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Two New Coordination Polymers of Cadmium with Bridging Thiocyanate Ligands: Composition and Structure

V. V. Kovalev[a], *, Yu. V. Kokunov[a], †, M. A. Shmelev[a], Yu. K. Voronina[a], M. A. Kiskin[a], A. A. Sidorov[a], and I. L. Eremenko[a, b]

[a] *Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, Moscow, Russia*
[b] *Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, Moscow, Russia*
**e-mail: kovavlad@igic.ras.ru*

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Abstract—Methods for the synthesis of new cadmium thiocyanate complexes with 3,5- and 2,6-lutidine (3,5- and 2,6-Lut, respectively), $[Cd(NCS)_2(3,5\text{-}Lut)_2]_n \cdot n$MeCN (**I**) and $[Cd(NCS)_2(2,6\text{-}Lut)]_n$ (**II**), are developed. The synthesized complexes are characterized. The use of 2,6-lutidine is shown to generate steric hindrances because of which only one molecule of the N-donor ligand can coordinate to the cadmium atom. The crystal packings of complexes **I** and **II** are stabilized by intermolecular π...π, S...S, and C–H...S interactions. The compounds are characterized by X-ray diffraction (XRD) (CIF files CCDC nos. 2034816 (**I**) and 2206062 (**II**)) and C,H,N-analysis data.

Keywords: cadmium thiocyanates, 2,6-lutidine, 3,5-lutidine, X-ray diffraction analysis

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INTRODUCTION

Self-assembling of organic compounds with metal centers is an efficient and widely used method for the design of coordination polymers. The synthesis of these compounds is actively developed in coordination chemistry due to a diversity of structures and important physicochemical properties. A series of coordination polymers with specific properties was prepared by the reactions of metal ion salts with organic ligands. The nature of the metal ion and anion of the salts, donor properties and geometric parameters of organic ligands, and the ligand to metal ion ratio exert the main effect on the properties and structures of the synthesized compounds [1–4].

High interest in these compounds of d^{10} metals is caused by their potential application in luminescence, nonlinear optics, molecular adsorption, and catalysis [5–7] and as corrosion inhibitors [8]. The study of the coordination polymers involving the Cd(II) ion is related to its electronic configuration and size and a broad variety of geometries and coordination numbers [9]. Cadmium and other d^{10} metals can efficiently affect both the enhancement and quenching of organic ligand emission [10, 11].

Coordination polymers with short bridging ligands, particularly, with thio- and selenocyanate anions, evoke increased interest in the recent time. These ligands manifest a diverse coordination behavior when added to the metal ion via both N- and S-, or Se-donor atoms [12].

The insertion of neutral ligands in the coordination polymer can change the structure, dimensionality, and properties of the compound [13, 14]. A number of cadmium thiocyanates with pyridine and its monosubstituted analogs has been prepared to the moment. The $Cd(NCS)_2(L)_2$ complexes (L is *N*-pyridine or its substituted analog) were found to be polymers with ambidentate bridging NCS ions coordinated to the Cd ions via the S and N atoms [15–19]. The coordination sphere of Cd consists of two NCS groups, two SCN groups, and two pyridine ligands. The linear structure of thiocyanate anions makes it possible to observe various steric effects induced by the influence of other ligands. It is much more difficult to obtain a similar information in the case of triatomic bridging fragments being a part of more bulky anions (carboxylate, mercaptoimidazolate, and hydroxypyridonate anions).

3,5-Lutidine (3,5-Lut) and 2,6-lutidine (2,6-Lut) were used as N-donor ligands in the present study. Both dimethyl derivatives of pyridine have the same two electron-donor substituents, but the coordination of 3,5-lutidine results in the formation of approximately the same structures as pyridine [20]. 2,6-Lutidine having a large Tolman cone angle occupies a much larger volume in the coordination environment of the metal and can form other structures [21].

† Deceased.

The purpose of this work is to study the influence of various disubstituted pyridine ligands on the composition, structure, and properties of the coordination polymers of cadmium thiocyanates.

