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4-(2-Methoxyphenyl)-5-(Thiophen-2-Ylmethyl)-2,4-Dihydro-1*H*-1,2,4-Triazole-3-Thione and Its Complex with Cadmium Chloride: Molecular and Crystal Structures

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Abstract—Compound 4-(2-methoxyphenyl)-5-(thiophen-2-ylmethyl)-2,4-dihydro-1*H*-1,2,4-triazole-3-thione (LH) and its complex with cadmium(II) $C_{42.12}H_{39.50}N_9O_{3.12}S_6Cl_2Cd$ (**I**) are synthesized. Their molecular and crystal structures are determined by X-ray diffraction analysis (CIF files CCDC nos. 1835776 (LH) and 1547251 (**I**)). Free ligand LH is thione and in the crystal forms H-bonded centrosymmetric dimers by two hydrogen bonds N—H···S. Complex **I** has a distorted trigonal bipyramidal structure: the sulfur atoms lie in the base and the chlorine atoms occupy the axial positions. Compound LH manifests itself as a monodentate ligand (S) when forming complex **I** and retains the thione form. The molecule of complex **I** is stabilized due to strong intramolecular contacts N—H···Cl. The crystal packing of compounds LH and **I** is formed due to the intermolecular contacts C—H···π, H···S, H···O, and H···N.

Keywords: 4-(2-methoxyphenyl)-5-(thiophen-2-ylmethyl)-2,4-dihydro-1*H*-1,2,4-triazole-3-thione, cadmium complex, X-ray diffraction analysis, crystal packings

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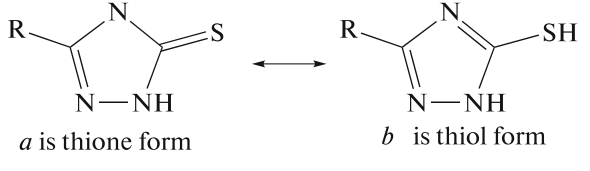
INTRODUCTION

As known from the literature data, 1,2,4-triazole-3-thiones and their derivatives exhibit a wide range of biological activity and find use as antibacterial, antiviral, analgesic, and fungicidal drugs [1–3]. These compounds are of scientific interest from the viewpoint of coordination chemistry since they can form various complexes with metal ions. Compounds of this type have several potentially active sites and can manifest themselves as monodentate (S or N) or bidentate (S,N or N,N) ligands forming polymer complexes or interacting with metal ions via their π-electron density [4, 5].

Similar heterocyclic compounds can exist in both thione and thiol forms. However, the thione form is more stable for mercaptotriazoles [6, 7].



a is thione form *b* is thiol form

Compound 4-(2-methoxyphenyl)-5-(thiophen-2-ylmethyl)-2,4-dihydro-1*H*-1,2,4-triazole-3-thione (LH) and its complex with cadmium(II) $C_{42.12}H_{39.50}N_9O_{3.12}S_6Cl_2Cd$ (**I**) were studied in this work. The structures of the synthesized compounds were determined by X-ray diffraction analysis.

EXPERIMENTAL

The following reagents were used as received: NaOH and $CdCl_2$ (reagent grade) and 2-thiophenacetic acid hydrazide and *o*-methoxyphenyl isothiocyanate (Acros Organics, Belgium).

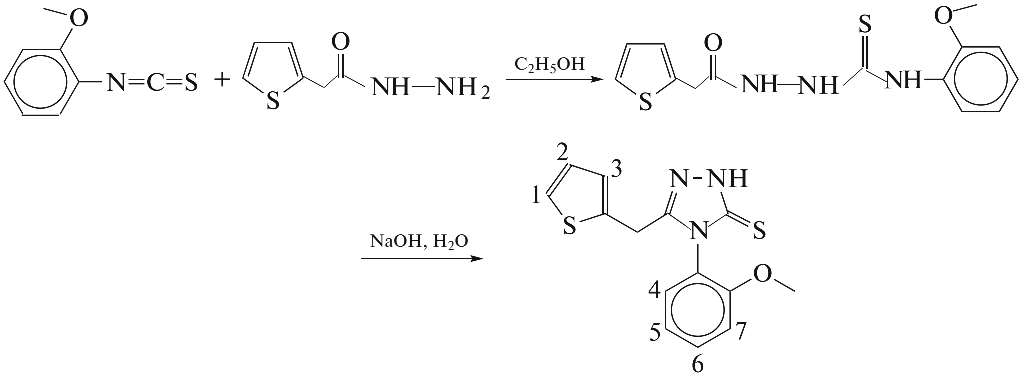
The melting points (or decomposition temperatures) were determined in evacuated sealed capillaries (presented without corrections).

