ISSN 1070-3284, Russian Journal of Coordination Chemistry, 2019, Vol. 45, No. 2, pp. 112–118. © Pleiades Publishing, Ltd., 2019.
Russian Text © R.K. Askerov, A.M. Magerramov, V.K. Osmanov, E.V. Baranov, G.N. Borisova, A.D. Samsonova, A.V. Borisov, 2019, published in Koordinatsionnaya Khimiya, 2019, Vol. 45, No. 2, pp. 99–105.

1-(2-Methoxyphenyl)-1,4-Dihydro-5*H*-Tetrazole-5-Thione and Its Complex with Cd(II): Molecular and Crystal Structures

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Received May 29, 2018; Revised August 21, 2018; Accepted August 24, 2018

Abstract—The molecular and crystal structures of 1-(2-methoxyphenyl)-1,4-dihydro-5*H*-tetrazole-5-thione (L) and its complex with cadmium(II) (**II**) are studied by X-ray diffraction analysis (CIF files CCDC nos. 1567109 (L) and 1547252 (**II**)). Free ligand L is nonplanar thione. The dihedral angle between the tetrazole and benzene cycles is 85.21(7)°. These cycles form centrosymmetric dimers in the crystal by two hydrogen bonds N–H···S. The dimers contain the central planar eight-membered ring {S=C–N–H···S=C–N–H···}. Complex **II** has a chain structure of the composition $[(C_8H_7N_4OS)_2Cd]_n$. The coordination mode of the Cd(II) atom is a distorted tetrahedron consisting of two nitrogen atoms and two sulfur atoms of four ligands L. The 1D chains contain the eight-membered rings {←S=C–N–Cd ← S=C–N–Cd} in the boat conformation. Weak intermolecular hydrogen bonds C–H···N are observed between the adjacent 1D chains along the *c* axis in the crystal.

Keyword: 1-(2-methoxyphenyl)-1,4-dihydro-5*H*-tetrazole-5-thione, crystal structure, polymer complex

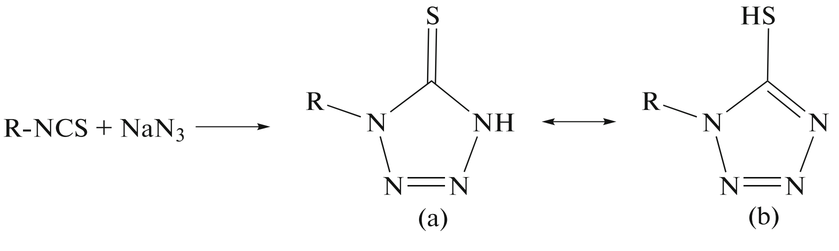
DOI: 10.1134/S1070328419020039

INTRODUCTION

The structures of 1-(2-methoxyphenyl)-1,4-dihydro-5*H*-tetrazole-5-thione (L) and its complex with cadmium(II) (**II**) were studied in this work.

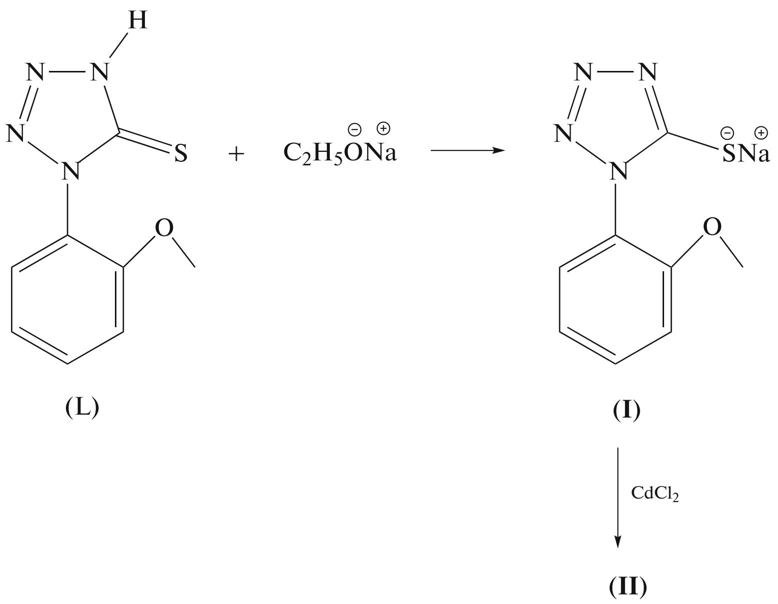
N-Substituted mercaptotetrazoles with several electron-donor centers can be used as ligands for the preparation of various coordination compounds [1–6].