EXPERIMENTAL

All procedures associated with the synthesis of the complexes were carried out in air using MeCN (99%), EtOH (96%), distilled water, $Cd(OH)_2$, NEt_4NCS, 2,6-lutidine (98%, Aldrich), 3,5-lutidine (98%, Aldrich), and trifluoroacetic acid (99%, Merck). Compound $Cd(OH)_2$ was synthesized by the reaction of stoichiometric amounts of KOH and $Cd(NO_3)_2 \cdot 6H_2O$ in water. Compound $Cd(CF_3COO)_2 \cdot 0.25H_2O$ was prepared by the treatment of an aqueous-alcohol suspension of $Cd(OH)_2$ with an equivalent amount of CF_3COOH.

Synthesis of $[N(Et)_4][Cd(NCS)_3]$. Weighed samples of NEt_4NCS (1.66 g, 8.81 mmol) and $Cd(CF_3COO)_2 \cdot 0.25H_2O$ (1.00 g, 2.92 mmol) were separately dissolved in acetonitrile (10 and 5 mL, respectively). The solutions were mixed and heated (50°C) to the evaporation of the most part of the solvent. Ethanol (8 mL) was added with stirring to the resulting saturated solution. The crystals precipitated in 3 days were separated from the mother liquor by filtration on a glass filter and washed with cold EtOH (T = ~5°C). According to the CHN-analysis results, the isolated crystals corresponded to the composition $[N(Et)_4][Cd(NCS)_3]$. The yield was 0.86 g (71.2% based on $Cd(CF_3COO)_2 \cdot 0.25H_2O$).

For $C_{11}H_{20}N_4S_3Cd$			
Anal. calcd., %	C, 31.7	H, 4.8	N, 13.4
Found, %	C, 31.8	H, 4.5	N, 13.3

Synthesis of $[Cd(NCS)_2(3,5\text{-Lut})_2]_n \cdot n$MeCN (I). A weighed sample of compound $[N(Et)_4][Cd(NCS)_3]$ (0.21 g, 0.50 mmol) was dissolved in MeCN (20 mL) at 60°C for 15 min, and 3,5-Lut (0.11 mL, 1.01 mmol) was added. The obtained reaction mixture was stored for 3 days in a closed bottle. The formed prismatic colorless crystals were separated by decantation, washed two times with small portions of cold MeCN (T = ~5°C), and dried in air. The yield was 0.16 g (66.9% based on $[N(Et)_4][Cd(NCS)_3]$).

For $C_{18}H_{21}N_5S_2Cd$			
Anal. calcd., %	C, 44.7	H, 4.4	N, 14.5
Found, %	C, 44.8	H, 4.0	N, 14.6

Synthesis of $[Cd(NCS)_2(2,6\text{-Lut})]_n$ (II) was carried out by a procedure similar to that for complex **I** using 3,5-Lut (0.11 mL, 1.01 mmol) instead of 2,6-Lut. The obtained colorless solution was left to evaporate slowly in air. Colorless crystals formed in 4 days suitable for XRD were separated from the mother liquor by decantation, washed with cold MeCN (T = ~5°C), and dried in air. The yield was 0.10 g (58.5% based on $[N(Et)_4][Cd(NCS)_3]$).

For $C_9H_9N_3S_2Cd$			
Anal. calcd., %	C, 32.2	H, 2.7	N, 12.5
Found, %	C, 32.4	H, 2.9	N, 12.6

XRD of single crystals was carried out on a Bruker Apex II diffractometer equipped with a CCD detector (MoK_α, λ = 0.71073 Å, graphite monochromator) [22]. A semiempirical absorption correction was applied using the SADABS program [23]. The structure was solved by a direct method and refined by least squares first in the isotropic and then anisotropic approximation for F^2_{hkl}. The positions of hydrogen atoms were calculated geometrically and refined in the isotropic approximation by the riding model. All calculations were performed using the SHELXL-2018/3 software [24]. The geometry of polyhedra of the metal atoms was determined using the SHAPE 2.1 program [25, 26].

