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Formation of New Unusual Cadmium Polymer with Bridging Thiocyanate Ions

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Abstract—The reaction of cadmium thiocyanate with 2-(methylamino)pyridine (2-Map) in an ethyl alcohol solution gave a new unusual coordination polymer $[Cd_2(NCS)_4(2\text{-}Map)_3]$. The structure of the polymer was determined (CIF file CCDC no. 1917586). The crystals are triclinic, space group $P\bar{1}$. The polymer elementary unit is composed of binuclear $[Cd_2\ (NCS)_4(2\text{-}Map)_3]$ moiety in which the Cd atoms are connected by μ-NCS bridges. The Cd(1) environment is completed to an octahedron (CdS_2N_4) via coordination of two pyridine nitrogen atoms of the 2-Map molecules in the apical positions. The Cd(2) coordination environment (CdS_2N_3) is a trigonal bipyramid supplemented by the pyridine nitrogen atom of the 2-Map molecule. The uncoordinated nitrogen atoms of the NH group are involved in the intrachain H-bonds with the NCS-group nitrogen atoms. The luminescence spectrum of the synthesized compounds was recorded.

Keywords: coordination polymer, cadmium thiocyanate, 2-methylaminopyridine, structure

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INTRODUCTION

The persistent interest in the structure and synthesis of new metal halides and thiocyanates modified with organic molecules is due to their structural diversity and potential applications in optics, electrochemistry, magnetic materials, and catalysis [1]. One of the modification methods is coordination of N-heterocycles to the metal ion [2]. Cadmium is one of the most widely used metals for the preparation of various types of polynuclear compounds. The cadmium C.N. and stereochemistry vary from 4 to 8 and are determined, as a rule, by the nature of ligands.

In the last two decades, considerable attention has been paid to cadmium thiocyanate compounds. The thiocyanate ion is known to be an ambidentate ligand able to be attached to metal ions (e.g., Zn, Cd, and Hg) via either N or S atom or via both atoms, thus occupying a bridging position [3]. Many cadmium compounds are used for the storage of gases, design of sensors, production of non-linear optical materials, and luminescence. The recent studies have been focused on the development of polynuclear metal halide and thiocyanate compounds with N-heterocyclic molecules. Pyridine and some its derivatives usually do not luminesce, but coordination polymers involving them, especially cadmium-containing ones, do show luminescent properties. Cadmium atoms can affect the emission wavelength of the coordinated organic compounds, which makes them good candidate luminescent materials [4–6].

It is known that steric and electronic effects of monodentate organic ligands have a modifying effect on thiocyanate-based polymeric structures and their properties [7, 8]. In most cases, the cadmium thiocyanate complexes tend to form double NCS bridges. Monodentate ligands occupy two *trans* positions in the octahedral environment of the Cd^{2+} ion. Some publications report the preparation and structure of Cd thiocyanate complexes with N-heterocyclic organic molecules. The structure depends on the $Cd(NCS)_2$: N-heterocycle ratio. When the ratio is 1 : 4, the molecular complexes $Cd(NCS)_2$(N-heterocycle)$_4$ with an octahedral environment of the metal ion are formed [9–12]. When the ratio is 1 : 2, the resulting complexes are polymeric and have double NCS bridges, with the octahedral environment of Cd^{2+} ions being composed of four bridging NCS groups and two neutral N-donor ligands. The $Cd(NCS)_2(Py)_2$ and $Cd(NCS)_2(4\text{-}EtPy)_2$ complexes were noted to exist as three forms, one stable and two metastable ones. They differ in the mode of coordination of the thiocyanate ion: (1) the S and N atoms occupy *trans* positions; (2) these atoms occupy *cis* positions; and (3) the same atoms occupy *cis–cis–trans* positions. The first and second forms are metastable [10–12]. As the $Cd(NCS)_2$: N-heterocycle ratio decreases to 1 : 1, a different structure is formed: $Cd(NCS)_2(Py)$. The octahedral Cd^{2+} ion is coordinated to two N atoms and three S atoms of NCS groups and one N-heterocycle.

The introduction of the electron-donating NH_2 group into the pyridine ring α position affects the geometric and electronic parameters of the ligand, which may induce a change in the structure of polynuclear compounds with this ligand. Furthermore, the ligands acquire the ability to form H-bonds [13, 14]. Examples of using these ligands in the coordination compounds of cadmium are very rare. Only one cadmium thiocyanate compound with α-aminopyridine is known, in which two organic ligands are attached to the Cd^{2+} ion in the monodentate fashion [15]. A compound of cadmium nitrate with α-aminopyridine was obtained [16]. Upon the reaction of cadmium pivalate with 2-amino-4-methylpyridine, a mononuclear complex with two monodentate pyridine derivatives was isolated [14]. The reactions of 2-amino-5-nitropyridine with cadmium chloride and bromide were studied. Both reactions gave coordination polymers with bridging halide ions and monodentate ligands coordinated via pyridine nitrogen atom [14, 17].