It is known from the literature data that similar heterocyclic compounds can exist in both the thione (a) and thiol (b) forms (Scheme 1). The thione form is considered to be more stable for mercaptotetrazoles [7]. These compounds should be transformed into alkaline metal thiolates to substitute them at the sulfur atoms.



Scheme 1.

We synthesized ligand L, which was transformed into the corresponding thiolate (**I**) by the treatment with sodium ethylate, and compound **I** was used without isolation in the reaction with cadmium chloride to form complex **II** (Scheme 2).



Scheme 2.

The structures of compounds L and **II** were determined by X-ray diffraction analysis.

EXPERIMENTAL

The starting reagents NaN_3, $CdCl_2$ (not lower than reagent grade), and *o*-methoxyphenyl isothiocyanate (Acros Organics, Belgium) were used without additional purification.

Synthesis of thione L. *o*-Methoxyphenyl isothiocyanate (6.431 g, 39 mmol) was added to a solution of NaN_3 (2.53 g, 39 mmol) in H_2O (50 mL) at 20°C. The reaction mixture was refluxed for 2 h, cooled to 20°C, and filtered to remove nondissolved impurities. A 10% aqueous solution of HCl was added with stirring to the obtained solution to pH 2. The precipitate formed was filtered off, washed with water (200 mL), and dried at 353 K. The product for X-ray diffraction analysis was recrystallized from ethanol. The yield of L as white crystals with mp = 162–164°C (with decomposition) was 7.036 g (33.82%).

For $C_8H_8N_4OS$ (L)

Anal. calcd., %	C, 46.15	H, 3.85	N, 26.92
Found, %	C, 46.28	H, 3.97	N, 26.43

Synthesis of compound II. A solution of sodium ethylate (0.136 g, 2 mmol) in anhydrous C_2H_5OH (15 mL) was added to a solution of thione L (0.416 g, 2 mmol) in anhydrous C_2H_5OH (25 mL). A solution of $CdCl_2$ (0.184 g, 1 mmol) in anhydrous C_2H_5OH (15 mL) was added. The reaction mixture was refluxed for 5 h and cooled to 20°C. The precipitate formed was filtered off, washed with C_2H_5OH (50 mL), and dried at 353 K. The product for X-ray diffraction analysis was recrystallized from ethanol. The yield of compound **II** as white crystals with mp = 202–204°C (with decomposition) was 0.093 g (18.06%).

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

Anal. calcd., %	C, 36.50	H, 2.66	N, 21.29
Found, %	C, 36.03	H, 2.48	N, 21.57

X-ray diffraction analyses of compounds L and **II** 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 [9] 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. The hydrogen atom involved in the intermolecular hydrogen bond $N-H\cdots S$ in L was localized from the difference electron density synthesis and refined in the isotropic approximation. Other hydrogen atoms in L and **II** were placed in geometrically calculated positions and refined isotropically with fixed thermal parameters $U_{iso}(H) = 1.2U_{iso}(C)$. The structure was refined and an absorption correction was applied using the SHELXTL [10] and SADABS [11] program packages. The crystallographic data and X-ray diffraction experimental parameters are presented in Table 1.

The structures were deposited with the Cambridge Crystallographic Data Centre (CIF files CCDC nos. 1567109 (L) and 1547252 (**II**); ccdc.cam.ac.uk/getstructures).

