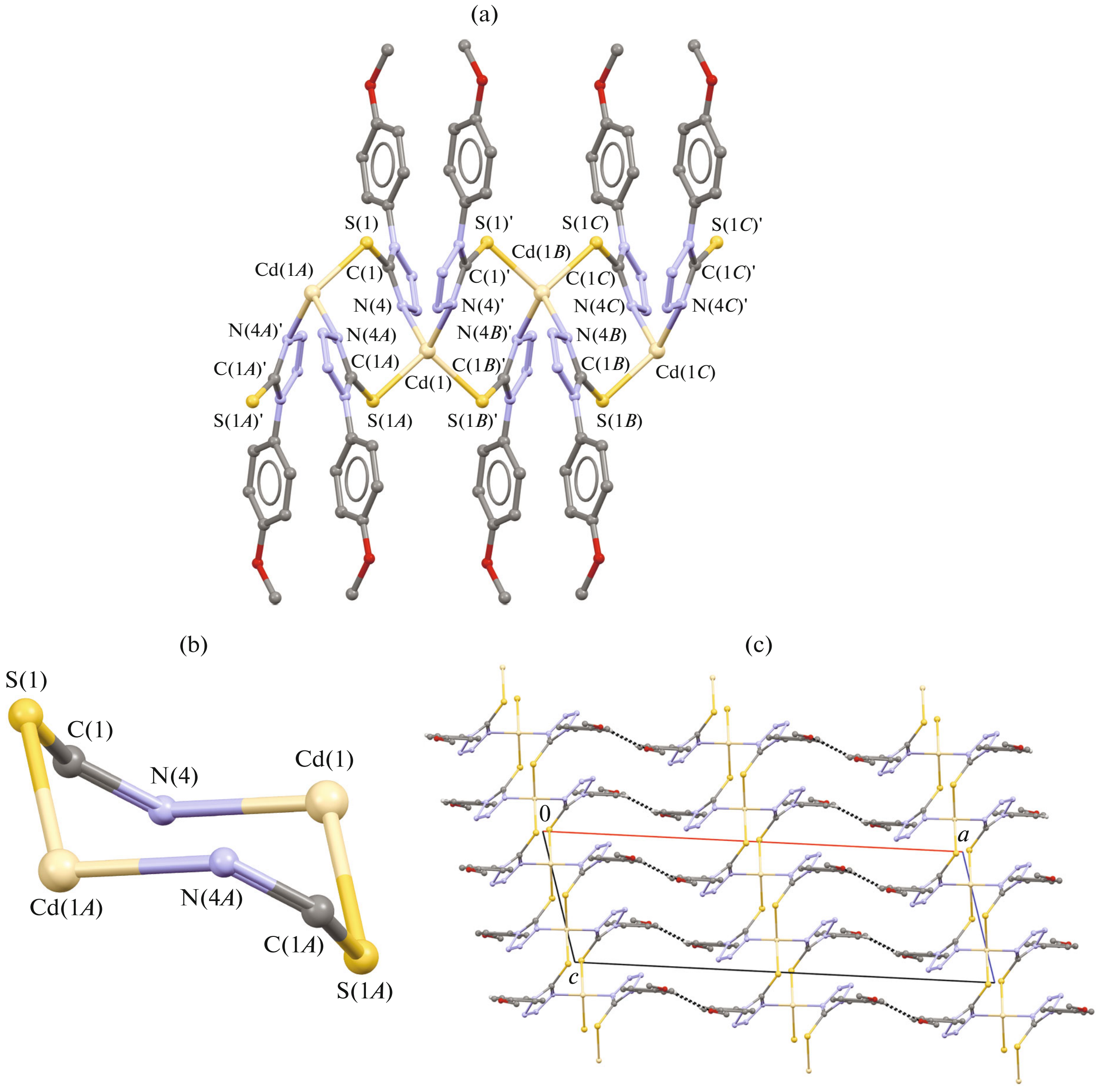


Fig. 1. (a) Fragment of the 1D chain of polymeric complex **I** (hydrogen atoms are omitted, thermal ellipsoids of 30% probability), (b) fragment of the framework of the 1D chain of complex **I** in the chair conformation, and (c) fragment of the crystal packing of complex **I** in the *a*0*c* projection (contacts O···H are shown by dotted lines; hydrogen atoms that are not involved in hydrogen contacts are omitted).

