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Coordination Compounds of Transition Metals with Rhodanine-3-acetic Acid

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Abstract—Seven compounds are synthesized by the reactions of the transition metals with rhodanine-3-acetic acid and studied by X-ray structure analysis. The compositions of the compounds can be presented by the formulas: $[Co(Rda)_2(H_2O)_4]$ (**I**), $[Ni(Rda)_2(H_2O)_4]$ (**II**), $[Zn(Rda)_2(H_2O)_4]$ (**III**), $[Zn(5,5'\text{-Rda-Rda})(Dmf)_2(H_2O)_2]_n$ (**IV**), $[Co(Rda)_2(bipy)(H_2O)_2]_n$ (**V**), $[Cd(Rda)_2(Bpe)]_n$ (**VI**), and $[Co(Gly)_3]\cdot H_2O$ (**VII**), where 5,5'-Rda-RdaH_2 is the new ligand (condensation product of two RdaH molecules), bipy is 4,4-bipyridine, Bpe is bis(4-pyridyl)ethane, and Gly is glycine (CIF files CCDC nos. 2070334–2070339 for **I**–**VI**, respectively). Compounds **I**–**III** and **VII** are mononuclear molecular complexes, and compounds **IV**–**VI** are 1D coordination polymers. In complexes **I**–**III**, Rda coordinates via one oxygen atom of the carboxyl group as the monodeprotonated monodentate ligand, whereas in compound **VII** this ligand undergoes decomposition due to the solvothermal synthesis to form glycine molecules. Polymer **IV** is formed by the new ligand $(5,5'\text{-Rda-Rda})^{2-}$ that coordinates as the bis(deprotonated) bidentate-bridging ligand, and molecules of the bis(pyridine) class (bipy and Bpe) act as bridging neutral ligands in compounds **V** and **VI.** In compound **V**, Rda coordinates as in complexes **I**–**III**, whereas in polymer **VI** two crystallographically independent Rda ligands coordinate via different modes: one ligand coordinates via the bidentate-chelating mode to one cadmium atom, and another coordinates via the tridentate-chelating mode to two metal atoms.

Keywords: transition metal complexes, rhodanine-3-acetic acid, coordination polymers, ligand condensation, X-ray structure analysis

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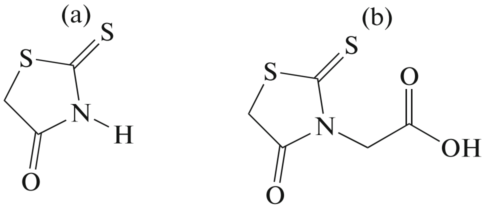
INTRODUCTION

The chemistry of rhodanine and its various derivatives evoke special interest as an important class of heterocyclic compounds with diverse donor atoms and a broad range of properties mainly associated with biological activity [1, 2], including their application as potential pharmaceuticals [1, 3–5]. The rhodanine compounds with various metals are also known as biologically active [6, 7], since it was found that the effect of drugs can be intensified if they were introduced in the form of metal complexes [8, 9]. An analysis of the Cambridge Structural Database [10] shows that such rhodanine-3-carboxylic acids as rhodanine-3-acetic acid and two its homologs (rhodanine-3-propionic and rhodanine-3-butyric acids) are used for the synthesis of various compounds [11]. The structures of rhodanine-3-acetic acid was determined as both anhydrous compound and monohydrate [12]. Various derivatives with antimicrobial and antidiabetic activities were synthesized by 1,3-dipolar cycloaddition [13–15]. The carboxylate-containing ligands bearing an additional donor heteroatom (e.g., N, O, or S) bound to the cycle, which are potentially tridentate ligands, were studied to reveal the influence of the heteroatom on the structures of the organotin compounds [16]. The electron-withdrawing derivative of rhodanine (Rd), rhodanine-3-acetic acid (RdaH, Scheme 1), was acknowledged to be a promising candidate as a component of sensibilized dyes for solar cells [17].



Rd RdaH

Scheme 1.

One of the most important trends in coordination chemistry of the assembling of molecules containing more than one metal atom in order to produce polymeric materials with a series of useful properties [18, 19]. The introduction of bidentate bridging ligands of the bipyridine class into the synthetic medium favors the formation of the bi- [20] or polynuclear complexes [21].

The synthesis and X-ray structure analysis (XSA) data for seven compounds formed via the reactions of various transition metal salts with rhodanine-3-acetic acid (RdaH) are presented in this work. The compositions of the Co(II), Ni(II), Zn(II), and Cd(II) complexes can be presented by the formulas: $[Co(Rda)_2(H_2O)_4]$ **(I)**, $[Ni(Rda)_2(H_2O)_4]$ **(II)**, $[Zn(Rda)_2(H_2O)_4]$ **(III)**, $[Zn(5,5'\text{-}Rda\text{-}Rda)(Dmf)_2(H_2O)_2]_n$ **(IV)**, $[Co(Rda)_2(bipy)(H_2O)_2]_n$ **(V)**, $[Cd(Rda)_2(Bpe)]_n$ **(VI)**, and $[Co(Gly)_3]\cdot H_2O$ **(VII)**, where 5,5'-Rda-$RdaH_2$ is the new ligand synthesized by the condensation of two RdaH molecules, bipy is 4,4-bipyridine, Bpe is bis(4-pyridyl)ethane, and Gly is glycine. Compound $[Co(Gly)_3]\cdot H_2O$ **(VII)** was formed due to the decomposition of the RdaH ligand.

EXPERIMENTAL

Commercial reagents and solvents (reagent grade) were used as received.

Synthesis of $[Co(Rda)_2(H_2O)_4]$ (I). Salt $Co(BF_4)_2\cdot 6H_2O$ (0.036 g, 1 mmol) and RdaH (0.039 g, 1 mmol) were dissolved in a mixture of water (4 mL), methanol (2 mL), and 10 droplets of dimethylformamide (DMF). The resulting solution was stired at room temperature (25°C) for 10 min. The formed yellowish solution was filtered and left to stay in a closed vessel. The slow evaporation of the solution led to the formation of single crystals, which were filtered off and dried at room temperature. The yield was ~20%.

For $C_{10}H_{16}N_2O_{10}S_4Co$

Anal. calcd., %	C, 26.53	H, 3.56	N, 6.19
Found, %	C, 26.36	H, 4.40	N, 5.98

Synthesis of $[Ni(Rda)_2(H_2O)_4]$ (II). A mixture of $NiCl_2\cdot 6H_2O$ (0.013 g, 1 mmol) and RdaH (0.039 g, 1 mmol) was dissolved in a mixture of water (4 mL), methanol (2 mL), and 10 droplets of DMF. The yellow solution obtained after stirring at room temperature (25°C) was left in a closed vessel. The slow evaporation gave single crystals, which were filtered off and dried at room temperature in air. The yield was ~25%.

For $C_{10}H_{16}N_2O_{10}S_4Ni$

Anal. calcd., %	C, 26.59	H, 3.56	N, 6.19
Found, %	C, 26.37	H, 4.42	N, 5.98

Synthesis of $[Zn(Rda)_2(H_2O)_4]$ (III). Salt $Zn(BF_4)_2\cdot 6H_2O$ (0.036 g, 1 mmol) and RdaH (0.039 g, 1 mmol) were dissolved in a mixture of water (4 mL), methanol (2 mL), and 10 droplets of DMF. The formed yellow solution was stirred at room temperature (25°C), filtered, and left in a closed vessel. The slow evaporation of the solution resulted in the formation of brown crystals, which were filtered off and dried at room temperature. The yield was ~40%.

For $C_{10}H_{16}N_2O_{10}S_4Zn$

Anal. calcd., %	C, 26.59	H, 3.56	N, 6.19
Found, %	C, 26.37	H, 4.42	N, 5.98

Synthesis of $[Zn(5,5'\text{-}Rda\text{-}Rda)(Dmf)_2(H_2O)_2]_n$ (IV). Weighed samples of $Zn(BF_4)_2\cdot 6H_2O$ (0.025 g, 1 mmol) and RdaH (0.078 g, 2 mmol) were dissolved in water (4 mL), methanol (2 mL), and 10 droplets of DMF. The yellow solution obtained after stirring at room temperature (25°C) was filtered and left in a closed vessel. The slow evaporation of the solution led to the formation of needle-like brown single crystals, which were filtered off, washed with diethyl ether, and dried at room temperature in air. The yield was ~70%.