Table 1. Main crystallographic data and refinement parameters for compounds L and **II**

Parameter	Value	
	L	**II**
Empirical formula	$C_8H_8N_4OS$	$C_{16}H_{14}N_8O_2S_2Cd$
FW	208.24	526.87
Crystal sizes, mm	0.21 × 0.17 × 0.10	0.65 × 0.074 × 0.06
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1/c$	*Pccn*
a, Å	5.0808(7)	12.8945(8)
b, Å	19.402(3)	18.9350(12)
c, Å	9.9024(14)	8.5599(6)
β, deg	90.967(3)	90
V, Å^3	976.0(2)	2090(6)
Z	4	4
ρ_{calcd}, g/cm^3	1.417	1.674
μ, mm^{-1}	0.303	1.274
F(000)	432	1048
Range of data collection over θ, deg	25	25
Measured reflections	10754	19754
Independent reflections	2793	2517
Number of refined parameters	131	133
R_1 ($I > 2\sigma(I)$)	0.0471	0.0216
wR_2 (all data)	0.0943	0.0565
GOOF	1.007	1.007
T_{min}; T_{max}	0.6474; 0.7461	0.384; 0.746
Residual electron density (ρ_{min}/ρ_{max}), e Å^{-3}	−0.318/0.378	−0.156/0.781

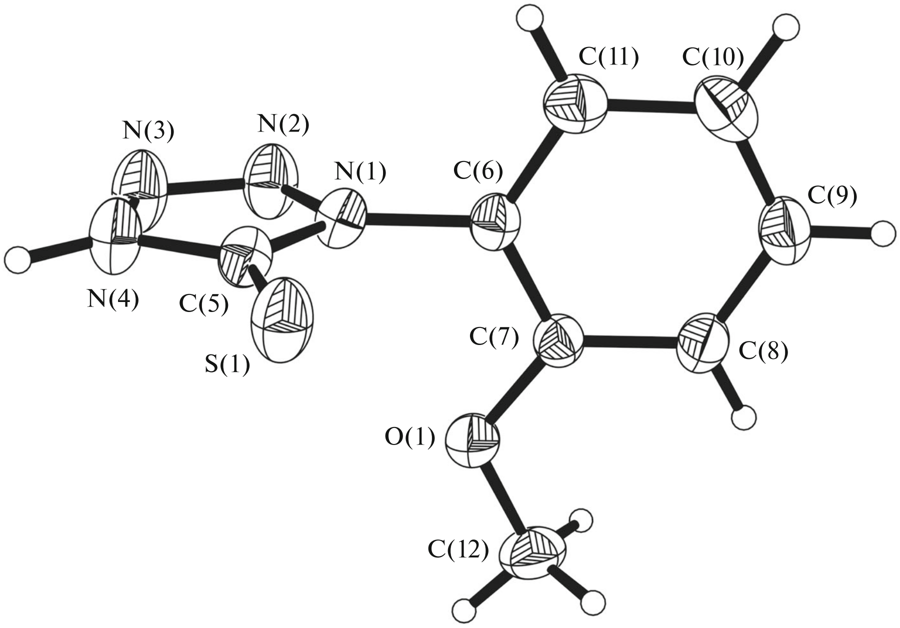


Fig. 1. Molecular structure of L. Thermal ellipsoids are presented with 30% probability.

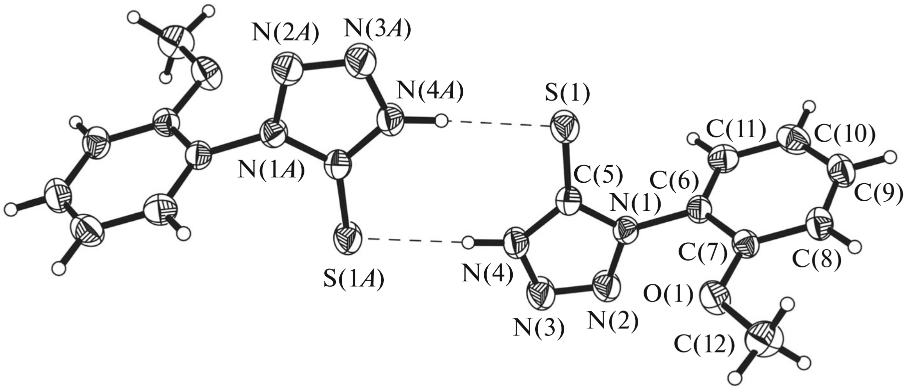


Fig. 2. Crystal structure of the H-bonded dimers in compound L. Thermal ellipsoids are presented with 30% probability.