The IR spectra of the samples were recorded on a Shimadzu IR Prestige-21 instrument in a range of 4000–400 cm^{-1} in KBr pellets (samples of the compounds were prepared by pressing pellets at the substance to KBr ratio equal to 1 : 200).

^1H NMR spectra were recorded on an Agilent DD2 400 spectrometer with a working frequency of 400 MHz in the internal stabilization mode of the 2H polar resonance line in $CDCl_3$ at 20°C. The signals were assigned using gradient 2D spectroscopy (proton–proton correlation GE-COSY). Chemical shifts are given in ppm relative to tetramethylsilane as an internal standard.

Synthesis of LH. *o*-Methoxyphenyl isocyanate (1.65 g, 10 mmol) was added to a solution of 2-thiophenacetic acid hydrazide (1.56 g, 10 mmol) in ethanol (50 mL) at 20°C. The reaction mixture was refluxed for 4 h and cooled to 20°C. The solvent was evaporated in vacuo, and a 10% aqueous solution of NaOH (50 mL) was poured to the obtained residue. The reaction mixture was refluxed for 6 h, cooled to 20°C, and filtered from nondissolved impurities. A 10% aqueous solution of HCl was added dropwise to the filtrate to reach acidic pH (pH = 2). A precipitate of compound LH that formed was filtered off, washed with H_2O (200 mL), and dried at 353 K. The substance for X-ray diffraction analysis was recrystallized from ethanol. The yield was 1.957 g (64.50%) (white crystals, mp = 175–176°C).

Ligand LH was synthesized according to the following scheme:



(LH)

IR (ν, cm^{-1}): 3439 (N–H), 1601 (Ph), 1574 (C=N), 1342 (C=S), 1022 (Ph–O–CH_3). ^1H NMR ($CDCl_3$), δ, ppm: 13.73 (s, 1H, NH), 7.48 (m, 1H, H^6), 7.32 (d, 1H, J = 5.4 Hz, H^1), 7.17 (d, 1H, J = 8.4 Hz, H^4), 7.13 (d, 1H, J = 7.7 Hz, H^7), 7.03 (m, 1H, H^5), 6.82 (dd, 1H, J = 5.4, 3.2 Hz, H^2), 6.53 (dd, 1H, J = 3.2, 1.2 Hz, H^3), 3.94 (q, 2H, CH_2), 3.65 (s, 3H, OCH_3).

For $C_{14}H_{13}N_3OS_2$

Anal. calcd, %	C, 55.42	H, 4.32	N, 13.85
Found, %	C, 55.78	H, 4.47	N, 13.73

Synthesis of complex I. A solution of $CdCl_2$ (0.184 g, 1 mmol) in anhydrous ethanol (15 mL) was added to a solution of thione LH (0.607 g, 2 mmol) in anhydrous ethanol (25 mL). The reaction mixture was refluxed for 5 h and cooled to 20°C. A precipitate of compound **I** that formed was filtered off, washed with ethanol (50 mL), and dried at 353 K. The substance for X-ray diffraction analysis was recrystallized from a DMSO–ethanol (1 : 1) mixture. The yield was 0.638 g (87.43%) (white crystals, mp = 151–152°C).

IR (ν, cm^{-1}): 3549 (N–H), 1603 (Ph), 1570 (C=N), 1342 (C=S), 1021 (Ph–O–CH_3). ^1H NMR ($CDCl_3$), δ, ppm: 13.74 (s, NH), 7.49 (m, 1H, H^6), 7.32 (d, 1H, J = 5.4 Hz, H^1), 7.17 (br.d, 1H, J = 8.4 Hz, H^4), 7.13 (br.d, 1H, J = 7.7 Hz, H^7), 7.02 (m, 1H, H^5), 6.82 (dd, 1H, J = 5.4, 3.2 Hz, H^2), 6.53 (br.d, 1H, J = 3.2 Hz, H^3), 3.94 (q, 2H, CH_2), 3.65 (s, 3H, OCH_3).