The crystallographic parameters and structure refinement details for compound **I**: $C_{18}H_{21}N_5S_2Cd$, FW = 483.92, crystal size 0.10 × 0.11 × 0.12 mm, colorless crystals, T = 150(2) K, monoclinic crystal system, space group $C2/c$, a = 18.0045(9), b = 13.7420(6), c = 9.5748(4) Å, β = 113.585(2)°, V = 2171.09(17) Å^3, Z = 4, ρ = 1.480 g/cm^3, μ = 1.209 mm^{-1}, θ = 2.26°–28.99°, $-32 \le h \le 32$, $-13 \le k \le 13$, $-21 \le l \le 21$; 19170 measured reflections, 4834 independent reflections, reflections with $I \ge 2\sigma(I)$ 4608, R_{int} = 0.0216, T_{min}/T_{max} = 0.786/0.817, R_1 = 0.0350, wR_2 = 0.0682 (for all data), R_1 = 0.0300, wR_2 = 0.0663 (for $I \ge 2\sigma(I)$), $\Delta\rho_{min}/\Delta\rho_{max}$ = –0.384/0.675 e Å^{-3}.

The crystallographic parameters and structure refinement details for compound **II**: $C_{27}H_{27}N_9S_6Cd_3$, FW = 1007.13, crystal size 0.03 × 0.06 × 0.15 mm, colorless crystals, T = 150(2) K, monoclinic crystal system, space group $C2/c$, a = 24.1763(15), b = 9.7493(6), c = 15.9745(12) Å, β = 103.495(2)°, V = 3661.3(4) Å^3, Z = 4, ρ = 1.827 g/cm^3, μ = 2.102 mm^{-1}, θ = 2.26°–30.56°, $-34 \le h \le 34$, $-13 \le k \le 13$, $-22 \le l \le 22$; 23144 measured reflections, 5335 independent reflections, reflections with $I \ge 2\sigma(I)$ 4470, R_{int} = 0.0397, T_{min}/T_{max} = 0.6334/0.7461, S = 1.055, R_1 = 0.0464, wR_2 = 0.0655 (for all data), R_1 = 0.0338, wR_2 = 0.0608 (for $I \ge 2\sigma(I)$), $\Delta\rho_{min}/\Delta\rho_{max}$ = –0.581/1.163 e Å^{-3}.

The atomic coordinates and other parameters of compounds **I** and **II** were deposited with the Cambridge Crystallographic Data Centre (CIF files CCDC nos. 2034816 and 2206062, respectively;

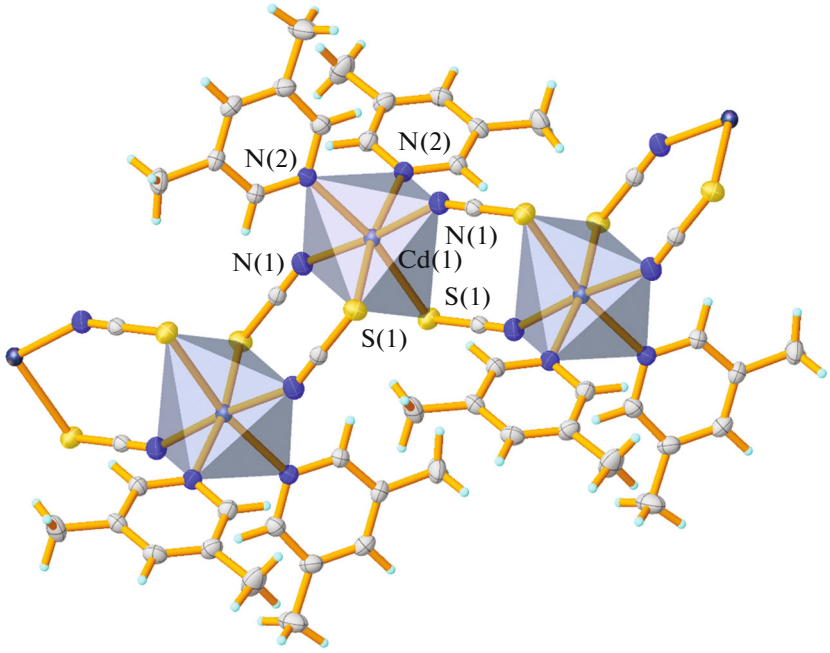

Fig. 1. Fragment of the polymer chain in complex **I**. Ellipsoids are shown with 50% probability.

deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/data_request/cif).

RESULTS AND DISCUSSION

Complex **I** in crystal has a polymer structure (Fig. 1) in which the coordination polyhedron of the central cadmium atom is an octahedron (O_h, SQ(P) = 1.404) and consists of two lutidine ligands and four bridging thiocyanate anions coordinated by the nitrogen atoms in two cases and by the sulfur atom in other two cases. The component moiety of the polymer structure exists in the partial position on the C_2 axis leading to the corresponding symmetry of the polyhedron. The cadmium ion forms the shortest bonds with the nitrogen atoms of the thiocyanate ligands, and the longest bonds are formed with the sulfur atoms (Table 1).