For $C_{16}H_{22}N_4O_{10}S_4Zn$

Anal. calcd., %	C, 30.80	H, 3.55	N, 8.98
Found, %	C, 30.62	H, 3.35	N, 8.82

Synthesis of $[Co(Rda)_2(Bipy)(H_2O)_2]_n$ (V). Salt $Co(BF_4)_2\cdot 6H_2O$ (0.036 g, 1 mmol), RdaH (0.039 g, 1 mmol), and bipy (0.019 g, 1 mmol) were dissolved in a mixture of water (4 mL), methanol (2 mL), and 10 droplets of DMF. The obtained yellow solution was stirred at room temperature (25°C) and left in a closed vessel. The slow evaporation of the solution gave brown single crystals, which were separated by filtration and dried at room temperature. The yield was ~35%.

For $C_{20}H_{20}N_4O_8S_4Co$

Anal. calcd., %	C, 41.94	H, 3.51	N, 9.78
Found, %	C, 41.76	H, 3.34	N, 9.69

Synthesis of $[Cd(Rda)_2(Bpe)]_n$ (VI). Weighed samples of $Cd(BF_4)_2\cdot 6H_2O$ (0.025 g, 1 mmol), RdaH (0.039 g, 1 mmol), and Bpe (0.018 g, 0.1 mmol) were dissolved in a mixture of water (4 mL), methanol (2 mL), and 10 droplets of DMF. The obtained yellow solution was stirred at room temperature (25°C), filtered off, and left in a closed vessel. The slow evaporation of the solution led to the formation of needle-like orange single crystals, which were filtered off, washed with diethyl ether, and dried at room temperature in air. The yield was ~30%.

For $C_{22}H_{20}N_4O_6S_4Cd$

Anal. calcd., %	C, 46.79	H, 3.59	N, 9.92
Found, %	C, 46.62	H, 3.42	N, 9.75

Synthesis of $[Co(Gly)_3]\cdot(H_2O)$ (VII). Salt $Co(BF_4)_2\cdot6H_2O$ (0.036 g, 1 mmol), RdaH (0.039 g, 1 mmol), and Bpe (0.018 g, 0.1 mmol) were dissolved in a mixture of water (4 mL), methanol (2 mL), and 10 droplets of DMF. The obtained solution was placed in a 8-mL Teflon vessel of a sealed metallic reactor and heated at 100°C for 48 h. After this, the solution was cooled to room temperature with a rate of 0.06°C/min. The obtained yellow solution was filtered off and left in a closed vessel. The slow evaporation of the solution gave needle-like brown single crystals, which were separated by filtration, washed with diethyl ether, and dried at room temperature in air.

For $C_6H_{12}N_3O_7Co$

Anal. calcd., %	C, 30.25	H, 5.07	N, 17.64
Found, %	C, 30.05	H, 4.96	N, 17.57

XSA. Experimental data for compounds **I–VII** were obtained at room temperature on an Xcalibur E diffractometer (graphite monochromator, MoK_α radiation). The unit cell parameters were determined and the experimental data were processed using the CrysAlis Oxford Diffraction Ltd. software [22]. The structures of the compounds were determined by direct methods and refined by least squares in the full-matrix anisotropic variant for non-hydrogen atoms using the SHELX-97 software [23]. The positions of the hydrogen atoms of the water molecules were revealed from the difference Fourier syntheses, and positions of other atoms were calculated geometrically. The coordinates of all hydrogen atoms were refined isotropically by the rigid body model with $U_{\text{eff}} = 1.2U_{\text{equiv}}$ or $1.5U_{\text{equiv}}$ of the corresponding C, N, and O atoms. The crystallographic data and experimental characteristics for the structures of compounds **I–VII** are presented in Table 1. Selected interatomic distances and bond angles in compounds **I–VI** are given in Table 2. The geometric parameters of intra- and intermolecular hydrogen bonds for compounds **I–VI** are listed in Table 3.

The positional and thermal parameters for the structures of compounds **I–VI** were deposited with the Cambridge Crystallographic Data Centre (CIF files CDCC nos. 2070334–2070339; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

Compounds $[Co(Rda)_2(H_2O)_4]$ (**I**), $[Ni(Rda)_2(H_2O)_4]$ (**II**), $[Zn(Rda)_2(H_2O)_4]$ (**III**), $[Zn(5,5'\text{-Rda-Rda})(Dmf)_2(H_2O)_2]_n$ (**IV**), $[Co(Rda)_2(bipy)(H_2O)_2]_n$ (**V**), $[Cd(Rda)_2(Bpe)]_n$ (**VI**), and $[Co(Gly)_3]\cdot H_2O$ (**VII**) were synthesized by the reactions of Co(II), Ni(II), Zn(II), and Cd(II) tetrafluoroborates with rhodanine-3-acetic acid (RdaH). The solvothermal synthesis was used only for compound **VII**. The ligands with the bridging function of the bis(pyridine) class were additionally involved for the preparation of coordination polymers in the synthesis of compounds **V–VII**. As a result, both the complexes (**I–III**, **VII**) and coordination polymers of the molecular type (**IV–VI**) were obtained.

The reaction of $M(BF_4)_2\cdot6H_2O$ (M = Co, Ni, Zn) with RdaH in a water–methanol mixture with the addition of several droplets of DMF afforded three isostructural isomorphous compounds **I–III**. These compounds crystallize in the space groups $P2_1/c$ and $P2_1/n$ of the monoclinic crystal system (Table 1). The Co(II), Ni(II), and Zn(II) molecular complexes are centrosymmetric (Fig. 1), and their two monodeprotonated organic ligands Rda^- coordinate via the monodentate mode through one oxygen atom of the carboxyl group and four water molecules supplementing the coordination polyhedron of the metal. As a result, the octahedral coordination polyhedra of the metals are formed by the same set (O_6) of donor atoms. The interatomic distances in compounds **I–III** are the following: Co(1)–O(1), Co(1)–O(1*w*), and Co(1)–O(2*w*) are 2.106(2), 2.141(2), and 2.087(2) Å, respectively; Ni(1)–O(1), Ni(1)–O(1*w*), and Ni(1)–O(2*w*) are 2.076(5), 2.114(5), and 2.042(5) Å, respectively; and Zn(1)–O(1), Zn(1)–O(1*w*), and Zn(1)–O(2*w*) are 2.112(2), 2.057(2), and 2.177(2) Å, respectively (Table 2). In three Sn(IV) compounds, the Rda^- ligand binds to the metal atoms via the bidentate-chelating or bidentate-bridging mode using both or one oxygen atom of the carboxyl group, respectively [16]. Thus, although this ligand has the O_3S set of donor atoms, only oxygen atoms of the carboxyl group are involved in coordination in both complexes **I–III** and the Sn(IV) compounds.

The coordinated water molecules in complexes **I–III** play an important role in the formation of the crystal structures (Table 3). First, one water molecule is involved in the formation of the intramolecular hydrogen bond O(*w*)–H···O with the uncoordinated oxygen atom of the carboxyl group to form the pseudohexametallocycle thus stabilizing the complex (Fig. 2a). The same water molecule is involved in intermolecular hydrogen bond formation joining the metal complexes into chains and involving the carbonyl oxygen atom bound to the pentacycle as the acceptor. The second water molecule participates in the formation of two intermolecular hydrogen bonds O(*w*)–H···O. As a result, one hydrogen bond stabilizes the formed chains, and another bond joins the chains into layers (Fig. 2b). The complexes are associated into the supramolecular 3D framework by the S···S interactions, and the distances in complexes **I–III** are 3.619, 3.608, and 3.615 Å, respectively (Fig. 3). The R-alkyl chain length and intermolecular S···S interactions affect the packing of the molecules in the crystal thus providing an excellent long-tern stability of thin-film transistors in air [24]. The involvement of the sulfur atoms in the

Table 1. Crystallographic data, experimental characteristics, and structure refinement parameters of compounds **I**–**VII**