For $C_{42.12}H_{39}N_9O_{3.12}S_6Cl_2Cd$ (**I**)

Anal. calcd., %	C, 46.07	H, 3.56	N, 11.52
Found, %	C, 46.23	H, 3.48	N, 11.67

The crystals suitable for X-ray diffraction analysis were obtained by the crystallization of H_2L and complex **I** from ethanol.

X-ray diffraction analyses of H_2L and complex **I** were carried out on a Bruker Smart Apex diffractometer (ω scan mode, MoK_α radiation, $\lambda = 0.71073$ Å, T = 296 K). Experimental sets of reflection intensities were collected and integrated using the SMART [8] and SAINT programs [9]. 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 by the difference electron density synthesis that the C(9) atom of the methylene group in the structure of ligand L and one of the thiophene fragments in molecules A and B of complex **I** were disordered over two positions in the population ratios 0.70 : 0.30 (L), 0.65 : 0.35 (A), and 0.50 : 0.50 (B) (**I**). The hydrogen atoms involved in the

Table 1. Main crystallographic data and refinement parameters for compounds LH and complex **I**

Parameter	Value	
	LH	**I**
FW	208.24	1097.48
Temperature, K	296	296
Crystal sizes, mm	0.89 × 0.79 × 0.43	0.17 × 0.15 × 0.14
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/c$	$P\bar{1}$
a, Å	7.4596(4)	12.7815(5)
b, Å	12.8917(8)	18.4884(6)
c, Å	15.6803(9)	21.4836(8)
α, deg	90	86.2509(6)
β, deg	100.0439(9)	74.6971(6)
γ, deg	90	86.1703(7)
V, Å^3	1484.82(15)	48798(3)
Z	4	4
ρ_{calcd}, g/cm^3	1.357	1.494
μ, mm^{-1}	0.357	0.862
F(000)	632	2233
Range of data collection over θ, deg	28	28
Measured reflections	14686	51033
Independent reflections	3573	24019
Number of refined parameters	197	1258
R_1, wR_2 ($I > 2\sigma(I)$)	0.0462, 0.1298	0.0557, 0.1269
R_1, wR_2 (all data)	0.0522, 0.1353	0.1195, 0.1518
GOOF	1.005	1.000
T_{min}, T_{max}	0.742, 0.862	0.867, 0.889
Residual electron density ($\Delta\rho_{min}/\Delta\rho_{max}$), e Å^{-3}	–0.498/0.334	–0.886/0.888

intermolecular hydrogen bonds N–H···S and N–H···Cl in ligand L and in complex **I** were localized from the difference electron density synthesis and refined in the isotropic approximation. The coordinates of other hydrogen atoms in ligand L and in compound **I** were calculated from geometric concepts and refined with fixed positional (riding model) and thermal parameters ($1.5U_{iso}$(C) for the methyl groups and U_{iso}(H) = $1.2U_{iso}$(C) for all other groups). The structures were refined and an absorption correction was applied using the SHELXTL [10] and SADABS program packages [11]. The crystallographic data and parameters of X-ray diffraction experiments for ligand L and compound **I** are presented in Table 1. Selected bond lengths and bond angles for ligand L and compound **I** are given in Tables 2 and 3, respectively.

The structures were deposited with the Cambridge Crystallographic Data Centre (CIF files CCDC nos. 1835776 (H_2L) and 1547251 (**I**); ccdc.cam.ac.uk/getstructures).

RESULTS AND DISCUSSION

Ligand LH consists of three planar cycles: triazole ring A (N(1)–C(1)–N(2)–N(3)–C(2)), phenyl ring B (C(3)–C(8)), and thiophene ring C (C(10)–C(11)–C(12)–C(13)–S(2)) (Fig. 1). The planes of cycles B and C are almost perpendicular to the plane of triazole cycle A. The dihedral angles between the cycles are as follows: A/B 73.57°, A/C 72.23°, and B/C 43.75°. The triazole fragment is nearly planar (±0.0067 Å).

The N(1)–C(1) (1.366(2) Å), N(1)–C(2) (1.376(2) Å), N(2)–C(1) (1.330(2) Å), and N(2)–N(3) (1.376(2) Å) bond lengths in the mercaptotriazole fragment correspond to the ordinary character, whereas the C(1)=S(1) (1.687(3) Å) and C(2)=N(3) (1.297(2) Å) bonds are double.