An interesting feature of the structure of studied polymer **I** is that the further growth of the chain occurs through the symmetry center located between two thiocyanate fragments due to which the polymer represents a zigzag chain where the lutidine fragments are arranged in pairs at different sides of the cadmium thiocyanate cage (Fig. 2). The packing of the molecules in crystal is that the polymer chains form infinite planar layers in which the metal atoms lie in one plane and the ligands are arranged symmetrically at both sides of the plane. An important feature of the crystals of the studied compound is that any significant noncovalent interaction is observed only between the layers, although this interaction is a rather weak π...π overlap of the pyridine fragments (the distance between the centroids of the rings is 3.686(1) Å, the distance between the planes is 3.480(1) Å, and the rings are rigidly parallel).

The search for cadmium complexes with the thiocyanate anion and 3,5-lutidine in the Cambridge Structural Database showed that only one structure of the composition, where only one 3,5-lutidine molecule was coordinated to the metal ion, was published to date [27]. An analysis of the crystal structures of related compounds shows that the structure of complex **I** is almost the same as the structure of the similar complex with the azide anion [28]. Some difference in the CdCdCd angles (116.51° in complex **I** and 94.74°

Table 1. Selected bond lengths (Å) and angles (deg) in compound **I**

Bond	*d*, Å	Bond	*d*, Å
Cd(1)–N(1)	2.328(2)	N(1)–C(1)	1.150(3)
Cd(1)–N(2)	2.338(2)	N(2)–C(3)	1.332(3)
Cd(1)–S(1)	2.710(1)	N(2)–C(7)	1.335(3)
S(1)–C(1)	1.649(2)		
Angle	ω, deg	Angle	ω, deg
N(1)Cd(1)N(2)	85.54(7)	N(2)Cd(1)S(1)	91.19(5)
N(1)Cd(1)N(2)	90.48(7)	N(1)Cd(1)S(1)	101.20(5)
CdCdCd	116.78(1)	N(2)Cd(1)S(1)	91.19(5)
N(1)Cd(1)N(2)	90.48(7)	N(2)Cd(1)S(1)	168.09(5)
N(2)Cd(1)N(2)	92.03(9)	S(1)Cd(1)S(1)	87.99(3)
N(1)Cd(1)S(1)	101.20(5)	N(1)C(1)S(1)	179.2(2)

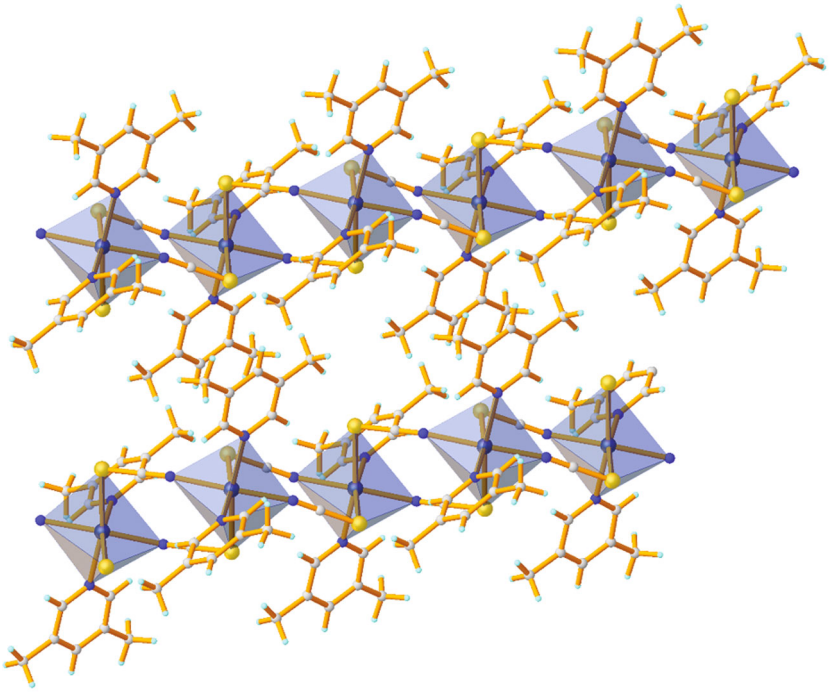

Fig. 2. Packing of molecules in crystal of complex **I**.

in the complex with azide) and Cd–Cd distances (5.629 and 5.142 Å, respectively) results in a slightly stronger compression of the polymer chain in the azide complex, which is easily explained by the difference in the sizes of the azide and thiocyanate fragments. An insignificant distinction in the crystal packings of these compounds is due, most likely, to the presence of acetonitrile molecules in the solvate shell of the crystal of compound **I**.