RESULTS AND DISCUSSION

The molecular structure of L is shown in Fig. 1. Selected bond lengths and bond and torsion angles in compounds L and **II** are presented in Table 2.

Compound L consists of two planar fragments: *o*-methoxyphenyl and mercaptotetrazole cycles. The dihedral angle between their planes is 85.21(7)°, and the torsion angle C(7)–C(6)–N(1)–C(5) is 93.3(2)°. The methyl group in the methoxyphenyl fragment lies in the cycle plane. The torsion angle C(8)–C(7)–O(1)–C(12) is 0.4(2)°. The N(1)–N(2) (1.3675(19) Å), N(1)–C(5) (1.351(2) Å), N(3)–N(4) (1.354(2) Å), and N(4)–C(5) (1.346(2) Å) distances in the mercaptotetrazole fragment correspond to ordinary bonds, whereas the N(2)=N(3) (1.2773(19) Å) and C(5)=S(1) (1.6680(18) Å) distances correspond to double bonds, which confirms the thione form of compound L in the free state. All bonds in the structure of L correspond to statistical averages [12].

In crystal molecules L form centrosymmetric dimers by two hydrogen bonds N(4)–H(4)···S(1) (1 – *x*, 1 – *y*, 1 – *z*) (N–H 0.93(2), H···S 2.30(2) Å, angle N–H–S 178(3)°) (Fig. 2).

The dimers contain the central planar (+0.0169 Å) eight-membered ring {S=C–N–H···S=C–N–H}. The dimers of compound L are linked into zigzag lay-

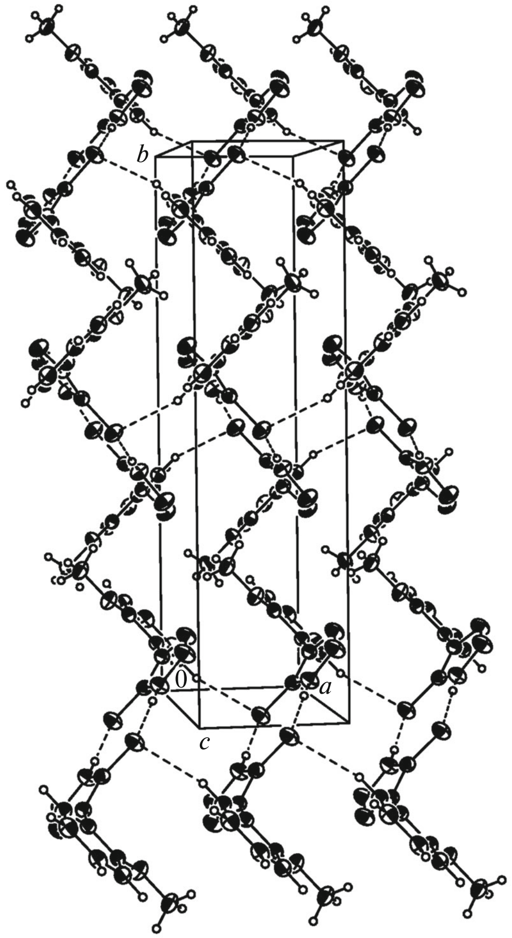


Fig. 3. Fragment of the crystal packing of zigzag layers in compound L along the *b* axis. Weak hydrogen bonds C—H···S are shown by dashed lines.

ers along the *b* axis. The layers are connected by weak intermolecular hydrogen bonds C(11)—H(11*A*···S(1) (*x* – 1, *y*, *z*) (C—H 0.930(2), H···S 2.915(2) Å, angle C—H···S 156(2)°) [13] along the *a* axis (Fig. 3).