Table 2. Selected bond lengths and bond and torsion angles in compound LH

Bond	*d*, Å	Angle	ω, deg
		S(1)C(1)N(1)	127.26(12)
		S(1)C(1)N(2)	129.10(12)
		C(1)N(1)C(2)	107.76(12)
S(1)–C(1)	1.677(2)	C(1)N(2)N(3)	113.72(13)
O(1)–C(4)	1.356(2)	N(1)C(2)N(3)	111.31(13)
O(1)–C(14)	1.417(3)	N(1)C(3)C(4)	117.71(15)
N(1)–C(1)	1.366(2)	N(1)C(3)C(8)	108.52(16)
N(2)–C(2)	1.376(2)	C(2)C(9)C(10)	112.9(2)
N(2)–N(3)	1.376(2)	C(3)C(4)O(1)	115.74(14)
N(3)–C(2)	1.297(2)	C(4)O(1)C(14)	118.57(17)
N(1)–C(3)	1.437(2)	Torsion angle	γ, deg
C(2)–C(9)	1.518(2)		
C(2)–C(9')	1.519(3)	S(1)C(1)N(1)C(3)	3.7(3)
C(9)–C(10)	1.515(2)	N(3)C(2)C(9)C(10)	26.7(7)
C(9')–C(10)	1.524(3)	C(1)N(1)C(3)C(8)	76.6(2)
		C(1)N(1)C(3)C(4)	102.33(2)
		C(5)C(4)O(1)C(14)	10.5(3)

Table 3. Selected bond lengths and bond and torsion angles in compound **I**

Bond	*d*, Å		Angle	ω, deg	
	A	B		A	B
Cd(1)–Cl(1)	2.7270(11)	2.5940(11)	Cl(1)Cd(1)Cl(2)	179.14(3)	176.11(4)
Cd(1)–Cl(2)	2.6292(11)	2.7492(11)	S(1)Cd(1)Cl(1)	81.00(3)	100.78(4)
Cd(1)–S(1)	2.5786(12)	2.5536(12)	S(1)Cd(1)Cl(2)	99.83(4)	76.04(4)
Cd(1)–S(3)	2.5609(11)	2.5879(12)	S(3)Cd(1)Cl(1)	98.24(3)	84.93(4)
Cd(1)–S(5)	2.5755(11)	2.6149(11)	S(3)Cd(1)Cl(2)	81.14(3)	98.79(4)
S(1)–C(1)	1.692(4)	1.693(4)	S(5)Cd(1)Cl(1)	98.31(3)	85.03(4)
S(3)–C(15)	1.692(4)	1.697(4)	S(5)Cd(1)Cl(2)	81.44(4)	94.50(3)
S(5)–C(29)	1.695(4)	1.688(4)	S(1)Cd(1)S(3)	124.41(4)	128.08(5)
O(1)–C(4)	1.363(5)	1.382(5)	S(1)Cd(1)S(5)	120.83(4)	118.54(4)
O(1)–C(14)	1.433(5)	1.444(6)	S(3)Cd(1)S(5)	114.30(4)	113.35(4)
O(2)–C(18)	1.348(7)	1.343(5)			
O(2)–C(28)	1.428(7)	1.423(6)	Torsion angle	γ, deg	
O(3)–C(32)	1.354(3)	1.354(5)			
O(3)–C(42)	1.415(6)	1.450(5)			
N(1)–C(3)	1.439(5)	1.436(5)		A	B
N(4)–C(17)	1.423(5)	1.427(5)			
N(7)–C(31)	1.432(5)	1.438(5)			
C(2)–C(9)	1.490(6)	1.493(7)			
C(9)–C(10)	1.504(6)	1.489(6)	Cd(1)S(1)C(1)N(2)	27.1(5)	4.1(5)
C(16)–C(23)	1.486(6)	1.487(6)	Cd(1)S(3)C(15)N(5)	18.0(5)	4.8(5)
C(23)–C(24)	1.496(7)	1.486(7)	Cd(1)S(5)C(29)N(8)	0.2(4)	23.0(5)
C(30)–C(37)	1.473(6)	1.497(6)			
C(37)–C(38)	1.474(5)	1.505(6)			