Compound	**I**	**II**	**III**	**IV**	**V**	**VI**	**VII**
Composition	$C_{10}H_{16}N_2O_{10}S_4Co$	$C_{10}H_{16}N_2O_{10}S_4Ni$	$C_{10}H_{16}N_2O_{10}S_4Zn$	$C_{16}H_{22}N_4O_{10}S_4Zn$	$C_{20}H_{20}N_4O_8S_4Co$	$C_{22}H_{20}N_4O_6S_4Cd$	$C_6H_{12}N_3O_7Co$
FW	511.42	511.20	517.86	639.98	631.57	677.06	297.12
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/n$	$P2_1/n$	$P2_1/c$	$C2/c$	$P\bar{1}$	$P2_1/c$
a, Å	5.2319(5)	5.2163(5)	5.2532(3)	15.6602(12)	11.1768(10)	9.4114(5)	6.2298(12)
b, Å	26.3588(18)	26.347(2)	26.3076(13)	5.1186(3)	11.3964(9)	11.6492(7)	14.230(2)
c, Å	7.1645(10)	6.9610(5)	7.0027(3)	17.3621(15)	21.0680(18)	13.1979(6)	12.128(2)
α, deg	90	90	90	90	90	110.653(5)	90
β, deg	113.342(9)	110.103(9)	110.365(5)	114.245(10)	99.367(8)	100.339(4)	101.46(2)
γ, deg	90	90	90	90	90	98.007(5)	90
V, $Å^3$	907.17(17)	898.38(14)	907.27(8)	1268.97(16)	2647.8(4)	1299.33(13)	1053.7(3)
Z	2	2	2	2	4	2	4
ρ_{calc}, g/cm^3	1.872	1.890	1.896	1.633	1.584	1.731	1.873
μ, mm^{-1}	1.461	1.600	1.869	1.354	1.015	1.208	1.660
F(000)	522	524	528	640	1292	680	608
Crystal sizes, mm	0.40 × 0.14 × 0.03	0.28 × 0.18 × 0.05	0.42 × 0.22 × 0.06	0.40 × 0.20 × 0.04	0.38 × 0.22 × 0.05	0.34 × 0.28 × 0.12	0.42 × 0.09 × 0.02
Range over θ, deg	3.09–25.04	3.09–25.05	3.10–25.50	2.96–24.99	3.05–25.50	3.02–25.50	3.34–25.05
Ranges of reflection indices	$-6 \le h \le 5$, $-29 \le k \le 30$, $-5 \le l \le 8$	$-5 \le h \le 6$, $-31 \le k \le 21$, $-6 \le l \le 8$	$-6 \le h \le 4$, $-20 \le k \le 31$, $-8 \le l \le 8$	$-18 \le h \le 17$, $-6 \le k \le 5$, $-13 \le l \le 20$	$-13 \le h \le 13$, $-7 \le k \le 13$, $-22 \le l \le 25$	$-11 \le h \le 9$, $-13 \le k \le 14$, $-15 \le l \le 15$	$-7 \le h \le 4$, $-7 \le k \le 16$, $-14 \le l \le 14$
Number of measured/ independent reflections (R_{int})	2908/1605 (0.0266)	2905/1582 (0.0319)	3222/1690 (0.0240)	3959/2216 (0.0311)	4751/2463 (0.0683)	8249/4807 (0.0268)	3431/1863 (0.0494)
Value, %	99.6	99.1	99.8	99.4	99.5	99.8	99.5
Number of reflections with $I > 2\sigma(I)$	1294	1284	1472	1547	1671	4204	1394
Number of refined parameters	124	125	125	162	171	335	154
GOOF	1.000	1.002	1.000	1.005	1.000	1.003	1.007
R factors ($I > 2\sigma(I)$)	$R_1 = 0.0384$ $wR_2 = 0.0787$	$R_1 = 0.0740$ $wR_2 = 0.2207$	$R_1 = 0.0369$ $wR_2 = 0.0886$	$R_1 = 0.0587$ $wR_2 = 0.1598$	$R_1 = 0.0706$ $wR_2 = 0.1721$	$R_1 = 0.0345$ $wR_2 = 0.0804$	$R_1 = 0.0646$ $wR_2 = 0.1526$
R factors (for all data)	$R_1 = 0.0529$ $wR_2 = 0.0841$	$R_1 = 0.0890$ $wR_2 = 0.2316$	$R_1 = 0.0438$ $wR_2 = 0.0926$	$R_1 = 0.0891$ $wR_2 = 0.1835$	$R_1 = 0.1031$ $wR_2 = 0.2052$	$R_1 = 0.0421$ $wR_2 = 0.0864$	$R_1 = 0.0889$ $wR_2 = 0.1688$
$\Delta\rho_{max}/\rho_{min}$, e $Å^{-3}$	0.294/–0.327	0.702/–0.689	0.307/–0.328	0.628/–0.543	0.908/–0.646	0.541/–0.501	1.501/–0.765

Table 2. Interatomic distances and bond angles in the coordination polyhedra of compounds **I–VI**

Bond	**I** (M = Co)	**II** (M = Ni)	**III** (M = Zn)	**IV** (M = Zn)	**V** (M = Co)	**VI** (M = Cd)
			d, Å			
M(1)–O(1)	2.106(2)	2.076(5)	2.112(2)	2.087(3)	2.062(3)	2.307(2)
M(1)–(1w)/O(2)**	2.141(2)	2.114(5)	2.177(2)	2.067(3)	2.144(3)	2.356(2)
M(1)–O(2w)/O(4)/N(2)	2.087(2)	2.042(5)	2.057(2)	2.138(4)	2.158(6)	2.380(2)
Me(1)–O(1w)/O(4)/N(3)*/O(5)					2.165(6)	2.397(2)
Me(1)–O(1)**						2.660(3)
Me(1)–N(3)						2.326(2)
Me(1)–N(4)*						2.300(2)
Angle			ω, deg			
O(1)Me(1)O(1w)/O(2)**	89.32(9)	90.2(2)	90.00(9)	88.8(1)	90.0(1)	123.50(10)
O(1)Me(1)O(1)**						74.91(9)
O(1)Me(1)O(2w)/O(4)/N(2)/O(4)	90.68(8)	91.5(2)	90.79(8)	92.3(2)	90.03(9)	91.07(10)
O(1)Me(1)O(1)*/O(5)	180	180	180	180	180.0(2)	146.01(10)
O(1)Me(1)O(1w)*/N(3)	90.68(9)	89.8(2)	90.00(9)	91.2(1)	90.0(1)	90.54(9)
O(1)Me(1)O(2w)*/N(3)*/N(4)*	89.32(8)	88.5(2)	89.21(8)	87.7(2)	89.97(9)	91.58(10)
O(1w)/O(2)**Me(1)O(2w)/O(4)*/N(2)/O(4)	89.59(9)	90.3(2)	89.56(8)	88.5(2)	87.37(10)	144.76(8)
O(1w)/O(2)**Me(1)O(1)*/O(5)	90.68(9)	89.8(2)	90.00(9)	91.2(1)	90.0(1)	90.13(8)
O(1w)/O(2)**Me(1)O(1w)*/N(3)	180	180	180	180	174.7(2)	85.56(8)
O(1w)/O(2)**Me(1)O(2w)*/O(4)*/N(3)*/N(4)*	90.40(9)	89.7(2)	90.45(8)	91.5(2)	92.63(10)	91.72(8)
O(2)**Me(1)O(1)**						51.05(8)
O(2w)/O(4)/N(2)Me(1)O(2w)*/O(4)*/N(3)*/O(5)	180	180	180	180	180	54.97(7)
O(4)Me(1)O(1)**						163.35(9)
O(4)Me(1)N(3)						87.65(9)
O(4)Me(1)N(4)*						94.16(9)
O(5)Me(1)N(3)						87.04(9)
O(5)Me(1)N(4)*						92.23(9)
O(5)Me(1)O(1)**						138.75(9)
N(3)Me(1)O(1)**						101.15(8)
N(4)*Me(1)O(1)**						77.62(8)
N(3)Me(1)N(4)*						177.19(8)

I: * –x – 2, –y, –z – 2; **II**: * –x + 2, –y, –z; **III**: * –x + 1, –y + 1, –z + 1; **IV**: * –x + 2, –y + 1, –z + 1; **V**: * –x, y, z + 1/2; ** x, y – 1, z; **VI**: * x – 1, y – 1, z; ** –x, –y + 1, –z + 1.