Complex **II** has the 1D chain structure and the composition $[(C_8H_7N_4OS)_2Cd]_n$. The coordination polyhedron of the cadmium(II) cation is a distorted tetrahedron containing two nitrogen atoms and two sulfur atoms of four ligands L [6]. The Cd—S and Cd—N distances (2.5035(4) and 2.2300(14) Å, respectively) and the NCdN and SCdS angles (119.80(7)° and 129.12(2)°, respectively) are correspondingly equal. It should be mentioned that the character of bonds in the tetrazole fragment of ligand L changes upon the formation of complex **II**, namely, the C(5)—S(1) bond (1.716(2) Å) becomes ordinary and the N(4)=C(5) bond (1.326(2) Å) becomes double (Table 2), which is determined by a higher chemical affinity of the cadmium cation to the sulfur atom than to the nitrogen atom. Therefore, unlike the free state, the tetrazole ligand L in complex **II** takes the thiol form. The dihedral angle between the planes of the phenyl and mercaptotetrazole fragments is 66.34(7)°, and the torsion angles C(7)—C(6)—N(1)—C(5) and C(8)—C(7)—O(1)—C(12) are 69.6(2)° and 4.5(3)°, respectively. The 1D chains in the crystal of compound **II** contain the eight-membered rings {←N=C—S—Cd—S—C=N → Cd} in the boat conformation. The Cd···Cd distance is 4.280 Å. The chains of complex **II** in the crystal are arranged along the *c* axis (Fig. 4).

Weak intermolecular hydrogen bonds C(10)—H(10*A*)···N(2) (–*x* + 3/2, *y*, –1/2 + *z*) (C—H 0.930(2), H···S 2.706(2) Å, angle C—H···N 148(2)° [13] (Fig. 5)) are observed between the adjacent 1D

Table 2. Selected bond lengths (d) and bond (ω) and torsion (γ) angles in compounds L and **II**

		L			
Bond	d, Å	Bond	d, Å	Bond	d, Å
S(1)–C(5)	1.6680(18)	N(3)–N(4)	1.354(2)	O(1)–C(12)	1.427(2)
N(1)–C(5)	1.351(2)	N(4)–C(5)	1.346(2)	C(6)–C(11)	1.374(2)
N(1)–N(2)	1.3675(19)	N(1)–C(6)	1.437(2)		
N(2)–N(3)	1.2773(19)	O(1)–C(7)	1.356(2)		
Angle	ω, deg	Angle	ω, deg	Angle	γ, deg
N(1)C(5)N(4)	102.11(15)	N(4)C(5)S(1)	129.35(14)	C(5)N(1)C(6)C(11)	87.3(2)
C(5)N(1)N(2)	111.00(14)	N(1)C(5)S(1)	128.53(13)	C(5)N(1)C(6)C(7)	93.3(2)
C(5)N(4)N(3)	111.79(16)	C(11)C(6)N(1)	118.52(15)	C(12)O(1)C(7)C(8)	0.4(3)
N(3)N(2)N(1)	107.48(15)	C(7)C(6)N(1)	117.65(14)	C(6)N(1)C(5)S(1)	3.0(3)
N(2)N(3)N(4)	107.62(15)	C(7)O(1)C(12)			
		II			
Bond	d, Å	Bond	d, Å	Bond	d,Å
Cd(1)–N(4)	2.228(4)	N(2)–N(3)	1.280(2)	C(6)–C(7)	1.392(3)
Cd(1)–S(1)	2.4972(11)	N(3)–N(4)	1.357(2)	C(6)–C(11)	1.374(2)
S(1)–C(5)	1.7155(16)	N(4)–C(5)	1.326(2)	O(1)–C(7)	1.354(2)
N(1)–C(5)	1.349(2)	N(1)–C(6)	1.434(2)	O(1)–C(12)	1.427(3)
N(1)–N(2)	1.3616(19)				
Angle	ω, deg	Angle	ω, deg	Angle	γ, deg
N(4)Cd(1)N(4*A*)	119.80(7)	C(11)C(6)N(1)	119.17(16)	C(7)C(6)N(1)C(5)	69.6(2)
S(1)Cd(1)S(1*E*)	129.12(2)	N(1)C(5)S(1)	127.52(12)	C(8)C(7)O(1)C(12)	4.5(3)
C(5)N(1)C(6)	131.99(14)	C(7)C(6)N(1)	119.16(15)		
N(2)N(1)C(6)	118.97(14)	N(4)C(5)S(1)	126.35(12)		