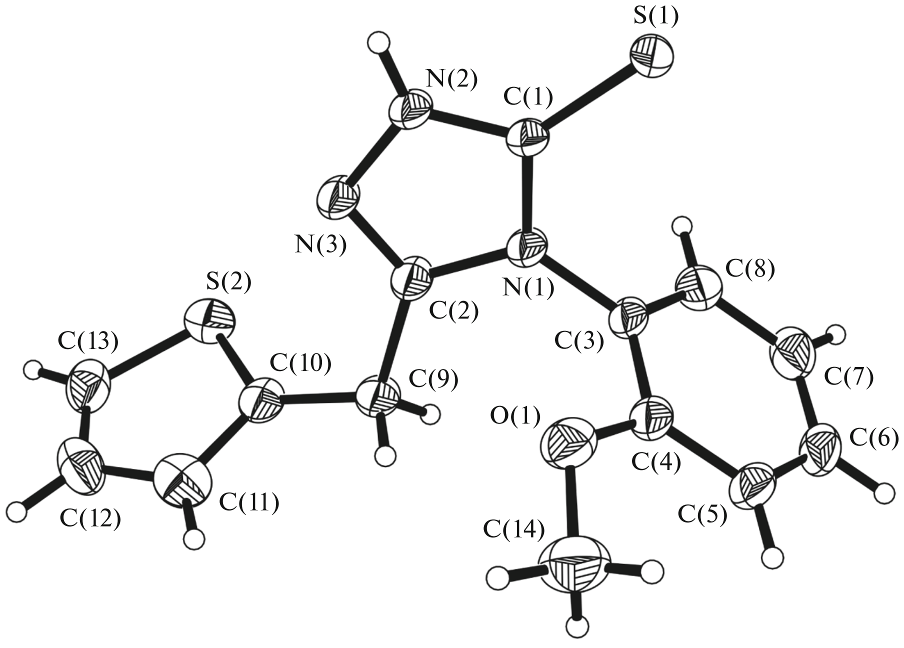


Fig. 1. Molecular structure of compound LH. Thermal ellipsoids are presented with 30% probability.

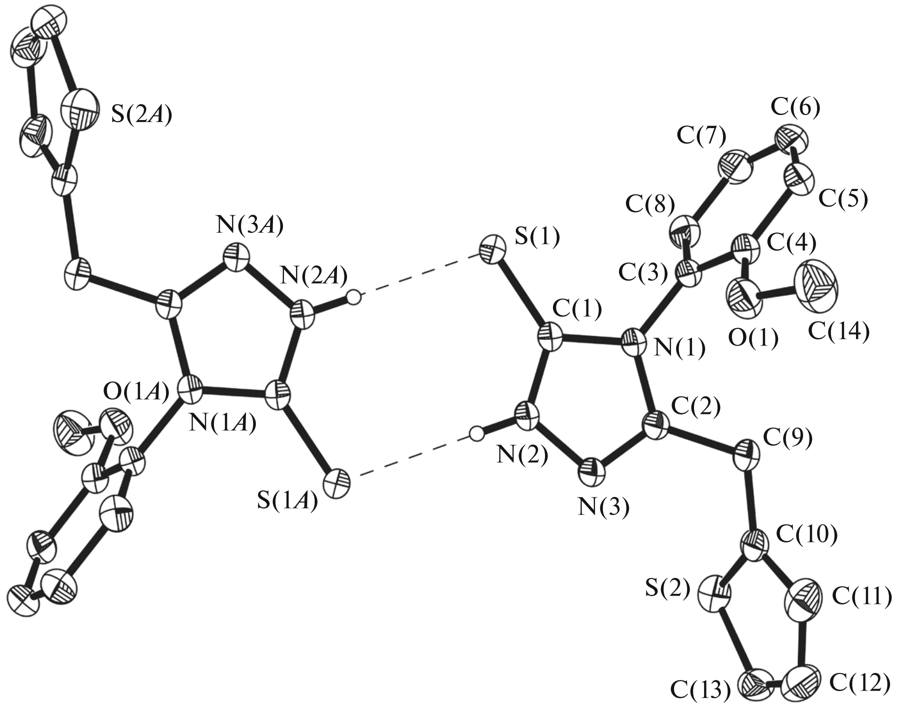


Fig. 2. Crystal structure of the H-bonded dimers in compound LH. Thermal ellipsoids are presented with 30% probability.