Table 3. Geometric parameters of the hydrogen bonds in compounds **I–VI**

D–H···A	Distance, Å			Angle DHA, deg	Symmetry transform for A
	D–H	H···A	D···A		
			I		
O(1*w*)–H(1)···O(1)	0.93	2.05	2.961(3)	165	$-x - 1, -y, -z - 2$
O(1*w*)–H(2)···O(2)	0.93	2.00	2.916(3)	168	$-x - 1, -y, -z - 1$
O(2*w*)–H(1)···O(2)	0.91	1.79	2.649(3)	157	x, y, z
O(2*w*)–H(2)···O(3)	0.80	2.03	2.821(3)	170	$-x - 1, -y, -z - 1$
C(4)–H(4)···S(2)	0.97	3.02	3.728(4)	131	$x + 1, -y + 1/2, z + 1/2$
			II		
O(1*w*)–H(1)···O(1)	0.83	2.22	2.969(7)	150	$x + 1, y, z$
O(1*w*)–H(2)···O(2)	0.88	2.03	2.912(7)	178	$x, y, z - 1$
O(2*w*)–H(1)···O(3)	0.86	1.95	2.798(8)	167	$-x + 2, -y, -z + 1$
O(2*w*)–H(2)···O(2)	0.86	1.83	2.637(8)	157	x, y, z
C(4)–H(4)···S(2)	0.97	3.03	3.728(9)	130	$x - 1/2, -y + 1/2, z + 1/2$
			III		
O(1*w*)–H(1)···O(1)	0.89	2.08	2.959(3)	172	$-x + 2, -y + 1, -z + 1$
O(1*w*)–H(2)···O(2)	0.89	2.04	2.908(3)	168	$-x + 1, -y + 1, -z$
O(2*w*)–H(1)···O(2)	0.89	1.85	2.634(3)	147	x, y, z
O(2*w*)–H(2)···O(3)	0.88	1.94	2.809(3)	168	$-x + 1, -y + 1, -z$
C(4)–H(4)···S(2)	0.97	3.00	3.714(3)	131	$x + 1/2, -y + 3/2, z - 1/2$
			IV		
O(1*w*)–H(1)···O(1)	0.82	2.32	3.129(5)	167	$-x + 2, -y, -z + 1$
O(1*w*)–H(1)···O(2)	0.86	1.94	2.608(5)	134	$-x + 2, -y + 1, -z + 1$
C(2)–H(2)···O(2)	0.97	2.54	3.424(7)	151	$x, y - 1, z$
C(6)–H(6)···O(1)	0.93	2.60	3.212(8)	124	x, y, z
C(7)–H(7*A*)···S(2)	0.96	2.91	3.553(10)	126	x, y, z
C(7)–H(7*B*)···O(2)	0.96	2.60	3.447(11)	147	$x, -y + 3/2, z - 1/2$
C(8)–H(8*A*)···O(1*w*)	0.96	2.56	3.450(11)	154	$x, y + 1, z$
			V		
O(1*w*)–H(1)···O(3)	0.85	1.99	2.837(6)	174	$x - 1/2, y - 1/2, z$
O(1*w*)–H(2)···O(2)	0.87	1.97	2.718(6)	144	x , y, z
C(4)–H(4)···O(2)	0.97	2.52	3.076(7)	117	$-x + 1/2, -y + 3/2, -z + 1$
C(7)–H(7)···O(1)	0.93	2.59	3.409(6)	147	$-x + 1/2, y + 1/2, -z + 1/2$
C(8)–H(8*A*)···O(1*w*)	0.96	2.56	3.450(11)	154	$x, y + 1, z$
			VI		
C(4)–H(1*B*)···O(6)	0.97	2.34	3.255(7)	157	$-x - 1, -y + 1, -z + 1$
C(9)–H(9*A*)···O(5)	0.97	2.45	3.015(4)	117	$-x, -y + 2, -z + 2$
C(9)–H(9*B*)···O(2)	0.97	2.52	3.298(5)	138	$x, y + 1, z + 1$
C(15)–H(15)···O(2)	0.93	2.51	3.158(4)	127	$-x, -y + 1, -z + 1$
C(22)–H(22)···O(4)	0.93	2.56	3.406(4)	151	$-x, -y + 2, -z + 1$

formation of weak intermolecular hydrogen bonds C(4)–H···S(2) can also be mentioned (Table 3).

Compound **IV** crystallizes in the monoclinic space group $P2_1/c$ (Table 1). The independent part of the unit cell contains one zinc atom localized at the symmetry center, 1/2 ligand (5,5'-Rda-Rda)$^{2-}$, one DMF molecule, and one water molecule. In the crystal, these components form the centrosymmetric 1D coordination polymer, whose bridging *exo*-bidentate function is performed by the doubly deprotonated new

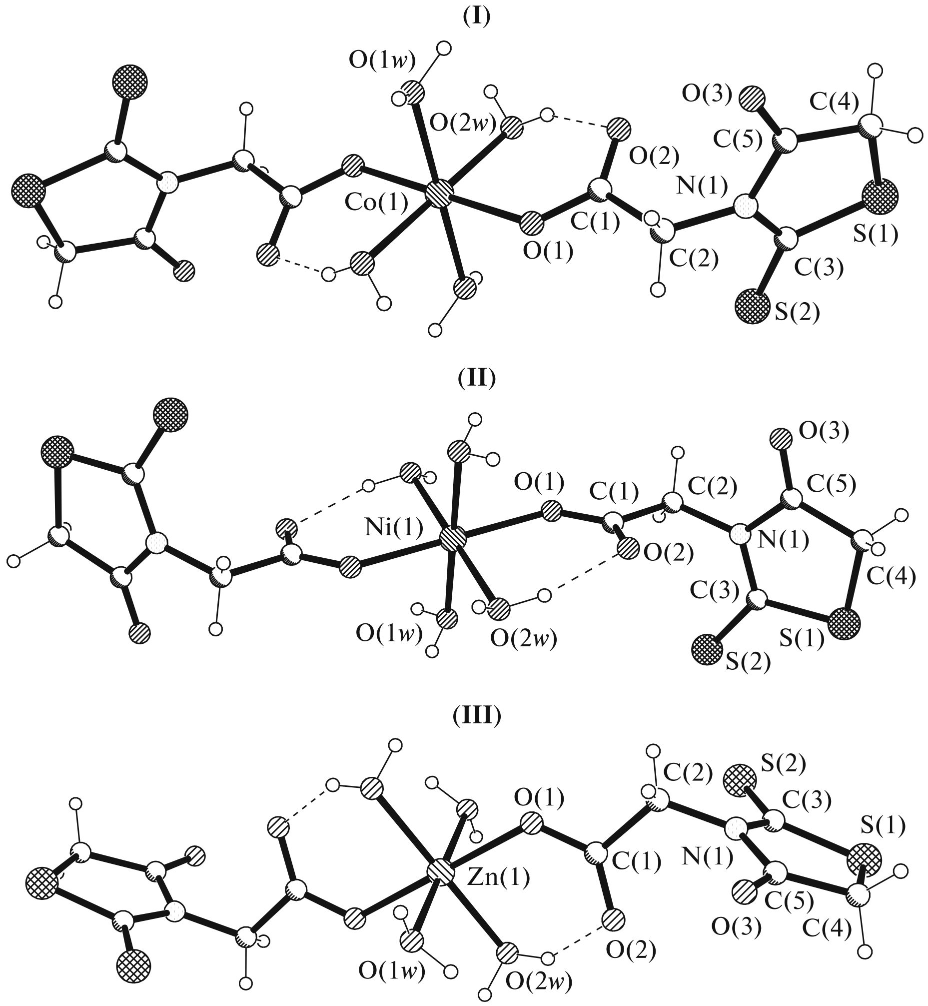
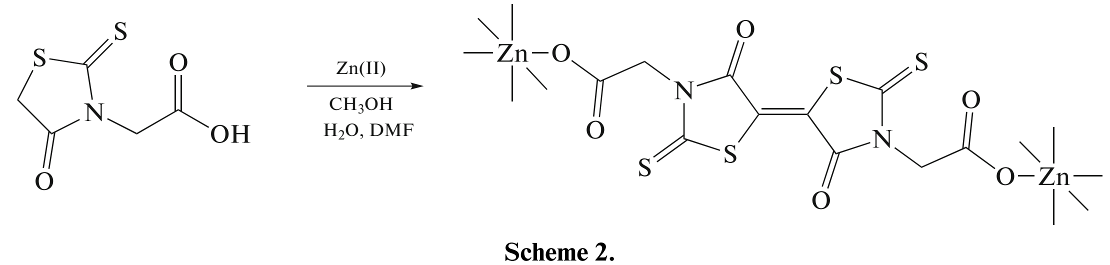


Fig. 1. Molecular structures of complexes **I**–**III**.

organic ligand 5,5'-Rda-Rda^{2-}, which was synthesized by the condensation of two Rda$^-$ ligands (Scheme 2). The condensation effect was revealed previously for various RdaH derivatives [25, 26].



