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Original Russian Text © 2018 R. K. Askerov, A. M. Maharramov, V. K. Osmanov, E. V. Baranov, G. N. Borisova, P. V. Dorovatovskii, V. N. Khrustalev, A. V. Borisov.

MOLECULAR AND CRYSTAL STRUCTURE OF 1-(4-FLUOROPHENYL)-1,4-DIHYDRO-1*H*-TETRAZOLE-5-THIONE AND ITS COMPLEX WITH CADMIUM(II)

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The molecular and crystal structures of 1-(4-fluorophenyl)-1,4-dihydro-1*H*-tetrazole-5-thione (**I**) and its complex with cadmium(II) (**II**) are studied by single crystal XRD. Free ligand **I** is thione; it has a non-planar structure (the torsion angle between the tetrazole and benzene rings is 54.99(7)°) and forms H-bonded centrosymmetric dimers via two N–H…S hydrogen bonds in the crystal. The dimers contain a central planar eight-membered {S=C–N–H…S=C–N–H…} ring. Complex **II** has a chain structure with the composition $[(C_7H_4N_4FS)_2Cd]_n$. The environment of the Cd(II) atom consists of two nitrogen atoms and two sulfur atoms from four ligands **I** and represents a distorted tetrahedron. When complex **II** forms, ligand **I** converts into the thiol form. Infinite 1D chains contain eight-membered {←S=C–N–Cd←S=C–N–Cd} rings in a *chair* conformation. The chains in the crystal are arranged in layers parallel to the (101) plane due to secondary intermolecular F…F and π–π-stacking interactions.

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INTRODUCTION

The article studies the structure of 1-(4-fluorophenyl)-1,4-dihydro-1*H*-tetrazole-5-thione (**I**) and its complex with cadmium(II) (**II**).

N-Substituted mercaptotetrazoles have several electron-donor centers and can be used as polydentate ligands in complexing reactions with different metals to produce various supramolecular architectures [1-6].

As is known from the literature data, these heterocyclic compounds can exist in both thione (a) and thiol forms (b). However, the thione form is considered to be more stable for mercaptotetrazoles [7].

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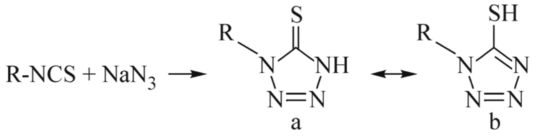

First we prepared initial compound **I** according to the known procedure and then synthesized complex **II** by the complexing reaction of organic ligand **I** with cadmium(II) chloride. The structure of synthesized compounds **I** and **II** was studied by single crystal X-ray diffraction (XRD).

EXPERIMENTAL

The initial NaN_3, $CdCl_2$ reagents were of at least chemically pure grade and used without additional purification. 4-Fluorophenylisothiocyanate was bought from Acros Organics (Belgium) and used without further purification.

Synthesis of 1-(4-fluorophenyl)-1,4-dihydro-1H-tetrazole-5-thione (I). To a solution of 1.9 g (29 mmol) of NaN_3 in 50 ml of H_2O 3 g (19.6 mmol) of 4-fluorophenylisothiocyanate were added at 20 °C. The reaction mixture was boiled for 2 h, cooled to 20 °C; then the aqueous solution was filtered from undissolved impurities and a 10% aqueous solution of HCl was added to it with stirring to pH = 2. The precipitate of compound **I** was filtered off, washed with 200 ml of water, and dried at 80 °C. Yield was 2.43 g (63.23%). White crystals. T_{melt} = 150-152 °C. Found (%): C 42.37, H 2.41, N 28.73. $C_7H_5FN_4S$. Calculated (%): C 42.85, H 2.57, N 28.56.

Synthesis of compound (II). To a solution of 0.392 g (2 mmol) of 1-(4-fluorophenyl)-1,4-dihydro-1H-tetrazole-5-thione **I** in 25 ml of 96% C_2H_5OH a solution of 0.112 g (1 mmol) of $CdCl_2$ in 15 ml of 96% C_2H_5OH was added. The reaction mixture was boiled for 2 h and cooled to 20 °C. The precipitate of compound **II** was filtered off, washed with 50 ml of C_2H_5OH, and dried at 80 °C. The substance was recrystallized from ethanol. Yield was 0.067 g (15.47%). White crystals. T_{melt} = 255-256 °C. Found (%): C 33.21, H 1.54, N 22.76. $C_{14}H_8CdF_2N_8S_2$. Calculated (%): C 33.44, H 1.6, N 22.63.