In the crystalline state molecules L are stabilized by strong intermolecular hydrogen bonds to form centrosymmetric dimers by two hydrogen bonds N(2)–H(2)···S(1) ($-x$, $1-y$, $-z$), N–H 0.86(2), H···S 2.38(3) Å, angle N–H···S 179(2)° [7] (the S···H contacts are shorter than the shortened contacts equal to 2.62 Å [12]) (Fig. 2). The dimers contain the central planar eight-membered cycle {S=C–N–H···S=C–N–H··· (±0.016 Å)}.

In the crystal the dimers of compound L form piles along the *a* axis. The hydrogen atoms of the methylene

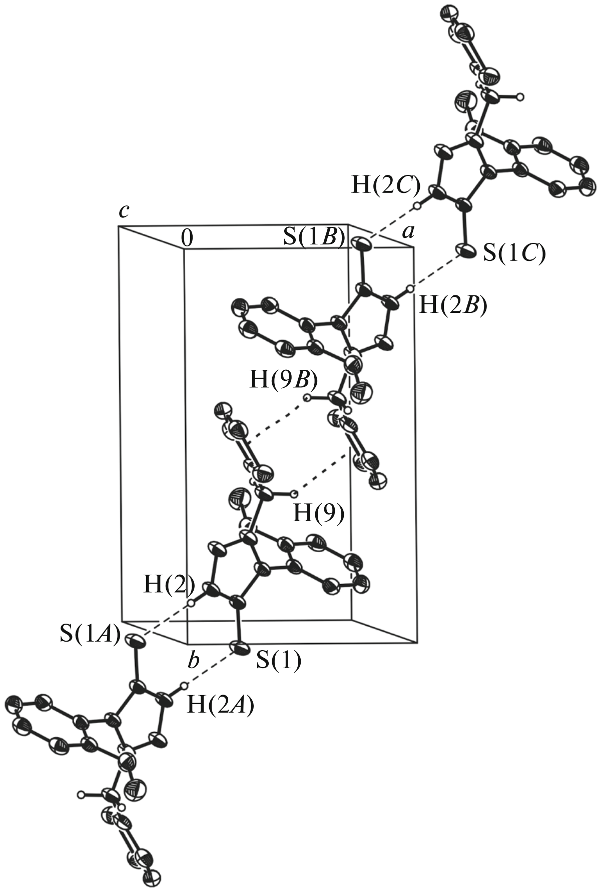


Fig. 3. Crystal packing of compound LH. Dashed lines show the centrosymmetric hydrogen bonds N–H···S and stacking interactions C–H···π along the *ab* diagonal.

groups are arranged between the dimers with a slight shift opposite to the center of the thiophene fragment. The distance from the H(9*A*) hydrogen atom of the methylene group to the plane of the thiophene cycle is 2.620 Å. The shortest C···H distances between the C(11) and H(9*A*) atoms (2.75 Å) indicate weak centrosymmetric stacking interactions C–H···π [13] propagating along the *ab* diagonal (Fig. 3).

In the single-crystal samples of complex **I** obtained after the crystallization of the compound from methanol, the asymmetric part of the crystal cell contains two crystallographically independent molecules of the complex (A and B). The crystal of compound **I** contains the solvate methanol molecule in a ratio of 1 : 8 to the cadmium complex. Thus, four molecules of complex **I** (two pairs of molecules A and B) are observed in the crystal cell. Molecules A and B have the identical structures (Table 3). The geometric characteristics of molecule A are presented in the discussion of the structure of complex **I**.

In complex **I**, the cadmium atom bound to two chlorine atoms additionally coordinates three neutral molecules of ligand L. The coordination polyhedron of the Cd atom is a distorted trigonal bipyramid, the base of which contains the sulfur atoms, and the chlorine atoms occupy the axial positions (Fig. 4). The Cd(1)–Cl(1,2) bond lengths were equal to 2.629(1) and 2.729(1) Å, respectively. The axial Cl(1)Cd(2)-Cl(2) angle was 179.14(4)°. The Cd–S bond lengths lie in a range of 2.561(1)–2.579(1) Å (average 2.572(1) Å). The equatorial SCdS angle range from 114.30(4)° to 124.41(4)° (average 119.85(4)°). The shift of the cadmium atom from the equatorial plane for molecules A and B is 0.075 and 0.020 Å, respectively. The dihedral angle between the planar cycles (A, B, C) in complex **I** lie in the ranges A/B 71.56°–85.50°, A/C 64.32°–76.19°, and B/C 30.02°–46.55°. The dihedral angles between the triazole fragments A/A in complex **I** lie in a range of 46.32°–87.89°.