The key interest in 3*d*-metal thiocyanate coordination polymers, which form 1D and 2D networks via NCS bridges, is related to the influence of their chemical and structural features on the magnetic properties. However, for some 3*d* metals, bridging structures are difficult to obtain. Therefore, studies of the systems with Zn and Cd thiocyanates may provide understanding of specific features of the chemical composition and structure of metal thiocyanate polymers.

We studied the reaction of cadmium thiocyanate with 2-(methylamino)pyridine (2-Map) containing an $NHCH_3$ group in position 2. Thus we obtained the coordination polymer $[Cd_2(NCS)_4(2\text{-Map})_3]_n$ (**I**) and studied its structure and photoluminescent properties.

EXPERIMENTAL

Reagent grade $Cd(NO_3)_2 \cdot 4H_2O$ (>99%), 2-(methylamino)pyridine (99%), and NH_4NCS and 96% ethanol were used in the synthesis.

The IR spectrum of a solid sample was recorded on a Perkin-Elmer Spectrum 65 Fourier transform IR spectrophotometer using the attenuated total reflection (ATR) mode in the 400–4000 cm^{-1} frequency range.

Elemental analysis was performed on an automatic Carlo Erba EA 1108 C,H,N,S analyzer.

Synthesis of I. A solution of $Cd(NO_3)_2 \cdot 4H_2O$ (0.95 g, 3.1 mmol) in ethanol (6 mL) was heated to 35–40°C, and a solution of 2-Map (0.33 g, 3.1 mmol) in ethanol (4 mL) was added with stirring. The precipitate that formed was not analyzed, and the obtained suspension was immediately used for the synthesis of the thiocyanate complex. For this purpose, a solution of NH_4NCS (0.47 g, 6.2 mmol) in ethanol (5 mL) was heated to 35–40°C and gradually added with stirring to the suspension. After 10 min, the solid phase completely dissolved, and the resulting transparent solution was kept at room temperature for 2 days for slow evaporation of the solvent. The prismatic crystals formed were separated by decantation, washed with ethanol, and dried in air. According to elemental analysis data, the crystals corresponded to the cadmium complex $[Cd_2(NCS)_4(2\text{-Map})_3]$. The yield was 35%.

For $C_{22}H_{24}N_{10}S_4Cd_2$

Anal. calcd., %	N, 17.86	C, 33.67	H, 3.08	S, 16.31
Found, %	N, 17.33	C, 33.64	H, 2.75	S, 15.31

IR (ν, cm^{-1}): 3415 w (ν_{as}(N–H(NH_2))), 3351 w (ν_s(N–H)), 2993 vw, 2927 vw, 2857 vw. and 2817 vw. (ν_{sym}(C–H)), 2124 m, 2095 s and 2072 s (ν_{as}(NCS)), 1664 w (δ(N–H)), 1611 s (ν(C=N and C=C)), 1571 s and 1527 m (ν_{as}(N–H)), 1460 s, 1448 s (ν(C=N and C=C)), 1419 s, 1335 m, 1288 s (δ(C–H)), 1165 m and 1073 w (ν(C=N)), 994 w, 927 vw (δ(C–H)), 763 s, 738 m, 637 w, 508 m.