Cd(1)–Cl(1, 1*C*) and Cd(1)–O(2, 2*C*) distances are 2.604(9), 2.718(9) and 2.369(3), 2.413(3) Å, respectively.

The dihedral angle between the planes of the tetrazole and phenyl cycles in compound **III** is 84.93(14)°. The methyl group in the *o*-methoxyphenyl fragment in complex **III** lies in the plane of the phenyl ring (rms 0.04 Å). The $MeOC^{Ph}C^{Ph}$ torsion angle is 4.3(6)° (Table 2).

The molecules of ligand L^2 in complex **III** manifest the bidentate properties being arranged alternately from the top and from the bottom along the 1D chain to form bridging bonds between two adjacent metal (Cd) atoms (Fig. 3a).

The repeated unit of the framework of the 1D chain of complex **III** exists in the chair conformation (Fig. 3b). The Cd(1*A*) and Cd(1*C*) cadmium atoms shift from the mean plane Cl(1)O(2)Cd(1)Cl(1*C*)O(2*C*) (rms 0.0352 Å) by 0.909 and 0.738 Å, respectively. The dihedral angles between the planes Cd(1*A*)Cl(1)O(2) and Cl(1)O(2)Cd(1), Cd(1)O(2*C*)Cl(1*C*) and O(2*C*)Cl(1*C*)Cd(1*C*) are the same and equal to 25.48(8)°. The distance between the cadmium atoms in the chain of complex **III** is 3.77(5) Å.

Table 3. SEM study of the composition of compound **II**

Element	S, at %	Cl, at %	Cd, at %
Averaging	31.98	33.14	34.88
Standard deviation	0.23	0.12	0.3
Normalization to Cd	0.92	0.95	1

In the crystal packing, the 1D chains of complex **III** are arranged along the *b* axis. The Cl···H contacts are observed between the neighboring 1D chains in complex **III** (distance Cl(1)···H(9*A*) is 2.866(11) Å and ranges from the shortened and van der Waals interactions (between 2.67 and 2.97 Å [14]) (Fig. 3c).

Unlike complex **III**, compound **IV** was synthesized by the reaction of HL^2 with cadmium chloride in an ethanol–DMSO (9 : 1) mixture during prolonged storage at 20°C. As complex **III**, complex **IV** contains DMSO molecules and chlorine atoms.

Compound **IV** crystallizes in the monoclinic crystal system in the space group $P2_1/n$ and has the 1D chain structure of the composition $[Cd_2(\mu\text{-}L^2)(\mu\text{-}Cl)_3(\mu\text{-}DMSO)DMSO/EtOH]_n$. The coordination polyhedron of the cadmium atom is a distorted octahedron, and two different coordination environments of the central Cd^{2+} atoms (Cd(1) and Cd(2)) are observed in complex **IV**. The N(4) atom of ligand L^2 and O(3) of the terminal DMSO molecule occupy the axial positions in the environment of Cd(2), whereas in the environment of Cd(1) the axial positions are occupied by the S(1) and N(3*A*) atoms of two L^2 ligands. Each equatorial position of the Cd(1) and Cd(2) atoms contains three chlorine atoms: Cl(1, 2*A*, 3*A*) and Cl(1–3), respectively, as well as the O(2) atom of the bridging DMSO molecule (Fig. 4a).

The Cd(2)–O(3) and Cd(2)–N(4) bond lengths are 2.323(9) and 2.3983(17) Å, respectively. The Cd(1)–S(1) and Cd(1)–N(3*A*) distances are 2.569(6) and 2.459(18) Å and close to similar distances in complex **III** (Cd(1)–S(1*C*) and Cd(1)–N(4) are 2.574(9) and 2.34(2) Å). The axial angles O(3)Cd(2)N(4) and S(1)Cd(1)N(3*A*) are 164.7(2)° and 175.49(5)°, respectively. The Cd–Cl and Cd–O distances for Cd(2) and Cd(1) are 2.560(6)–2.564(6) and 2.334(2) Å, 2.579(7)–2.598(6) and 2.373(1) Å, respectively. The sums of bond angles between the equatorial substituents for Cd(2) is 360°.

The dihedral angles between the planes of the tetrazole and phenyl cycles in compound **IV** is 60.67(9)°. The methyl group in the *o*-methoxyphenyl fragment of complex **IV** lies in the plane of the phenyl ring (rms 0.0027 Å). The $MeOC^{Ph}C^{Ph}$ torsion angle is −1.3(4)° (Table 2).