Scheme 2.

The octahedral coordination polyhedron of the metal in compound **IV** is formed by the donor set of atoms (O_6) of which two oxygen atoms belong to two organic dianions 5,5'-Rda-Rda^{2-} and other four atoms belong to two coordinated DMF molecules and two water molecules (Fig. 4a). The interatomic distances in the coordination polyhedron of the metal are as follows: Zn–O(1) 2.087(3) Å, Zn–O(Dmf) 2.138(4) Å, and Zn–O(*w*) 2.067(3) Å (Table 2).

The 1D coordination polymers in the crystal are stabilized by the intramolecular hydrogen bonds O(1*w*)–H···O(1), where the water molecule acts as the proton donor and the uncoordinated oxygen atom of the carboxyl group of the 5,5'-Rda-Rda^{2-} ligand

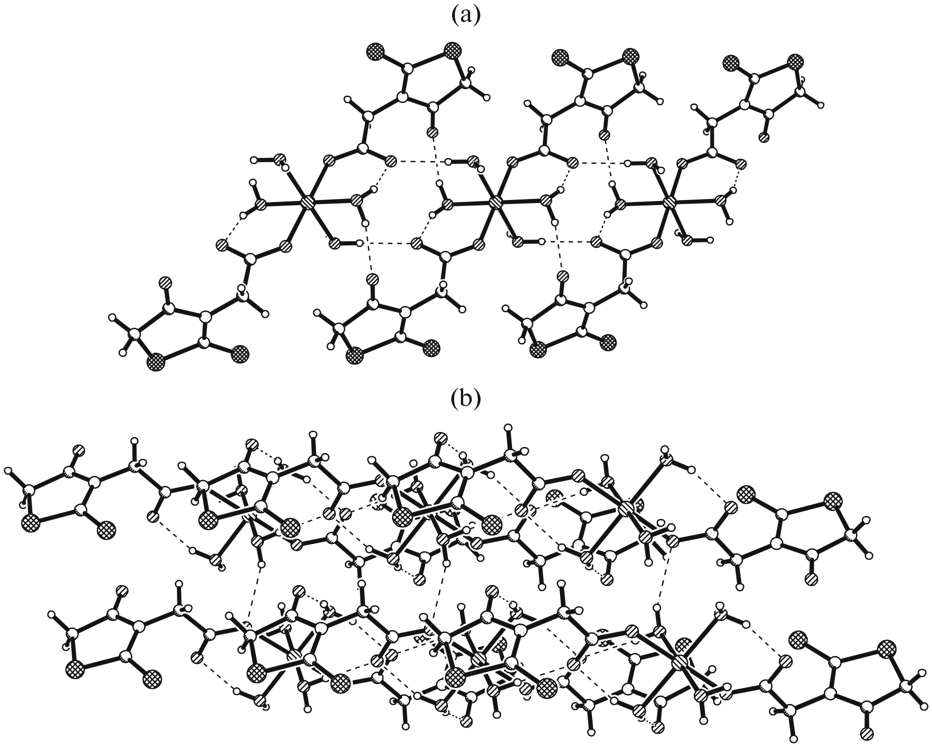


Fig. 2. (a) Structure of the chain in compound **II** and (b) joining of the chains from the Ni(II) complexes with layer formation in complex **II**.

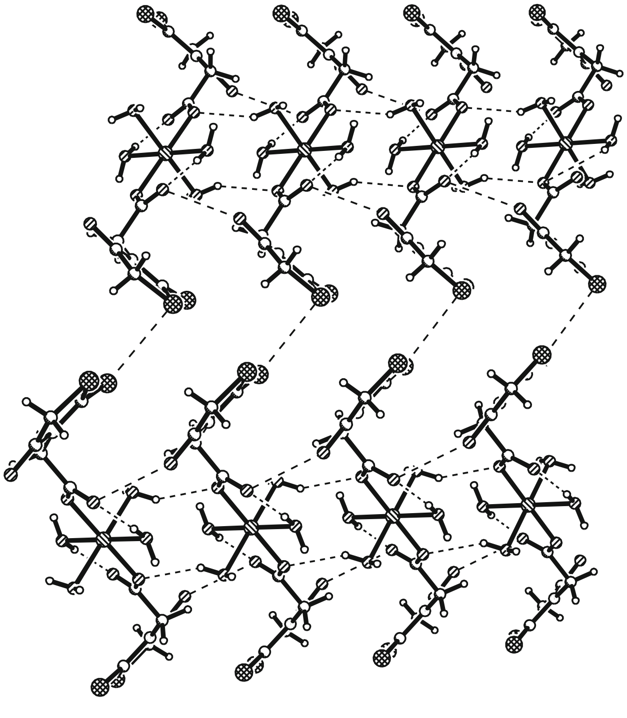


Fig. 3. Formation of the supramolecular 3D polymer due to the S···S interaction in the crystal of complex **II**.

serves as the acceptor with the formation of the pseudohexametallocycle similar to those observed in complexes **I**–**III**. The same water molecule is involved in the formation of a weaker intermolecular hydrogen bond O(*w*)–H···O(1)* as well (Table 3). As a result, the chain in the crystals are joined by both O(*w*)–H···O(1) and C–H···O intermolecular hydrogen bonds into the layers (Fig. 4b). The three-dimensional framework is built by the S···S interactions (3.493 Å) forming SCSSCS hexamacrocycles between the organic ligands of the coordination polymers (Fig. 5).

Attempts to synthesize the transition metal complexes with RdaH and additional bridging ligands of the bis(pyridine) class led to the formation of two new 1D coordination polymers **V** and **VI**. However, the reaction of the Co(II) salt with RdaH and Bpe afforded the already known Co(II) complex with glycine (**VII**) [27].

Compound **V** crystallizes in the monoclinic space group *C*2/*c* (Table 1). The independent part of the unit cell contains the metal atom and bipy ligand with the C_2 symmetry, one monodeprotonated Rda$^-$ ligand, and one water molecule, and the latter are localized in the common position. The octahedral coordination polyhedron of Co(II) is formed by the set of donor atoms N_2O_4 (Fig. 6a). All oxygen atoms lie in the