Single crystal X-ray diffraction study of compound **I** was performed on a Bruker SMART APEX II diffractometer (CD detector, MoK_α, $\lambda = 0.71073$ Å, graphite monochromator) [18]. Semiempirical absorption corrections were applied [19]. The structure was solved by direct methods and refined by full-matrix least squares method in the anisotropic approximation for all non-hydrogen atoms. The hydrogen atoms at the carbon atoms of organic ligands were generated geometrically and refined in the riding model. The disorder of one of the coordinated 2-Map molecules over two positions with occupancies of 0.715(3) and 0.285(3) was considered using the DFIX and FLAT constraint functions. The calculations were carried out using the SHELX-2014 program package [20]. Crystallographic parameters and structure refinement details of **I**: $M = 781.55$, colorless crystal of $0.20 \times 0.10 \times 0.07$ mm size, $T = 150(2)$ K, triclinic system, space group $P\bar{1}$, $a = 8.87830(10)$ Å, $b = 11.4684(2)$ Å, $c = 15.8755(3)$ Å, $\alpha = 105.7300(10)°$, $\beta = 101.1300(10)°$, $\gamma = 103.6360(10)°$, $V = 1453.88(4)$ Å^3, $Z = 2$, ρ(calcd.) = 1.785 g/cm^3, $\mu_{Mo} = 1.782$ mm^{-1}, $\theta = 1.93°–30.57°$, $-11 \le h \le 12$, $-16 \le k \le 16$, $-22 \le l \le 22$. Altogether 18167 reflections were collected; 8834 reflections were unique; and 7613 reflections had $I \ge 2\sigma(I)$; $R_{int} = 0.023$, $T_{min}/T_{max} = 0.600/0.746$, $S = 0.957$, $R_1 = 0.0497$, $wR_2 = 0.0928$ (for all data), $R_1 = 0.0407$, $wR_2 = 0.0883$ (for $I \ge 2\sigma(I)$), $\Delta\rho_{min}/\Delta\rho_{max} = -1.210/2.101$ e Å^{-3}.

The full set of X-ray diffraction data for **I** is deposited with the Cambridge Crystallographic Data Centre (no. 1917586; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/data_request/cif).

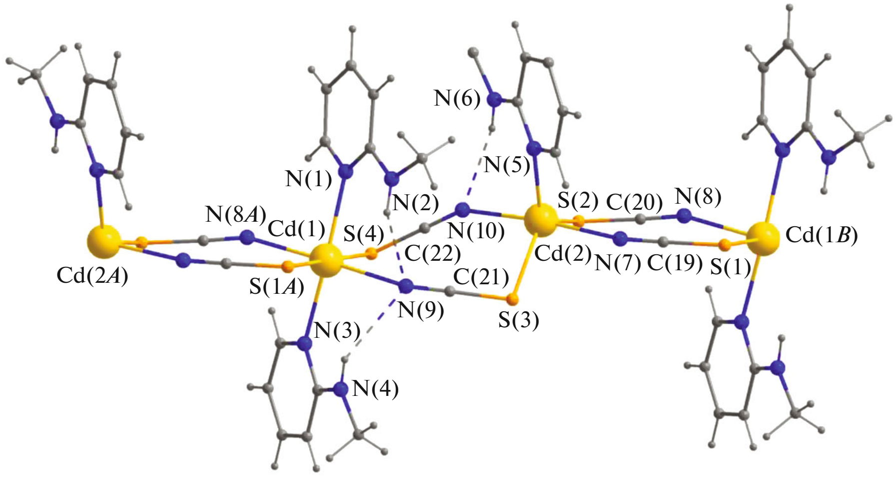

Fig. 1. Fragment of the polymer chain of the coordination compound [$Cd_2(NCS)_4(2\text{-Map})_3$]. Symmetry codes: (*A*) *x*, –1 + *y*, *z*: (*B*) *x*, 1 + *y*, *z*.

Powder X-ray diffraction study of **I** was carried out on a Bruker D8 Advance diffractometer (CuK_α, Ni filter, LYNXEYE detector, reflection geometry). The excitation and emission spectra for the solid samples of [$Cd_2(NCS)_4(2\text{-Map})_3$] were measured at room temperature in the visible range on a Perkin-Elmer LS-55 spectrometer.

RESULTS AND DISCUSSION

Coordination compound **I** is a 1D coordination polymer. The polymer elementary unit is the binuclear [$Cd_2(NCS)_4(2\text{-Map})_3$] moiety in which the Cd atoms are connected by NCS bridges (Cd···Cd, 5.877; Cd–N, 2.321(3), 2.326(3); Cd–S, 2.5814(9), 2.7016(11) Å) (Fig. 1). The phase purity of the sample was confirmed by powder X-ray diffraction (Fig. 2). The binuclear moieties are connected into a chain by pairs of μ-NCS bridges (Cd···Cd, 5.704; Cd–N, 2.331(3), 2.366(3); Cd–S, 2.5965(10), 2.7379(11) Å). The Cd(1) environment is completed to an octahedron (CdS_2N_4) by coordination of two pyridine nitrogens of the 2-Map molecule in the apical positions (Cd–N, 2.366(3), 2.375(3) Å). The Cd(2) coordination environment (CdS_2N_3) is a trigonal bipyramid (τ = 0.79) [20], which is supplemented by the pyridine nitrogen of the 2-Map molecule (Cd–N, 2.266(3) Å). The uncoordinated nitrogen atoms of the NH groups are involved in intrachain H-bonds with the NCS-group nitrogen (NH···N, 3.071–3.173 Å; N–H···N, 131°–150°) (Fig. 1). These data are comparable with the results obtained for the $Cd(HPz)_2(NCS)_2$ complex in which the NH group is also located in position 2 to the coordinated N atom (NH···N, 3.150 Å; NHN, 131°) [21]. Selected bond lengths and bond angles of compound **I** are summarized in Table 1.