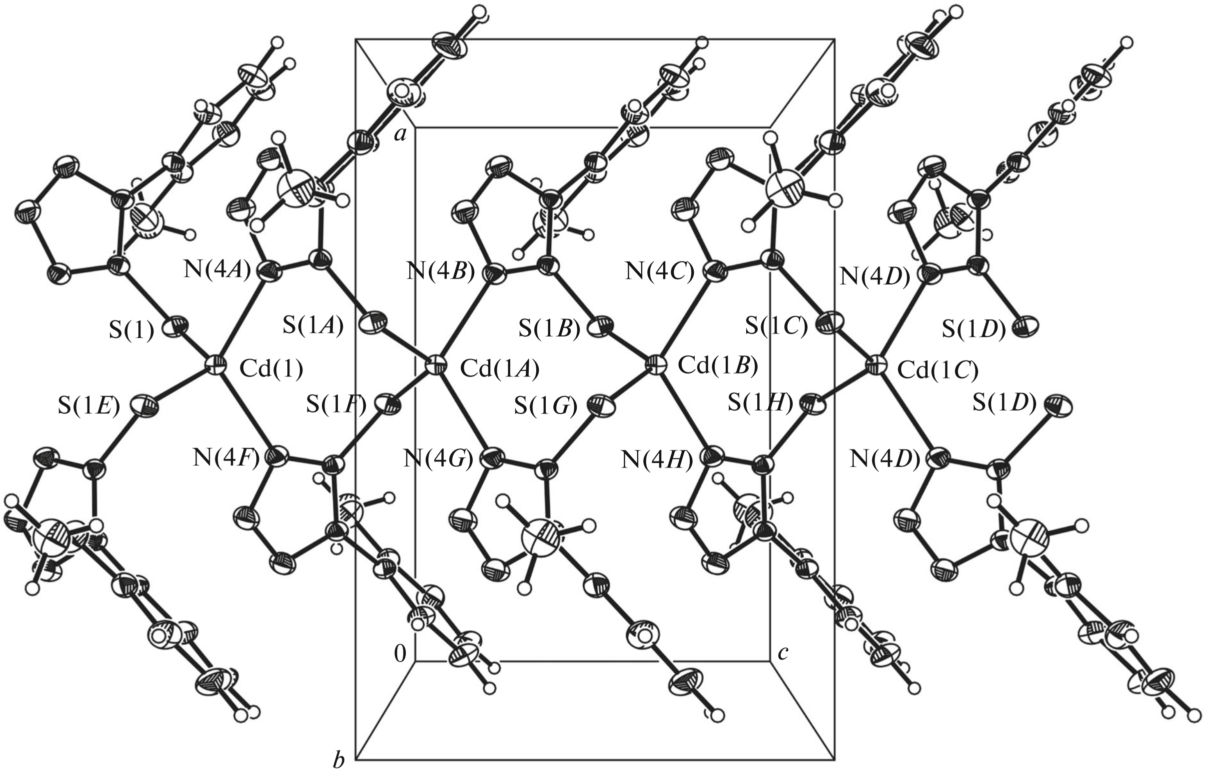


Fig. 4. Crystal structure of 1D polymer chains in compound **II** along the *c* axis.