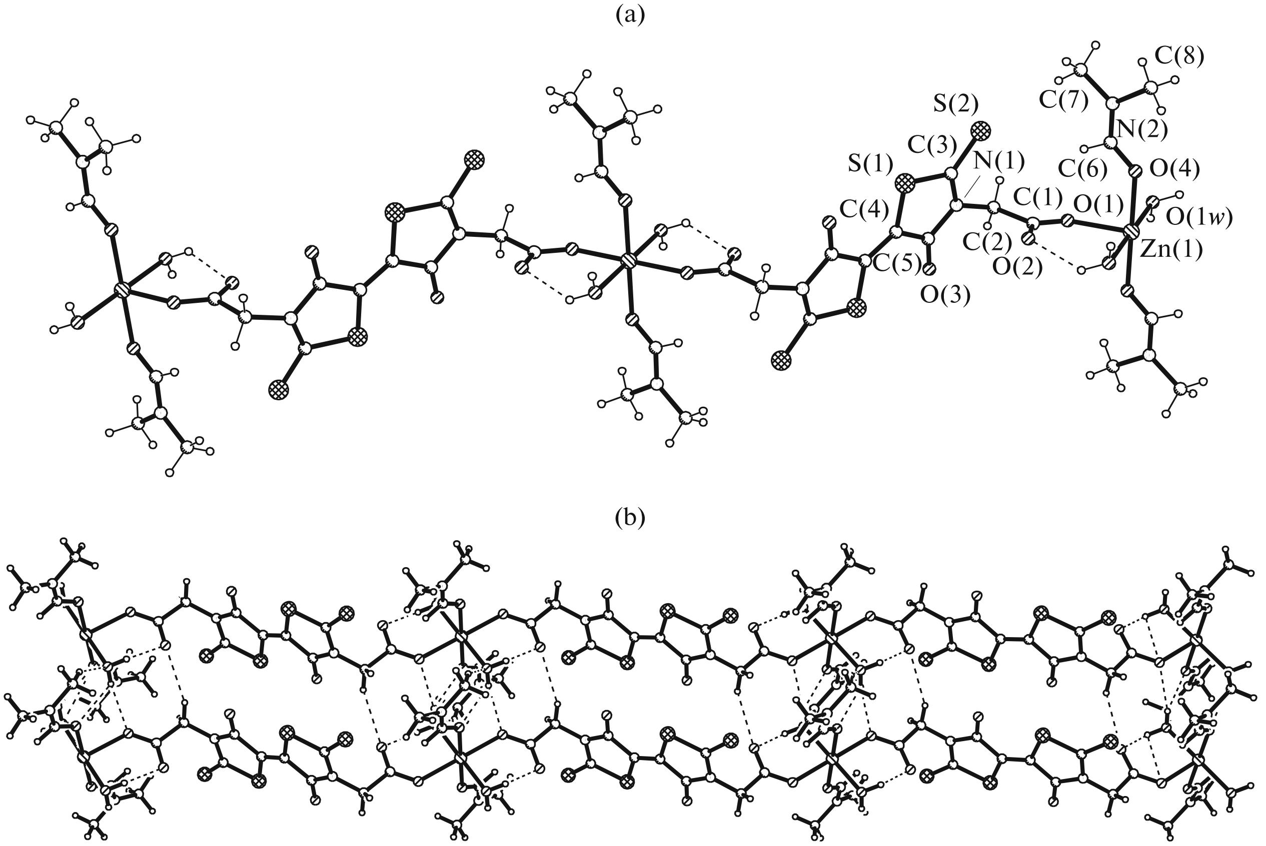


Fig. 4. (a) Formation of the 1D coordination polymer in compound **IV** and (b) joining of the coordination polymers into the layers in compound **IV** by hydrogen bonds.

equatorial plane of the polyhedron, two of them belong to two organic anions Rda⁻ and two water molecules, and the interatomic distances Co–O(Rda) and Co–O(*w*) are 2.062(3) and 2.144(3) Å, respectively (Table 2). Two nitrogen atoms belonging to two bipy ligands are arranged in the axial positions of the polyhedron, and the Co–N interatomic distance is 2.158(6) Å. Since bipy coordinates to two metal atoms as an *exo*-bidentate ligand, the chains of 1D coordination polymers are revealed in the crystal. The interatomic distance between two metal atoms linked by the bipy ligand is 11.396 Å, and the dihedral angle

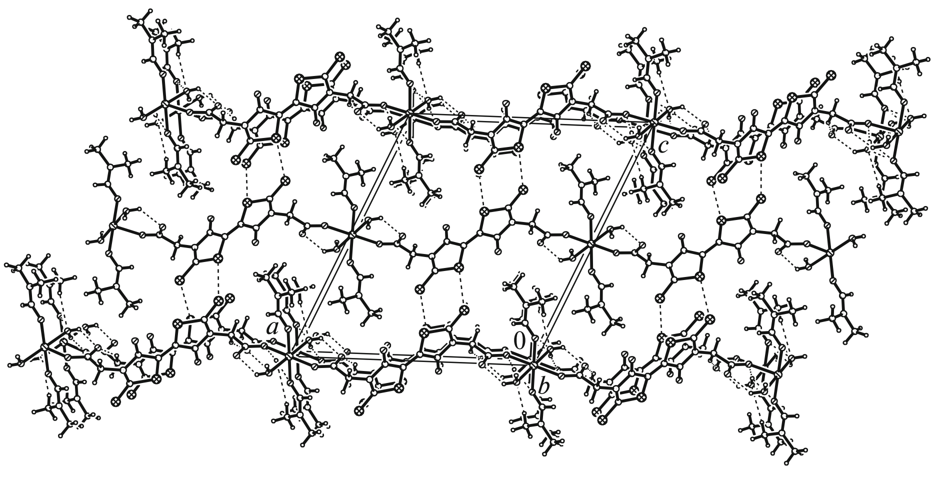


Fig. 5. Fragment of the crystal structure of compound **IV**.

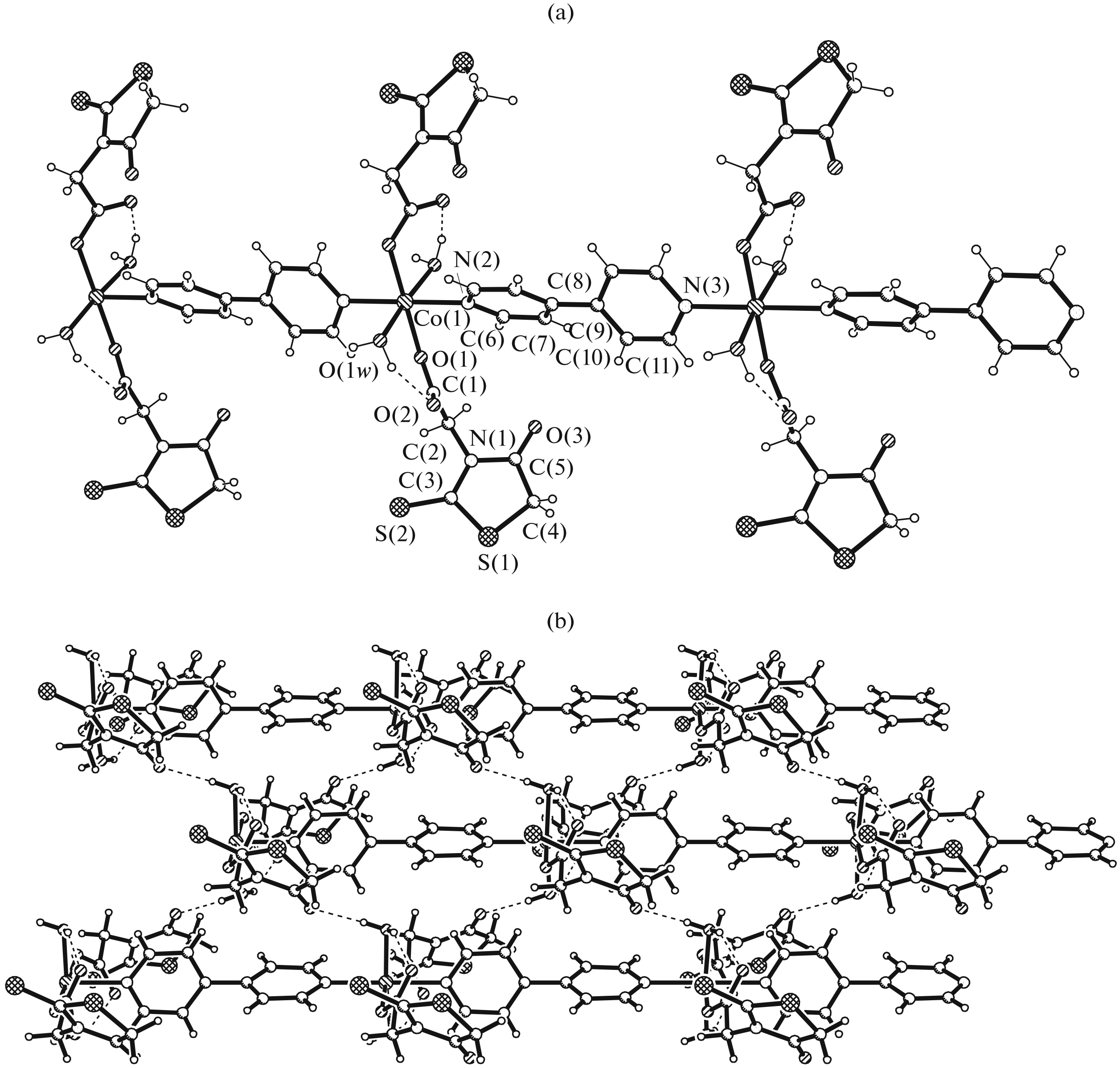


Fig. 6. (a) Formation of the 1D coordination polymer by Bipy in compound **V** and (b) layer formation by the intermolecular O(*w*)–H···O hydrogen bonds between the coordination polymers in compound **V**.

between the aromatic rings of the latter is 121.18°. Since the Rda$^-$ ligands coordinate to the metal atom via the monodentate mode involving only one oxygen atom of the carboxyl group, and the ligands along with water molecules only decorate the coordination chains in the crystal rather than develop them.