The obtained coordination polymer **I** has an unusual structure incorporating simultaneously five- and six-coordinate cadmium ions. It can be seen that a decrease in the Cd : L ratio from 1 : 2 to 1 : 1.5 induces a considerable structural rearrangement. The six-coordinate cadmium ion has four bridging NCS groups, which coordinate cadmium ions via the N and S atoms with the *trans* positions of chemically identical atoms. Two *trans* positions in the octahedron are occupied by pyridine nitrogen atoms. In the five-coordinate moiety, the cadmium ion also has four bridging NCS groups; however, only nitrogen atoms are located in the *trans* positions, while the SCdS angle is 126°. The Cd–N(NCS) distances in the octahedron are 2.326–2.366 Å; these values in the five-coordinate

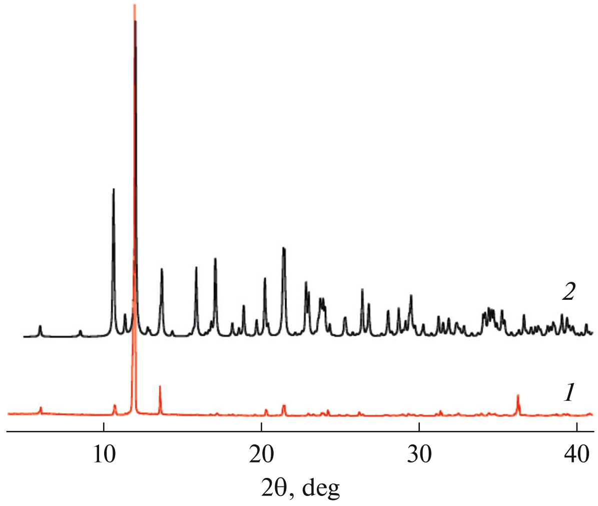

Fig. 2. Powder X-ray diffraction pattern of [$Cd_2(NCS)_4(2\text{-Map})_3$] (*1* is experimental, *2* is calculated X-ray diffraction pattern, λ = 1.541 Å).

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

Bond	*d*, Å	Angle	ω, deg
Cd(1)–N(8)	2.326(3)	N(8)Cd(1)N(9)	178.45(14)
Cd(1)–N(9)	2.366(3)	N(8)Cd(1)N(3)	84.06(14)
Cd(1)–N(3)	2.366(3)	N(9)Cd(1)N(3)	94.74(14)
Cd(1)–N(1)	2.375(3)	N(8)Cd(1)N(1)	88.46(14)
Cd(1)–N(3*X*)*	2.403(7)	N(9)Cd(1)N(1)	92.91(13)
Cd(1)–S(1)	2.7016(11)	N(3)Cd(1)N(1)	165.95(11)
Cd(1)–S(4)	2.7379(11)	N(8)Cd(1)N(3)	105.4(2)
Cd(2)–N(5)	2.266(3)	N(9)Cd(1)N(3*X*)	73.1(2)
Cd(2)–N(7)	2.321(3)	N(1)Cd(1)N(3*X*)	164.3(2)
Cd(2)–N(10)	2.331(3)	N(8)Cd(1)S(1)	92.46(8)
Cd(2)–S(2)	2.5814(9)	N(9)Cd(1)S(1)	86.77(9)
Cd(2)–S(3)	2.5965(10)	N(3)Cd(1)S(1)	99.38(9)
N(1)–C(1)	1.341(5)	N(1)Cd(1)S(1)	92.79(8)
N(1)–C(5)	1.349(5)	N(3*A*)Cd(1)S(1)	79.7(2)
N(2)–C(1)	1.362(6)	N(8)Cd(1)S(4*A*)**	90.91(8)
N(2)–C(6)	1.447(6)	N(9)Cd(1)S(4*A*)	89.89(9)
N(3)–C(11)	1.370(5)	N(3)Cd(1)S(4*A*)	82.16(8)
N(3)–C(7)	1.371(5)	N(1)Cd(1)S(4*A*)	86.09(8)
N(4)–C(7)	1.348(5)	N(3*A*)Cd(1)S(4*A*)	100.6(2)
N(4)–C(11)	1.424(7)	S(1)Cd(1)S(4)	176.42(3)
N(3*A*)–C(11*X*)	1.386(7)	N(5)Cd(2)N(7)	90.66(11)
N(3*A*)–C(7*X*)	1.384(7)	N(5)Cd(2)N(10)	95.52(11)
N(4*A*)–C(7*X*)	1.350(8)	N(7)Cd(2)N(10)	173.80(12)
N(4*A*)–C(12*X*)	1.34(3)	N(5)Cd(2)S(2)	124.34(7)
N(5)–C(17)	1.353(4)	N(7)Cd(2)S(2)	92.55(8)
N(5)–C(13)	1.361(4)	N(10)Cd(2)S(2)	84.40(8)
N(6)–C(13)	1.350(5)	N(5)Cd(2)S(3*B*)***	108.93(7)
N(6)–C(18)	1.453(5)	N(7)Cd(2)S(3*B*)	82.39(9)
N(7)–C(19)	1.150(4)	N(10)Cd(2)S(3*B*)	95.08(8)
N(8)–C(20)	1.159(5)	S(2)Cd(2)(3*B*)	126.57(4)
N(9)–C(21)	1.151(5)	C(19)S(1)Cd(1)	98.83(13)
N(10)–C(22)	1.153(4)	C(20)S(2)Cd(2)	100.34(13)
C(19)–S(1)	1.641(3)	C(21)S(3)Cd(2*B*)	100.05(12)
C(20)–S(2)	1.644(4)	C(22)S(4)Cd(1*A*)	94.96(12)
C(21)–S(3)	1.643(3)	N(7)C(19)S(1)	178.8(4)
C(22)–S(4)	1.635(4)	N(8)C(20)S(2)	177.8(4)
		N(9)C(21)S(3)	178.6(3)
		N(10)C(22)S(4)	179.5(3)