Compound **II** is a polymer chain consisting of two independent Cd atoms linked to each other by pairs of the bridging NSC anions (Fig. 3). The 2-fold axis C_2 passes through the Cd(1) atom and the N(5) and C(13) atoms belonging to the 2,6-lutidine molecule. Each cadmium atom coordinates two S atoms and two N atoms of the NSC^- anions, as well as one N atom of the 2,6-lutidine molecule is coordinated to each cadmium atom. The geometry of the CdN_3S_2 coordination polyhedra was examined using the Shape2.1 program and corresponds to a trigonal bipyramid (S_q(Cd(1)) = 0.720, S_q(Cd(2)) = 1.066). In the polyhedron of the Cd(1) ion, the equatorial positions are occupied by the S(1), S(1*A*), and N(5) atoms, and N(2) and N(2*A*) occupy the axial positions. For the polyhedron of the Cd(2) atom, the S(2), N(3), and N(4) atoms occupy the equatorial positions, and the axial positions are occupied by N(1) and S(3*B*). Selected bond lengths and angles are given in Table 2. The pentacoordination environment of the cadmium ion in the form of a trigonal bipyramid is rather rare for the thiocyanate complexes. As found recently [17], compound $[Cd_2(SCN)_4(2\text{-MeNH-Py})_3]$ (2-MeNH-Py is 2-(methylamino)pyridine) contains two nonequivalent Cd(II) ions with the coordination numbers 6 and 5 in the form of an octahedron and a trigonal bipyramid. It is shown [29] that the cadmium ion in compound $[Cd(NCS)_2(TPPO)]_n$ (TPPO is triphenylphosphine oxide) has the trigonal bipyramidal coordination environment.

Table 2. Selected bond lengths and bond angles in compound **II**

Bond	*d*, Å	Bond	*d*, Å
Cd(1)–N(2)	2.293(2)	Cd(2)–S(2)	2.5862(7)
Cd(2)–N(3)	2.209(2)	Cd(1)–N(5)	2.308(3)
Cd(1)–S(1)	2.6202(8)	Cd(2)–N(4)	2.266(2)
Angle	ω, deg	Angle	ω, deg
N(1)Cd(2)S(3*B*)	175.30(7)	S(2)Cd(2)N(1)	92.95(7)
S(1)Cd(1)S(1)	108.23(4)	S(2)Cd(2)N(2)	87.99(6)
S(1)Cd(1)N(5)	125.89(2)	N(3)Cd(2)N(4)	123.92(10)
N(2)CdN(2*A*)	178.22(12)	Cd(1)Cd(2)Cd(1)	130.97(1)

The crystal packing of compound **II** also exhibits the formation of C–H...S interactions (inside the chain and interchain, Table 3) and S···S interactions (interchain, the S(2)...S(3C) distance (3.593(1) Å) is