It should be mentioned that compound LH behaves as a monodentate ligand (S) when forming complex **I** and retains the thione form.

In the crystal of complex **I**, molecules A and B are stabilized by strong intramolecular hydrogen bonds N–H···Cl (for A, N–H 0.98, H···Cl 2.09–2.14 Å, angles N–H···Cl 155°–164°; for B, N–H 0.98, H···Cl 2.08–2.18 Å, angles N–H···Cl 155°–164°) (contacts Cl···H in complex **I** are substantially shorter than the shortened interactions of the Cl and H atoms (2.67 Å) [12]).

Thus, the Cl(1) chlorine atom is involved in two intramolecular N–H···Cl contacts from two triazole ligands, and the Cl(2) atom participates in one analogous contact from the third triazole substituent.

The molecules of complex **I** in the crystal are packed in piles along the crystallographic *a* axis. The following C(67)–H(67*A*)···N(12) contacts are observed in these piles between the molecules: $x + 1$, y, z (C–H 0.93, H···N 2.49 Å, angle C–H···N 164° with the intermediate distance between the shortened and van der Waals interactions (between 2.64 and 2.34 Å [12])) (Fig. 5). The Cd···Cd distance in the pile is 12.782 Å. The following weak contacts exist between the parallel piles along the *c* axis: C(5)–H(5*A*)···S(7) (C–H 0.93, H···S 2.93 Å, angle C–H···S 156°, somewhat longer than the van der Waals interactions of the S and H atoms (2.92 Å [12])) and C(34)–H(34*A*)···O(1) (C–H 0.93, H···O 2.45 Å, angle C–H···O 134°, comparable with the van der Waals interactions of the O and H atoms (2.45 Å [12])).

To conclude, it was found by the X-ray diffraction method that in the crystalline state ligand L existed as thione and formed the H-bonded dimers. The reaction of LH with cadmium(II) chloride affords complex **I** with the distorted trigonal bipyramidal coordination mode of the Cd atom. The molecules of ligand L are coordinated with the cadmium atom in complex **I** and manifest themselves as a monodentate ligand (S) with the retention of the thione form. In the crystalline state the molecules of ligand L and complex **I** are sta-