The molecules of ligand L^2 in complex **IV** manifest the tridentate properties and are arranged, as in complex **III**, alternatively from the top and from the bottom along the 1D chain to form bridging bonds between three cadmium atoms.

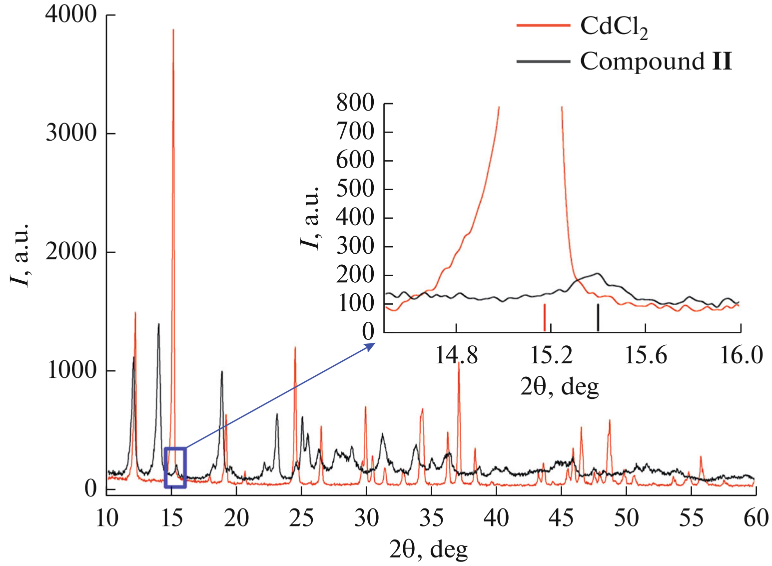


Fig. 2. Powder XRD patterns of compound **II** and $CdCl_2$.