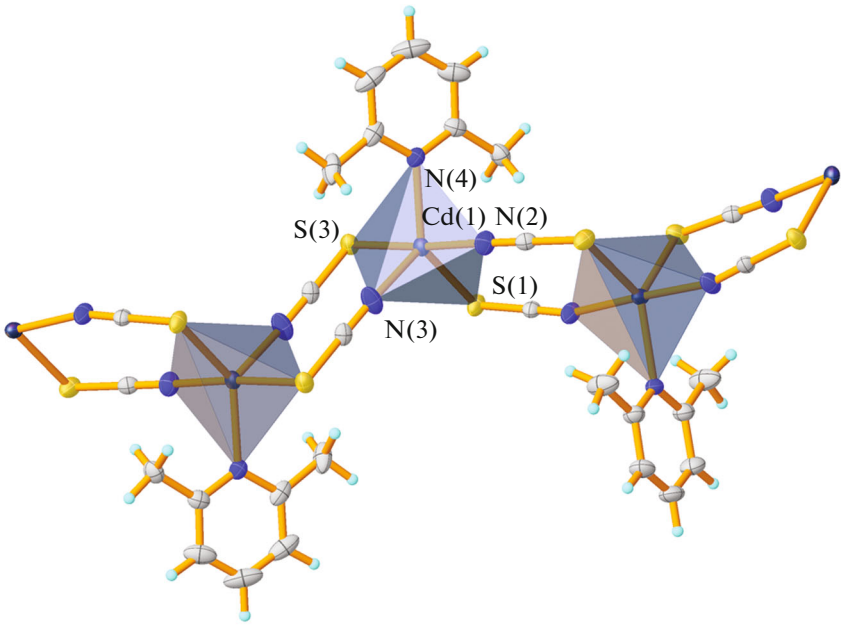

Fig. 3. Fragment of the polymer chain in complex **II**.

shorter than the sum of the van der Waals radii [30]), which favors the formation of the three-dimensional supramolecular structure (Fig. 4).

An analysis of the literature data shows that the composition and structure of compound **I** are characteristic of the cadmium thiocyanate complexes with pyridine and its monosubstituted analogs where the polymer structure is formed due to the bridging N,S-thiocyanate ions and cadmium builds up its environment to the octahedral one [32, 33]. In the case of compound **II**, the use of 2,6-lutidine made it possible to generate steric hindrances because of which only one molecule of the pyridine derivative can coordinate to the cadmium atom. The coordination number of cadmium decreased to five, and the coordination polyhedron corresponds to a strongly distorted trigonal bipyramid. This indicates that the steric parameters of the neutral N-ligands exert a decisive effect on the composition and structure of the compounds compared to their basicity and donor ability. It is most likely that these metal centers can be accessible for coordination only to small molecules, which can be used in the development of selective sensor materials.

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Table 3. Geometric parameters of hydrogen bonds in crystal of complex **II**

D–H···A	Distance, Å			Angle DHA, deg	Symmetry index
	D–H	H···A	D···A		
C(5)–H(5*A*)···S(3*D*)	0.95	3.01	122.5	3.614	$x, -y + 1, z + 1/2$
C(7)–H(7*A*)···S(3*E*)	0.95	2.88	159.4	3.782	$x, y + 1, z$
C(10)–H(10*B*)···S(3*F*)	0.95	3.03	140.5	3.833	$-x + 3/2, -y + 1/2, -z + 1$

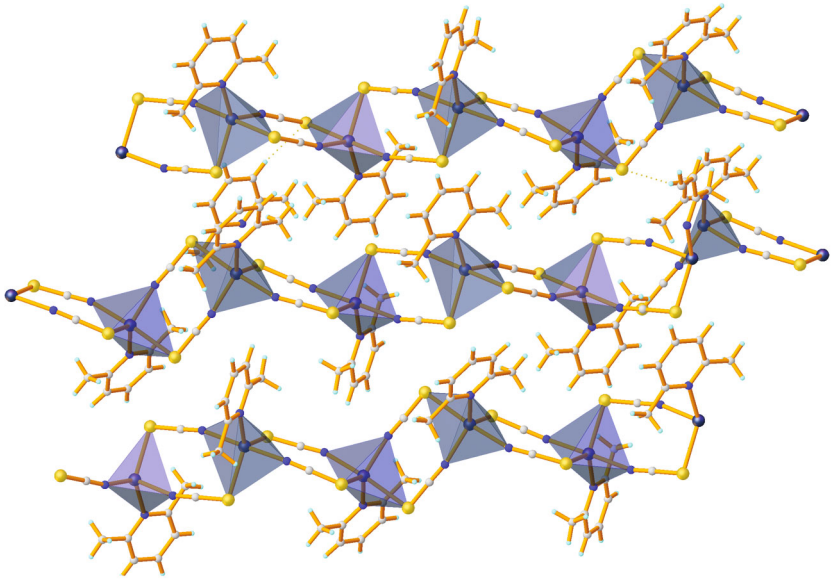

Fig. 4. Packing fragment of complex **II** in crystal, projection on the *ac* plane (S···S and C···S interactions are shown by dash).

CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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