Single crystal XRD. Crystals for XRD experiments were obtained by recrystallization of **I** and **II** from ethanol. The single crystal XRD study was carried out on the “BELOK” synchrotron beamline at the National Research Center “Kurchatov Institute” (λ = 0.96990 Å, Rayonix SX165 CCD detector, φ-scanning) (compound **I**) and a Bruker Smart Apex diffractometer ($\text{Mo}K_\alpha$ radiation, λ = 0.71073 Å, φ- and ω-scanning) (compound **II**). Importantly that it is synchrotron radiation that allowed us to determine the structure of compound **I** with a high accuracy of measuring geometric parameters because the single crystals of this compound were of rather poor quality which we failed to improve. The experimental sets of reflection intensities were collected and integrated using the MARCCD [8] and iMOSFLM programs respectively, being the subroutines of the CCP4 program suite [9] (for compound **I**), and SMART [10] and SAINT [11] (for compound **II**). The structures were solved by a direct method and refined by full-matrix LSM against F^2_{hkl} in the anisotropic approximation for non-hydrogen atoms. The hydrogen atom of the amino group in **I** was identified objectively in the difference Fourier maps and refined isotropically with fixed displacement parameters ($U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{N})$). The positions of the other hydrogen atoms in **I** and **II** were calculated geometrically and included in the refinement with fixed positional parameters (riding model) and isotropic displacement parameters ($U_{\text{iso}}(\text{H}) = 1.2U_{\text{iso}}(\text{C})$). X-ray absorption correction was applied using the Scala [12] (compound **I**) and SADABS [13] (compound **II**) softwares respectively. All calculations related to the crystal structure refinement were performed using the SHELXTL software [14]. The crystallographic data and the parameters of the single crystal XRD experiments are given in Table 1. The structures have been deposited with CCDC under numbers 1479807 (**I**), 1479766 (**II**) and are available at the address: ccdc.cam.ac.uk/getstructures.

RESULTS AND DISCUSSION

The selected valence bond lengths, bond and torsion angles for compound **I** are given in Table 2.

TABLE 1. Main Crystallographic Data and Refinement Parameters for Compounds **I** and **II**

Parameters	**I**	**II**
Chemical formula	$C_7H_5FN_4S$	$C_{14}H_8CdF_2N_8S_2$
Molecular weight	196.21	502.80
Temperature, K	100	100
Crystal size, mm	0.15×0.15×0.10	0.21×0.16×0.16
Crystal symmetry	Triclinic	Monoclinic
Space group	*P*-1	*C*2/*c*
a, *b*, *c*, Å	3.8649(8), 10.705(2), 11.130(2)	26.4468(13), 8.9421(4), 7.3009(3)
α, β, γ, deg	65.71(3), 86.29(3), 82.21(3)	β 101.856(1)
V, Å^3	415.83(17)	1689.76(13)
Z	2	4
d(calc.), g/cm^3	1.567	1.976
μ, mm^{-1}	0.844	1.579
F(000)	200	984
θ range of data collection, deg	38	25
Meas. / indep. reflections	5814 / 1301	8303 / 1996
Refined parameters	122	123
R_1 [I > 2σ(I)] / wR_2 (all data)	0.0534 / 0.1265	0.0421 / 0.0909
GOOF	1.000	1.047
$T_{\min}$; $T_{\max}$	0.868; 0.909	0.384; 0.746
Residual electron density, ($\rho_{\min}$ / $\rho_{\max}$), e/Å^3	–0.463 / 0.366	–1.331 / 2.484

TABLE 2. Selected Valence Bond Distances, Bond and Torsion Angles in Compound **I**

Bond	*d*, Å	Bond	*d*, Å	Bond	*d*, Å
S(1)–C(5)	1.676(3)	N(3)–N(4)	1.363(3)	C(6)–C(7)	1.386(4)
N(1)–C(5)	1.370(3)	N(4)–C(5)	1.361(3)	C(6)–C(11)	1.397(3)
N(1)–N(2)	1.380(3)	N(1)–C(6)	1.444(3)	F(1)–C(9)	1.364(3)
N(2)–N(3)	1.287(3				
Angle	ω, deg	Angle	ω, deg	Torsion angle	ω, deg
C(5)–N(1)–C(6)	128.9(2)	N(1)–C(5)–S(1)	129.03(19)	C(5)–N(1)–C(6)–C(11)	57.3(4)
N(2)–N(1)–C(6)	120.38(19)	C(7)–C(6)–N(1)	119.0(2)		
C(11)–C(6)–N(1)	119.0(2)	N(4)–C(5)–S(1)	129.14(18)		

Compound **I** is 1-(4-fluoro-phenyl)-1,4-dehydro-5H-tetrazole-5-thione and consists of two planar moieties: *n*-fluorophenyl and mercaptotetrazole rings. The angle between these planes is 54.99(7)°. The N(1)–N(2) (1.363(3) Å), N(1)–C(5) (1.370(3) Å), N(3)–N(4) (1.361(3) Å), and N(4)–C(5) (1.380(3) Å) bond lengths in the mercaptotetrazole moiety correspond to single bonds, while the N(2)=N(3) (1.287(3) Å) and C(5)=S(1) (1.676(3) Å) bonds are double (Table 2), which confirms the existence of compound **I** in thione form in the free state. The C(5)–N(1)–C(6)–C(11) torsion angle is 57.3(4)°. The analysis of bond lengths in the structure of **I** showed that all of them correspond to average values [15].