The positions of all components of the coordination polymer are stabilized by the intramolecular hydrogen bonds O(*w*)–H···O to form hexametallocycles in which the water molecules serve as proton donors and the uncoordinated oxygen atoms of the carboxyl groups act as acceptors (Table 3). In the crystal, the coordination chains are joined into the layers by the intermolecular hydrogen bonds O(*w*)–H···O in which the water molecules are the proton donors, whereas the acceptors are the carbonyl oxygen atoms of the Rda$^-$ ligand linked with the pentacycle (Table 3, Fig. 6b). The formation of the three-dimensional framework in the crystal is provided only by weak interactions of the C–H···O (Table 3) and O(2)···S(1)* (3.122 Å) types between the bridging organic ligands of the adjacent coordination polymers (Fig. 7).

The use of the Cd(II) salt and Bpe instead of the Co(II) salt and bipy resulted in the formation of compound **VI**, which is new in both composition and structure. Compound **VI** crystallizes in the triclinic space group $P\overline{1}$ (Table 1). One metal atom, two

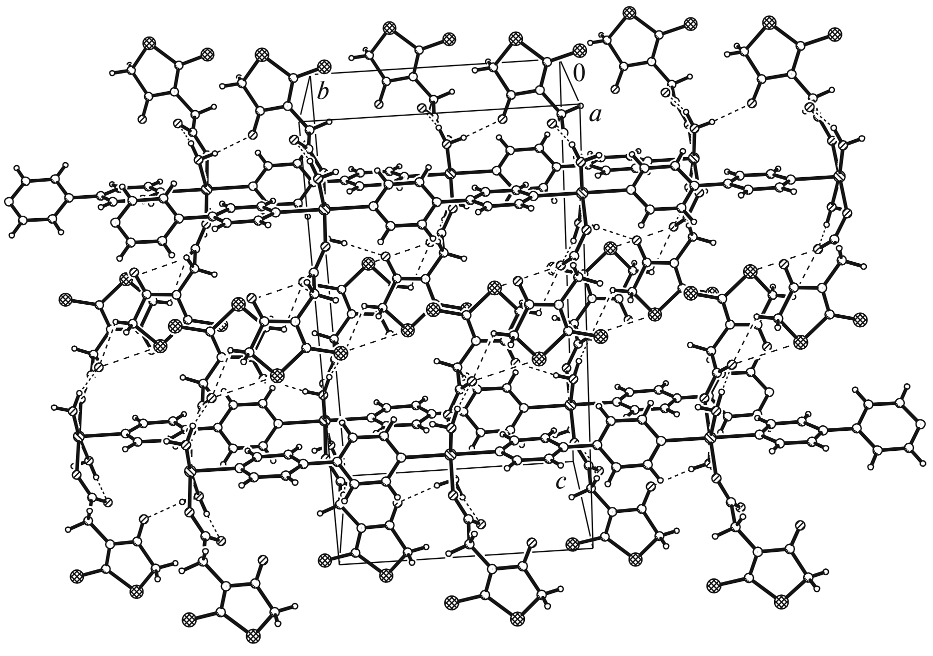


Fig. 7. Fragment of the crystal structure of compound **V**.

monoprotonated Rda⁻ ligands, and one Bpe ligand in the common positions were revealed in the unit cell of the crystal. As a result of both different coordination modes for two crystallographically independent Rda⁻ ligands and the mode differed from that found for compounds **I**–**III** and **V**, the centrosymmetric binuclear fragments $[Cd(Rda)_2]_2$ are formed in the crystal, and their two organic ligands coordinate via the tridentate-bridging mode: the bidentate-chelating mode to one metal atom and monodentate mode to another metal atom, whereas two ligands coordinate via only the bidentate-chelating mode to one metal atom, and all the four ligands use the oxygen atoms of the carboxyl groups only (Fig. 8a). These coordination modes for this ligand were found earlier in the Sn(IV) compounds [16]. The binuclear fragments develop further to form 1D coordination polymers as ribbons via the bridging *exo*-bidentate ligands Bpe. The coordination polyhedron of the Cd(1) atom is formed by a set of donor atoms N_2O_5; that is, the coordination number of the metal atom is 7 and the coordination polyhedron is a pentagonal bipyramid (Fig. 8a). The interatomic Cd–O(Rda) distances range from 2.307(2) to 2.660(3) Å, and the Cd–N distances are 2.300(2) and 2.326(2) Å (Table 2). The interatomic Cd···Cd distance in the centrosymmetric binuclear fragment is 3.949 Å, and that along the Bpe ligand is 13.919 Å (Fig. 8b). In the crystal, the ribbon 1D coordination polymers are linked with each other only by weak intermolecular hydrogen bonds C–H···O involving the donor groups of both the Rda⁻ and Bpe ligands, whereas the oxygen atoms of the Rda⁻ ligand participate as acceptors (Table 3, Fig. 9).

An attempt to synthesize the Co(II) complexes with RdaH and Bpe by the solvothermal method resulted in the decomposition of the RdaH ligand and formation of the compound with glycine **(VII)** (Fig. 10), which is already known in the literature but was earlier synthesized by the direct method [27].

Thus, the structural study of compounds $[Co(Rda)_2(H_2O)_4]$ (**I**), $[Ni(Rda)_2(H_2O)_4]$ (**II**), $[Zn(Rda)_2(H_2O)_4]$ (**III**), $[Zn(5,5'\text{-}Rda\text{-}Rda)\text{-}(Dmf)_2\text{-}(H_2O)_2]_n$ (**IV**), $[Co(Rda)_2(bipy)(H_2O)_2]_n$ (**V**), and $[Cd(Rda)_2(Bpe)]_n$ (**VI**) showed that rhodanine-3-acetic acid (RdaH) in the complexes behaved as a monodeprotonated ligand that can coordinate to the metal atoms via the mono-, bi-, or tridentate mode using only the oxygen atoms of the carboxyl group. Under certain conditions, the condensation of two similar ligands led to the formation of the new ligand with the *exo*-bridging function. However, the coordination polymers with RdaH can mainly be synthesized using additional ligands of the bis(pyridine) class with the bridging function.

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CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