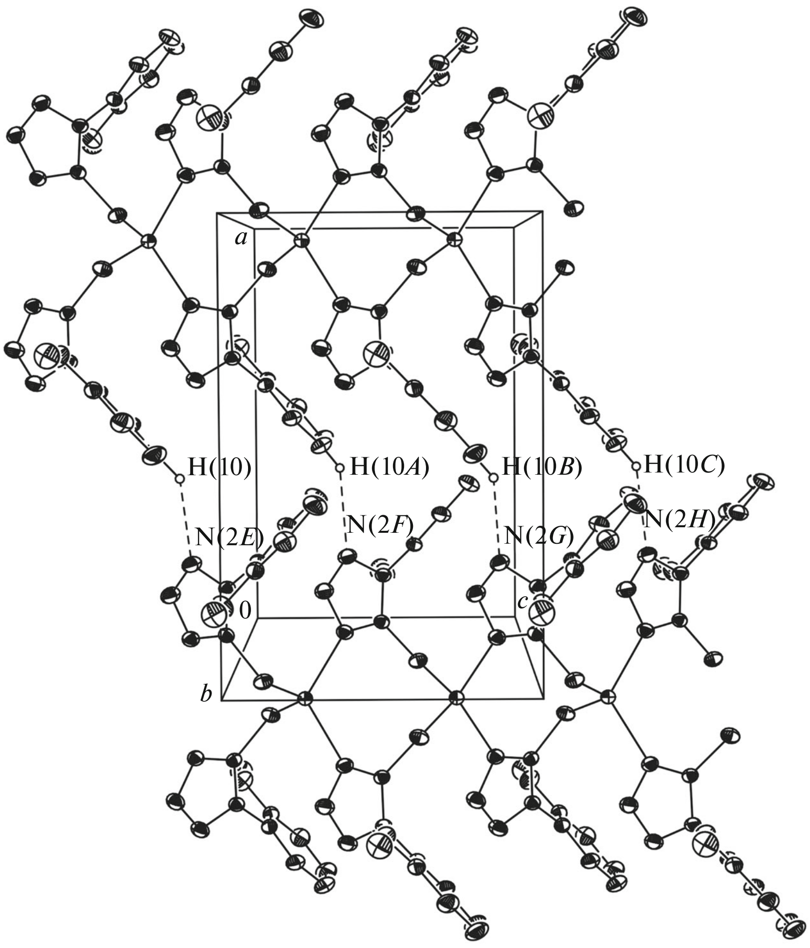


Fig. 5. Fragment of the crystal packing of compound **II** in the projection onto the *a*0*c* plane. Weak hydrogen bonds C–H···N between the adjacent polymer chains along the *c* axis are shown by dashed lines.

chains along the *c* axis in the crystal packing of complex **II**.

REFERENCES

1. Ma, C.L., Zhang, Q., Sun, J.F., and Zhang, R.F., *J. Organomet. Chem.*, 2006, vol. 691, p. 2567.
2. Ilie, A., Rat, C.I., Scheutzow, S., Kiske, C., et al., *Inorg. Chem.*, 2011, vol. 50, p. 2675.
3. Li, Y., Wang, C.Q., Bian, H.D., et al., *J. Coord. Chem.*, 2012, vol. 65, no. 20, p. 3665.
4. Sanina, N.A., Kozub, G.I., and Kondrat, T.A., *J. Mol. Struct.*, 2013, vol. 1041, p. 183.
5. Bharty, M.K., Dani, R.K., and Kushawaha, S.K., *Polyhedron*, 2015, vol. 88, p. 208.
6. Song, J.F., Wang, J., and Li, S.Z., *J. Mol. Struct.*, 2017, vol. 1129, p. 1.
7. Shtefan, E.D. and Vvedenskii, V.Yu., *Usp. Khim.*, 1995, vol. 65, no. 4, p. 326.
8. SMART. Bruker Molecular Analysis Research Tool. Version 5.632, Madison: Bruker AXS, 2005.
9. SAINT. Data Reduction and Correction Program. Version 8.34A, Madison: Bruker AXS, 2014.
10. Sheldrick, G.M., SADABS. Program for Absorption Correction, Göttingen: Univ. of Göttingen, 1996.
11. Sheldrick, G.M., *Acta Crystallogr., Sect C: Struct. Chem.*, 2015, vol. 71, p. 3.
12. Allen, F.H., Watson, D.G., Brammer, L., et al., *International Tables for Crystallography*, 2006, ch. 9.5, p. 790.
13. Zefirov, Yu.V. and Zorkii, P.M., *Usp Khim.*, 1995, vol. 64, no. 4, p. 446.

Translated by E. Yablonskaya