In the crystal, molecules of **I** form H-bonded centrosymmetric dimers via two N(4)–H(4)…S(1) (1–*x*, 1–*y*, 1–*z*) hydrogen bonds (N–H is 0.91(2) Å, H…S is 2.34(2) Å, the N–H… angle is 177(2)°) (Fig. 1) [16-18]. The dimers contain a central planar eight-membered ring {S=C–N–H…S=C–N–H… (rms = 0.009 Å)}. The C(5)=S(1) bond length (1.676(2) Å) corresponds to that of double bonds.

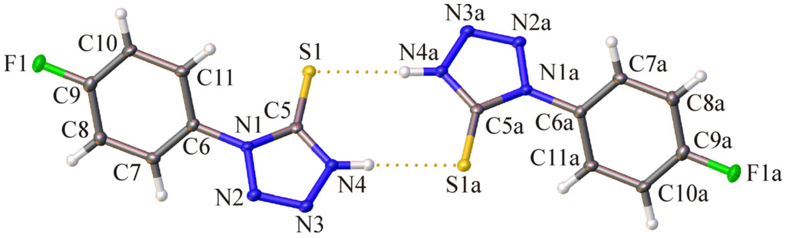

Fig. 1. Structure of H-bonded dimers in the crystal of compound **I**.

The dimers of compound **I** are located in the crystal in such a way that the phenyl and tetrazole rings are arranged in pairs parallel to each other to form stacks along the ***a*** axis (Fig. 2). The distance between the ring centers is 3.865(2) Å, which exceeds the geometric criterion of the π–π stacking interaction [19].

The bond lengths, bond and torsion angles in complex **II** are given in Table 3.

Complex **II** has a one-dimensional chain structure of the composition $[(C_7H_4N_4FS)_2Cd]_n$. The coordination environment of the cadmium cation is a distorted tetrahedron containing two nitrogen atoms and two sulfur atoms from four ligands **I**. The Cd–S and Cd–N distances are 2.4972(11) Å and 2.228 (4) Å respectively. The N–Cd–N and S–Cd–S angles are 103.44(19)° and 105.06(5)° respectively. Note that the character of bonds in the mercaptotetrazole moiety of ligand **I**

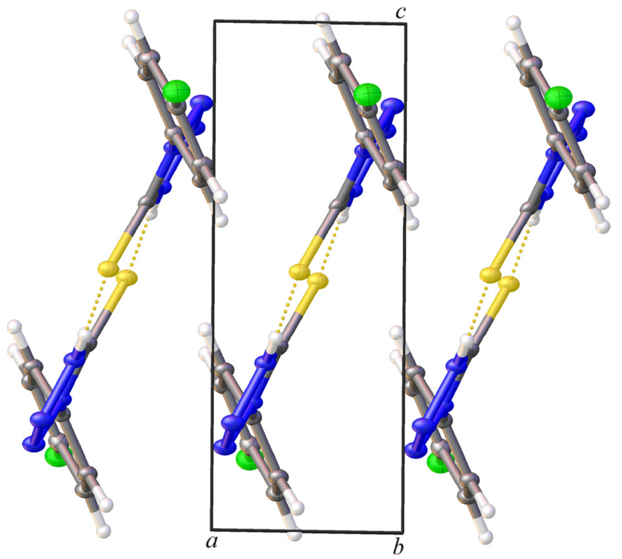

Fig. 2. Fragment of the crystal packing of **I** along the ***a*** axis.

TABLE 3. Selected Valence Bond Distances, Bond and Torsion Angles in Complex **II**