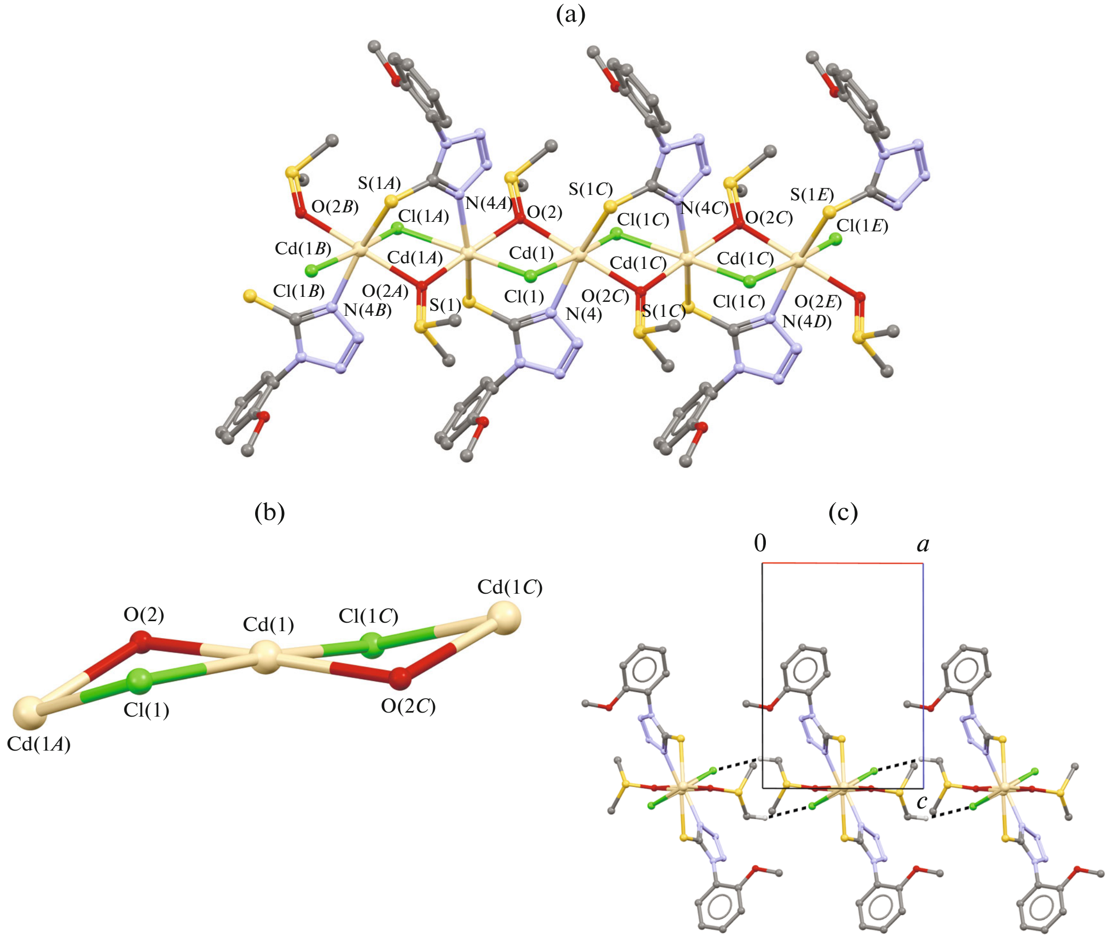


Fig. 3. (a) Fragment of polymeric 1D complex **III** (hydrogen atoms are omitted), and (b) fragment of the framework of the crystal packing of complex **III** in the chair conformation, and (c) fragment of the crystal packing of complex **III** in the *a*0*c* projection (contacts Cl···H are shown by dotted lines; hydrogen atoms that are not involved in hydrogen contacts are omitted).

The repeated unit of the framework of the 1D chain in complex **IV** has the boat conformation at the central Cd(2) atom (Fig. 4b). The Cd(1) and Cd(1*C*) atoms shift from the mean plane Cl(1)O(2)Cd(2)Cl(3)Cl(2) (rms 0.0688 Å) by 0.994 and 1.332 Å. The dihedral angles between the planes Cd(1)Cl(1)O(2) and Cl(1)O(2)Cd(2), Cd(2)Cl(2)Cl(3) and Cl(2)Cl(3)-Cd(1*C*) are 29.90(6)° and 40.76(3)°, respectively. The distance between the cadmium atoms (Cd(1)···Cd(2) and Cd(2)···Cd(1*C*)) in the chain of compound **IV** is 3.511(4) and 3.569(4) Å, respectively.

In the crystal, the 1D chains of complex **IV** are arranged along the crystallographic axis *b*. The Cl···H contacts are observed between the adjacent 1D chains in complex **IV** (distances Cl(1)···H(4*A*) and Cl(2)···H(5*A*) are 2.750(6) and 2.742(8) Å and range from the shortened to van der Waals interactions (between 2.67 and 2.97 Å [14]) (Fig. 4c).

The detailed analysis of the crystal packing of complex **IV** shows that the shortened nonvalent C···S contacts forming a 2D network in the (001) plane (distance C(6)···S(3) is 3.106(4) Å, which is substantially smaller than the shortened interactions of the S and C atoms (3.40 Å) [14]) are observed between the adjacent 1D chains along the *b* axis (Fig. 4d).

To conclude, it is established by XSA that ligands HL^1 and HL^2 possess several electron-donating centers in the complex formation reactions with cadmium chloride and manifest the bi- and tridentate properties to form 1D polymeric complexes **I**, **III**, and **IV**. It was found that, under other equivalent conditions, depending on the used ligands HL^1 or HL^2, which exist in the thione form under the reaction conditions, complexes **I** or **II** of different composition and structure were formed by the complex formation reactions with cadmium chloride in ethanol. It was revealed by the SEM method that compound **II** contained chlorine atoms in a ratio of 1 : 1 : 1 to cadmium and sulfur atoms, whereas complex **I**, whose structure was determined by XSA, contained no chlorine atoms. The XSA results for complex **III** showed that DMSO molecules are involved in complex formation along with