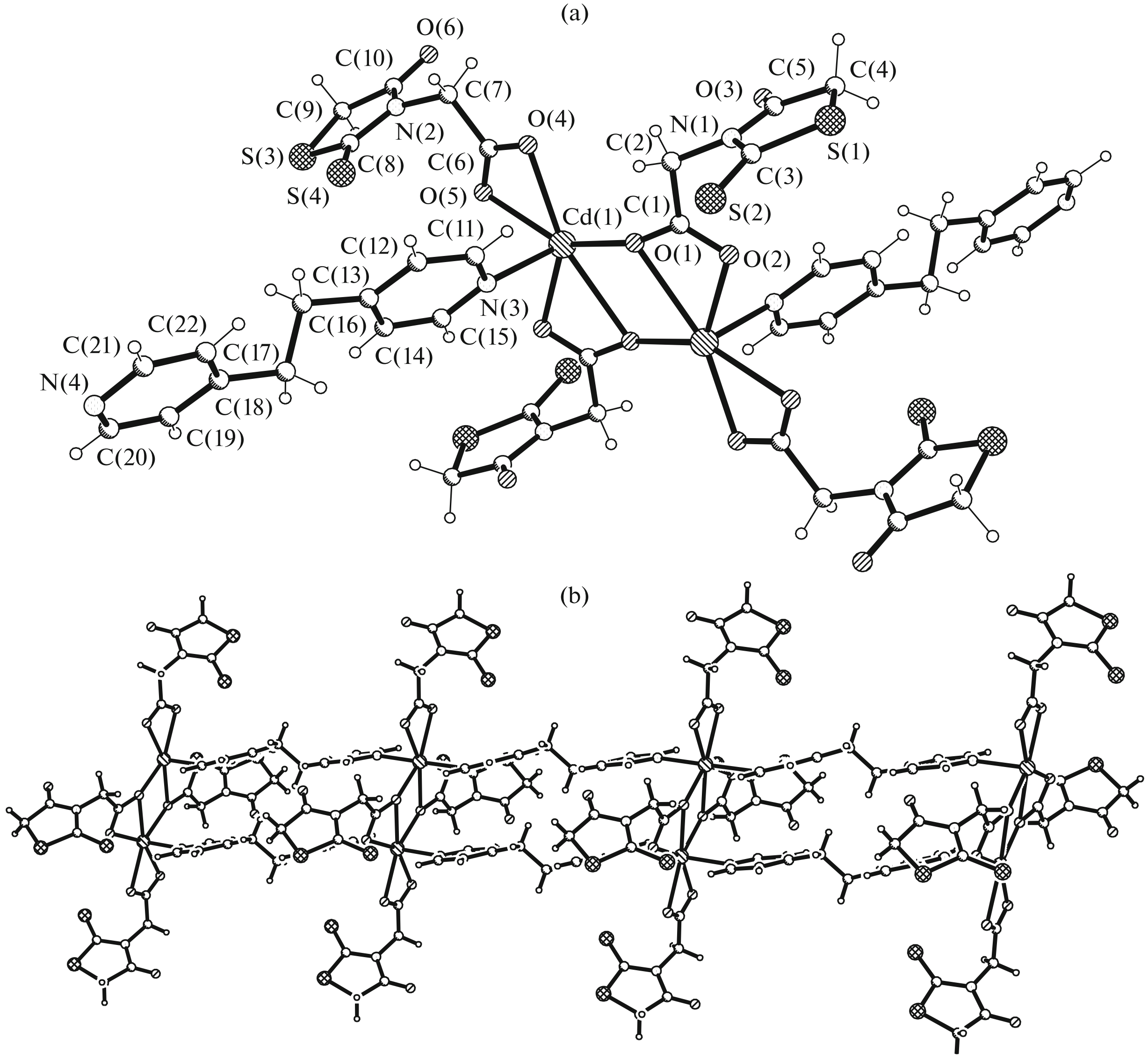

Fig. 8. (a) Formation of the binuclear fragment in compound **VI** and (b) joining of the binuclear fragments by Bpe with the formation of the binary 1D coordination polymer in compound **VI**.

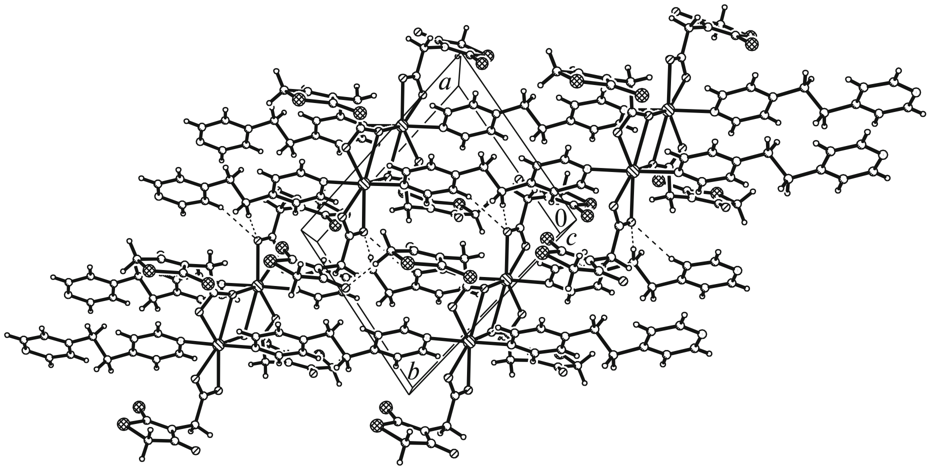

Fig. 9. Fragment of the crystal structure of compound **VI**.

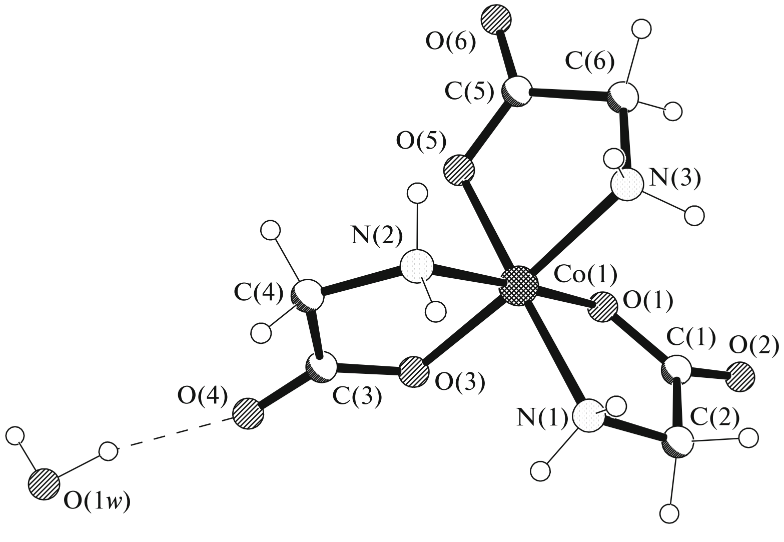

Fig. 10. Molecular structure of complex **VII**.

REFERENCES

1. Gendy, El.Z., Abdel Rahman, R.M., Fazy, M.M., and Mahmoud, M.B., *J. Ind. Chem. Soc.*, 1990, vol. 67, p. 927.
2. Shah, V., Pant, C.K., and Joshi, P.C., *Asian J. Chem.*, 1993, vol. 5, p. 83.
3. Vicini, P., Geronikaki, A., Anastasia, K., et al., *Bioorg. Med. Chem.*, 2006, vol. 14, p. 3859.
4. Zervosen, A., Lu, W.P., Chen, Z., et al., *Antimicrob. Agents Chemother.*, 2004, vol. 48, p. 961.
5. Liu, H.L., Li, Z., and Anthonsen, T., *Molecules*, 2000, vol. 5, p. 1055.
6. Sen, M. and Sathya, C.D., *Indian J. Exp. Biol.*, 1994, vol. 13, p. 279.
7. Kshirsagar, V., Gandhe, S., and Gautam, M.D., *Asian J. Chem.*, 2008, vol. 20, no. 6, p. 4955.
8. Gupta, P.N. and Raina, A., *Asian J. Chem.*, 1990, vol. 2, p. 73.
9. Kodama, M., Mahatma, A.B., and Raut, A.K., *Bull. Chem. Soc.*, 1994, vol. 63, p. 592.
10. Allen, F.H., *Acta Crystallogr., Sect. B: Struct. Sci.*, 2002, vol. 58, nos. 1–3, p. 380.
11. Tejchman, W., Skorska-Stania, A., and Zeslawska, E., *J. Chem. Crystallogr.*, 2016, vol. 46, p. 181.
12. Barakat, A., Ali, M., Al-Majid, A.M., and Ghabbour, H.A., *Z. Kristallogr. New Crystal Struct.*, 2017, vol. 232, p. 141.
13. Barakat, A., Ghabbour, H.A., Al-Majid, A.M., et al., *Z. Kristallogr. New Crystal Struct.*, 2016, vol. 231, p. 319.
14. Jin, X., Zheng, C.J., Song, M.X., et al., *Eur. J. Med. Chem.*, 2012, vol. 56, p. 203.
15. Murugan, R., Anbazhagan, S., and Sriman Narayanan, S., *Eur. J. Med. Chem.*, 2009, vol. 44, no. 8, p. 3272.
16. Zhang, R., Sun, J., and Ma, C., *J. Organomet. Chem.*, 2005, vol. 690, p. 4366.
17. Liang, M., Xu, W., Cai, F., et al., *J. Phys. Chem.*, 2007, vol. C111, p. 4465.
18. Coropceanu, E., Croitor, L., Gdaniec, M., et al., *Inorg. Chim. Acta*, 2009, vol. 362, no. 7, p. 2151.
19. Croitor, L., Coropceanu, E.B., Siminel, A.V., et al., *CrystEngComm*, 2012, vol. 14, p. 3750.
20. Coropceanu, E., Rija, A., Lozan, V., et al., *Cryst. Growth Des.*, 2016, vol. 16, no. 2, p. 814.
21. Croitor, L., Coropceanu, E., Chisca, D., et al., *Cryst. Growth Des.*, 2014, vol. 14, no. 6, p. 3015.
22. CrysAlis RED. O.D.L. Version 1.171.34.76, 2003.
23. Sheldrick, G., *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 2008, vol. 64, no. 1, p. 112.
24. Iijima, K., Le Gal, Y., Lorcy, D., and Mori, T., *RSC Adv.*, 2018, vol. 8, p. 18400.
25. Allendorf, M.D., Bauer, C.A., Bhakta, R.K., and Houk, R.J., *Chem. Soc. Rev.*, 2009, vol. 38, p. 1330.
26. Mohamed, G., Omar, M., and Ibrahim, A., *Eur. J. Med. Chem.*, 2009, vol. 44, no. 12, p. 4801.
27. Zhao, X.-J., Du, M., Wang, Y., and Bu, X.-H., *J. Mol. Struct.*, 2004, vol. 692, nos. 1–3, p. 155.

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