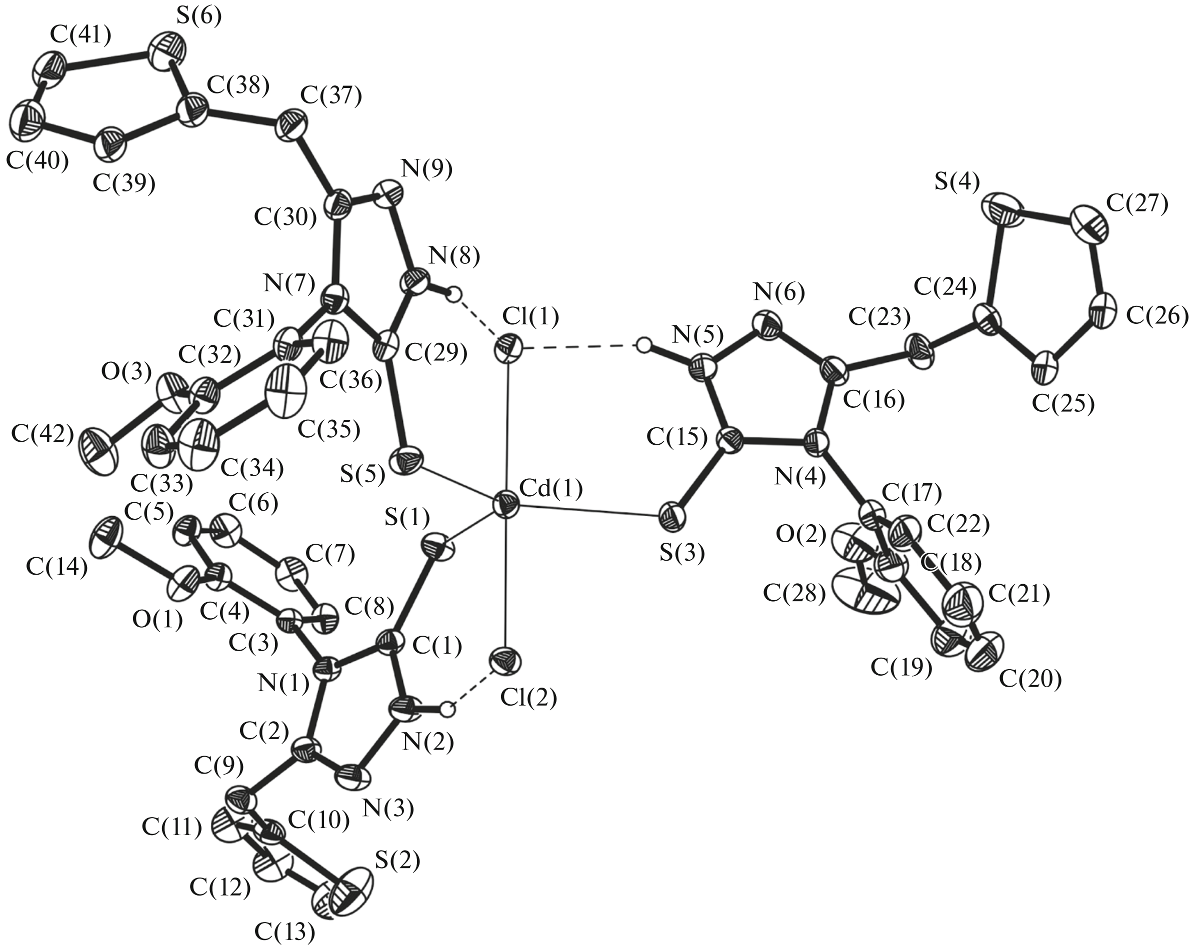


Fig. 4. Molecular structure of complex **I**. Hydrogen atoms that are not involved in intramolecular hydrogen bonds are omitted for clarity. Thermal ellipsoids are presented with 30% probability.

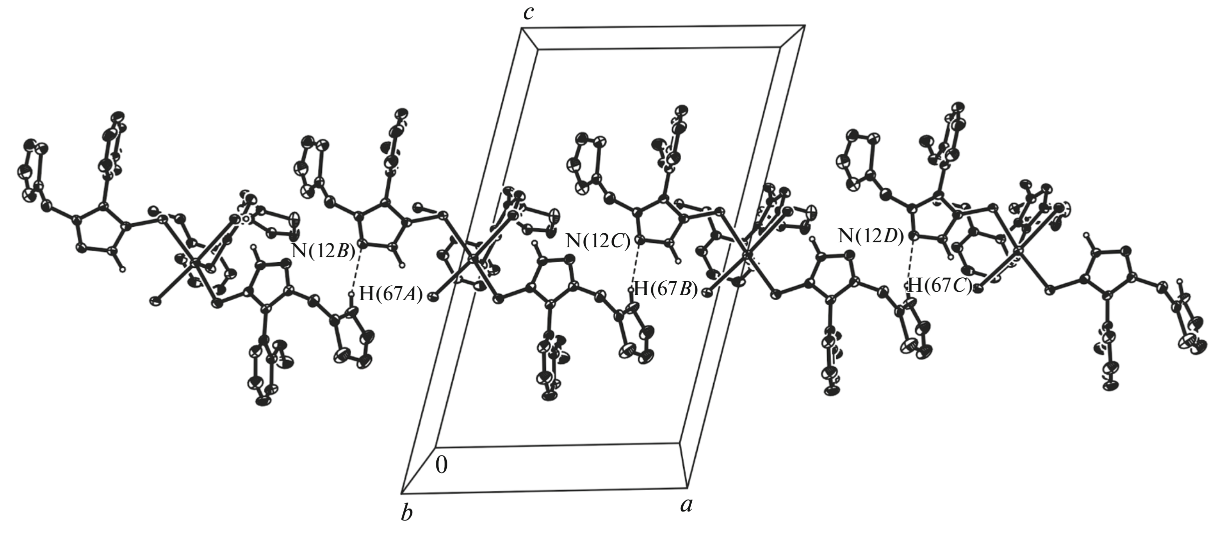


Fig. 5. Fragment of the crystal packing of complex **I** in the projection onto the *a*0*c* plane. Dashed lines show the H···N contacts.

bilized due to strong both inter- and intramolecular H···S and H···Cl contacts.

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