Bond	*d*, Å	Bond	*d*, Å	Bond	*d*, Å
Cd(1)–N(4)#1	2.228(4)	S(1)–C(5)	1.728(4)	N(4)–C(5)	1.332(5)
Cd(1)–N(4)	2.228(4)	N(1)–C(5)	1.354(5)	N(1)–C(6)	1.432(5)
Cd(1)–S(1)#2	2.4972(11)	N(1)–N(2)	1.371(5)	C(6)–C(7)	1.390(6)
Cd(1)–S(1)#3	2.4972(11)	N(2)–N(3)	1.288(5)	C(6)–C(11)	1.388(6)
Cd(1)#3–S(1)	2.4972(11)	N(3)–N(4)	1.365(5)	F(1)–C(9)	1.357(5)
Angle	ω, deg	Angle	ω, deg	Torsion angle	ω, deg
N(4)#1–Cd(1)–N(4)	103.44(19)	C(11)–C(6)–N(1)	119.9(4)	C(5)–N(1)–C(6)–C(11)	46.5(6)
S(1)#2–Cd(1)–S(1)#3	105.06(5)	N(1)–C(5)–S(1)	125.7(3)		
C(5)–N(1)–C(6)	128.9(2)	C(7)–C(6)–N(1)	118.5(4)		
N(2)–N(1)–C(6)	120.38(19)	N(4)–C(5)–S(1)	128.1(3)		

changes when complex **II** forms. Thus, the C(5)–S(1) bond (1.728(4) Å) becomes single and the N(4)=C(5) bond (1.332(5) Å) becomes double (Table 3) due to a higher chemical affinity of the cadmium cation to a sulfur atom than to a nitrogen atom. Hence, unlike the free state, in complex **II** mercaptotetrazole ligand **I** takes the thiol form. The angle between the planes of the phenyl and mercaptotetrazole moieties is 45.56(16)°. Infinite 1D chains contain eight-membered {←S=C–N–Cd←S=C–N–Cd} rings in a *chair* conformation. The distance between the metal atoms Cd…Cd is 4.165 Å. One-dimensional polymer chains of complex **II** in the crystal are arranged along the *c* axis (Fig. 3).

The detailed analysis of the crystal packing of complex **II** shows that between the neighboring one-dimensional chains along the *b* axis there is a parallel packing of phenyl moieties of the chains extending along the *c* axis. The shortest C…C distances are observed between the carbon atoms C(7)…C(10) (3.404(3) Å) and C(6)…C(9) (3.479(3) Å) and indicate the presence of weak π–π stacking interactions [19]. The distance between the ring centers is 3.651(3) Å, which only slightly exceeds the geometric criteria of the said π–π stacking interactions [19].

In addition, it was revealed that there were short intermolecular fluorine-fluorine contacts between the adjacent chains along the *a* axis. The F…F distances are 2.736(2) Å and correspond to weak secondary F…F interactions (between 2.80 Å and 2.65 Å [20]) (Fig. 3).

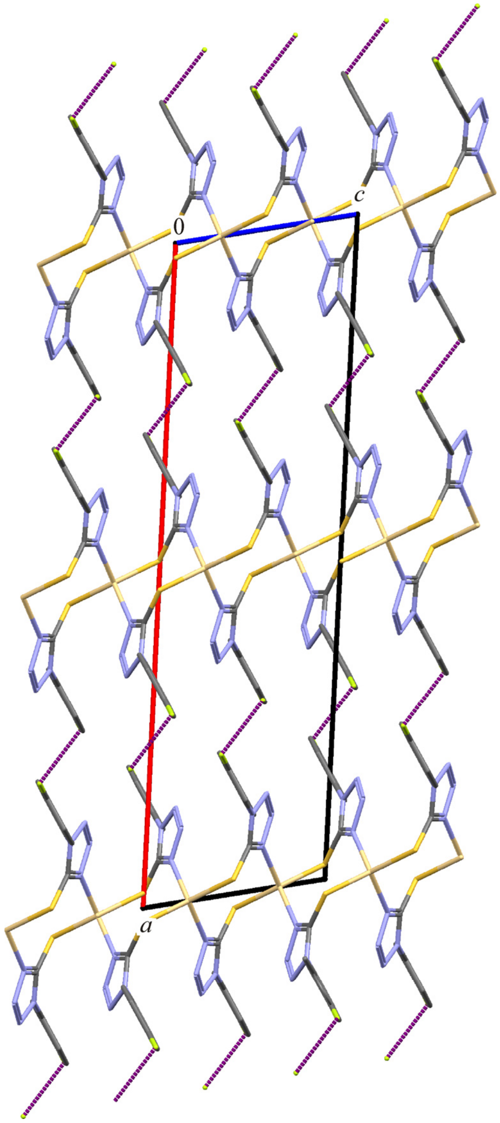

Fig. 3. F…F contacts in the crystal of complex **II**.

CONCLUSIONS

Thus, by single crystal XRD it is established that in the crystal compound **I** is in the thione form. These heterocyclic compounds have several electron-donor centers and the use of **I** as a ligand in the complexing reaction with cadmium(II) chloride gives complex **II**, which has a 1D polymeric chain structure. It is shown that when complex **II** forms, mercaptotetrazole ligand **I** converts into the thiol form. The crystal structure of **II** is stabilized by intermolecular secondary F…F and π–π stacking interactions.

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