* *X* stands for atoms of the disordered form of the 2-Map molecule.
** *A* stands for atoms with the symmetry *x*, *y* – 1, *z*.
*** *B* stands for atoms with the symmetry *x*, *y* + 1, *z*.

moiety are similar: 2.32–2.331 Å. In the trigonal bipyramid, the equatorial plane is occupied by two bridging S(NCS) atoms and the N(2-Map) atom, while the apical positions contain the N atoms of bridging NCS groups. The Cd–S distances in the octahedral moiety are 2.7016 and 2.7379 Å, while these distances in the trigonal bipyramid are much shorter (Cd–S, 2.581 and 2.596 Å). Previously [11], in

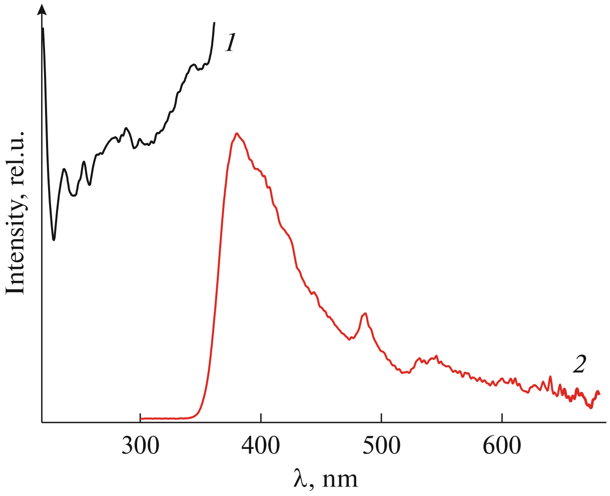

Fig. 3. (*1*) Excitation (λ_{excit} = 380 nm) and (*2*) emission (λ_{em} = 290) spectra of solid samples of $[Cd_2(NCS)_4(2\text{-}Map)_3]$ at room temperature.

analysis of the structure of $[Cd(NCS)_2(Py)_2]$ isomers, it was noted that pyridine rings in one of them are rotated relative to each other. In the compound studied here, this rotation is absent, probably due to the formation of N—H···N H-bonds stabilizing the structure.

Study of the luminescent properties of solid $[Cd_2(NCS)_4(2\text{-}Map)_3]$ at room temperature showed that the excitation spectrum at 380 nm wavelength exhibits bands at 237, 253, 279, 290, and 345 nm (Fig. 3). The emission spectrum at the excitation wavelength of 290 nm shows a broad band with a peak at 380 nm and shoulders at 398, 420, and 444 nm and less intense bands at 487, 530, and 546 nm. According to [5], the coordination compounds of cadmium with pyridine ligands exhibit intense fluorescence, which is usually attributed to the *n*—π transitions of the aromatic ring of the organic ligand upon its coordination to cadmium.

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CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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