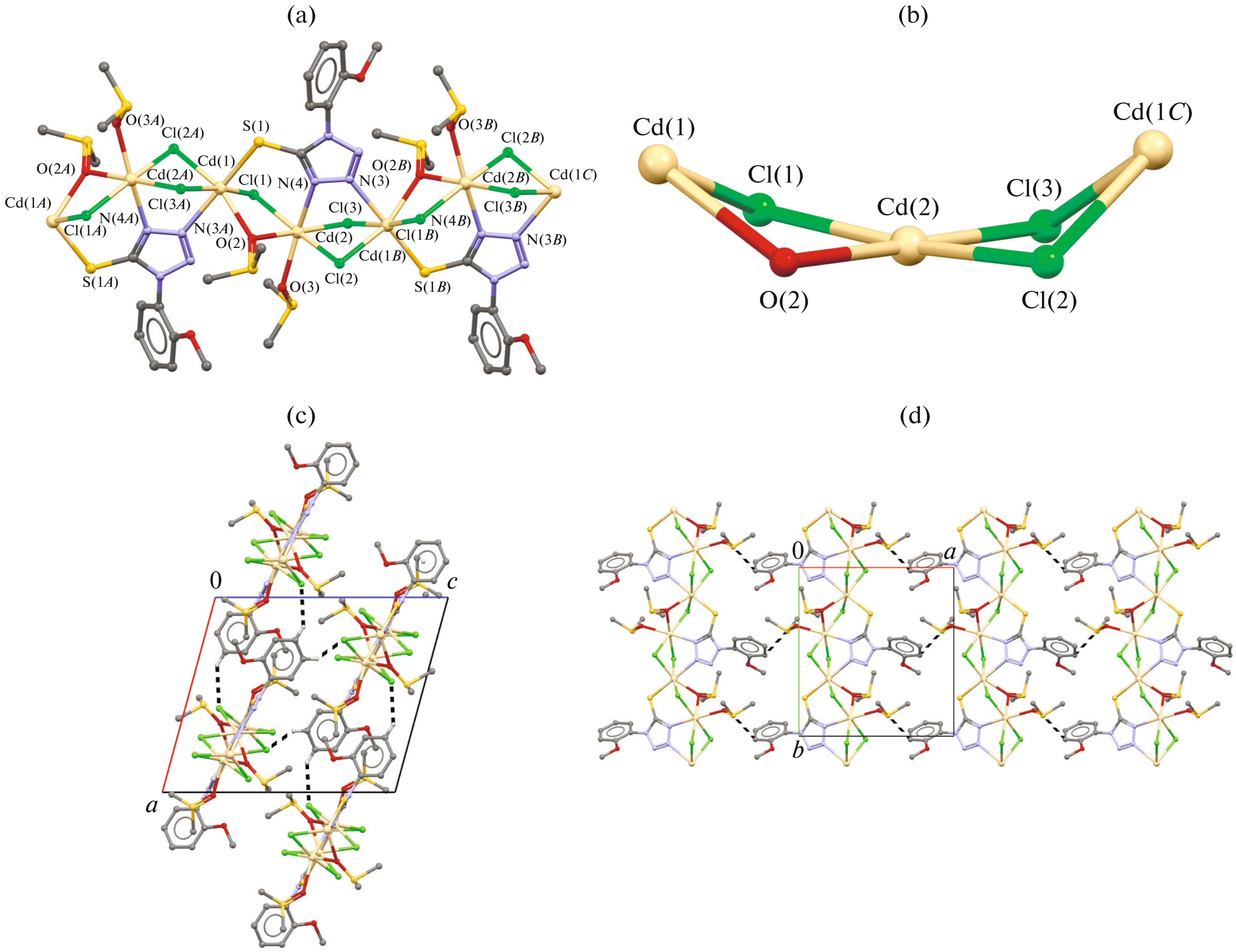


Fig. 4. (a) Fragment of polymeric 1D complex **IV** (hydrogen atoms and terminal EtOH molecules disordered with DMSO are omitted), (b) fragment of the framework of the 1D chain of complex **IV** in the boat conformation, (c) fragment of the crystal packing of complex **IV** in the *a*0*c* projection (contacts Cl···H are shown by dotted lines; hydrogen atoms that are not involved in hydrogen contacts are omitted), and (d) fragment of the crystal packing of complex **IV** in the *a*0*b* projection (contacts C···S are shown by dotted lines; hydrogen atoms are omitted).

chlorine atoms. Complex **IV** also contains DMSO molecules along with chlorine atoms. Whence it follows that the initial participation in the coordination of chlorine atoms in complexes **II**, **III**, and **IV** is caused by the structure of ligand L^2, namely, by the position of the methoxy group in the phenyl fragment of L^2 differed from L^1. It is most likely that the position of the MeO group also affects complex formation involving DMSO molecules, which predetermines the structures of 1D polymeric complexes **III** and **IV** differed from the structure of complex **I**. The crystal packings of complexes **I**, **III**, and **IV** are formed due to the O···H contacts and shortened Cl···H and C···S contacts.

ACKNOWLEDGMENTS

This work was carried out using equipment of the Center for Collective Use “Novel Materials and Resource Saving Technologies” (Lobachevskii State University, Nizhny Novgorod, Russia).

CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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Translated by E. Yablonskaya