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The authors congratulate Academician I.L. Eremenko on his 70th birthday

Synthesis, Structure, and Magnetic Properties of Heterospin Polymers $M^{I}[M^{II}(Hfac)L_2]$

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Abstract—Heterospin polymeric complexes based on Ni(II) and Co(II) hexafluoroacetylacetonates and deprotonated iminonitroxide, 2-(2-hydroxy-5-nitrophenyl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazole-1-oxyl (HL), were synthesized. The $[M^{II}(Hfac)L_2]^-$ anions (Hfac = 1,1,1,5,5,5-hexafluoro-2,4-pentanedionate) in the complexes are linked into 1D–3D polymers by Na^+, K^+, Rb^+, or Cs^+ cations (**I**–**V**). An X-ray diffraction study of $M^{I}[M^{II}(Hac)L_2] \cdot n(Me_2CO)$ ($n = 0$–2.5) demonstrated that the polymer structural motif is determined by alkali metal cation (CIF files CCDC nos. 1974139–1974143 for **I**–**V**). According to magnetic measurements, ferromagnetic interactions in the {LML} exchange clusters predominate in the solid phase, which gives rise to increase in the effective magnetic moment with decreasing temperature.

Keywords: nickel, cobalt, sodium, potassium, rubidium, cesium, hexafluoroacetylacetonate, nitroxide, polymers, X-ray diffraction, magnetic properties

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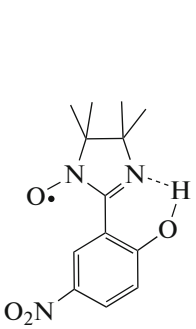
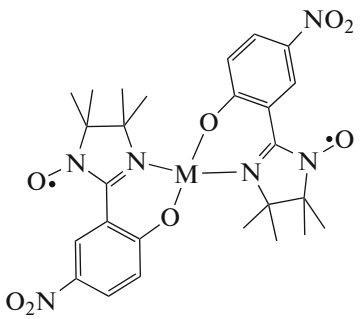
INTRODUCTION

Recently, it was shown that the iminonitroxide, 2-(2-hydroxy-5-nitrophenyl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazole-1-oxyl (HL), reacts with transition metal pivalates with initiation of redox processes accompanied by partial reduction of the iminonitroxide followed by the formation of coordination compounds containing both the initial radical and the nitrone resulting from its reduction [1, 2]. Attention was drawn by the existence of ferromagnetic exchange clusters within the formed mono- and polynuclear molecules [2, 3], which generated interest in the development of synthetic routes for connecting ferromagnetic exchange clusters into high-dimensional structures, in which cooperative ordering of spins is potentially possible. It is noteworthy that the ferromagnetic exchange also occurs in bis-chelate molecular matrices with the spin-labeled Schiff bases $[ML_2]$ (M = Ni, Cu, Co) containing no additional organic ligands [4, 5]. However, homoleptic $[ML_2]$ are, first, poorly soluble in organic solvents and, second, possess low acceptor ability needed for the development of high-dimensional structures. Therefore, for increasing the acceptor properties of metals in $[ML_2]$, it is necessary to either introduce appropriate substituents into the L molecule or add acceptor ligands into the metal coordination sphere. It is noteworthy that there exist few reported examples of polymeric complexes formed by 3*d* metal hexafluoroacetylacetonates with nitroxides, most of which behave as magnets, but do not contain *s*-elements [6–18]. We made an attempt to study the products formed in the reaction of the strong acceptor metal-containing matrix {M(Hfac)2} with HL. The study demonstrated that mononuclear $[M(H_2O)_2(Hfac)_2]$, where M = Ni or Co, react with HL in organic media only in the presence of alkali. As a result, polymeric heterometallic different-ligand complexes are separated into the solid phase; the dimensionality of the complexes was found to depend on the alkali metal ion used in the reaction (Na, K, Rb, or Cs). The complexes were obtained as single crystals and studied by X-ray diffraction.

Here we investigated the effect of the nature of alkali metal on the structure of the resulting polymer. Since all isolated polymeric heterometallic complexes contain ferromagnetic exchange clusters, a suggestion was made how these polymers can be used to prepare solid phases with cooperative magnetic ordering.



HL



ML_2

EXPERIMENTAL

The reagents used in the study include iminonitroxide, 2-(2-hydroxy-5-nitrophenyl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazole-1-oxyl (HL), synthesized by a reported procedure [4], reagent grade KOH, analytical grade NaOH, RbOH (50% aqueous solution, Sigma-Aldrich), CsOH (50% aqueous solution, Sigma-Aldrich), high-purity grade acetone, reference heptane, and methanol (distilled prior to use). The complexes $[Co(H_2O)_2(Hfac)_2]$ and $[Ni(H_2O)_2(Hfac)_2]$ were prepared by the reactions of $[Co(H_2O)_4(OAc)_2]$ and $[Ni(H_2O)_4(OAc)_2]$ with 1,1,1,5,5,5-hexafluoro-2,4-pentanedione (Hfac) and KOH in water followed by recrystallization of the products from high-purity grade EtOAc.

Synthesis of $K[Ni(Hfac)L_2] \cdot Me_2CO$ (I). At room temperature, a solution of HL (0.055 g, 0.2 mmol) in acetone (3 mL) and then a solution of KOH (0.011 g, 0.2 mmol) in MeOH (0.5 mL) were added to a solution of $[Ni(H_2O)_2(Hfac)_2]$ (0.05 g, 0.1 mmol) in acetone (1 mL). The reaction mixture acquired a dark brown color. After 2 days, complex **I** precipitated as brown prismatic crystals, which were collected on a filter and washed with acetone. The yield was 0.08 g (45%).

For $C_{34}H_{37}N_6O_{11}F_6KNi$

Anal. calcd., %	C, 44.5	H, 4.1	N, 9.2	F, 12.4
Found, %	C, 44.4	H, 3.9	N, 9.2	F, 12.6

The compounds $Na[Ni(Hfac)L_2] \cdot Me_2CO$ (**II**), $Rb[Ni(Hfac)L_2] \cdot 2.5Me_2CO$ (**III**), and $Cs[Ni(Hfac)L_2]$ (**IV**) were prepared by a similar procedure using NaOH, RbOH, and CsOH, respectively.

II: red-brown prismatic crystals (60% yield).

For $C_{34}H_{37}N_6O_{11}F_6NaNi$

Anal. calcd., %	C, 45.3	H, 4.1	N, 9.3	F, 12.6
Found, %	C, 45.4	H, 4.4	N, 9.5	F, 12.7

III: fine red-brown prismatic crystals (60% yield).

For $C_{34}H_{37}N_6O_{11}F_6RbNi$ (partly desolvated)

Anal. calcd., %	C, 42.4	H, 3.9	N, 8.7	F, 11.8
Found, %	C, 42.6	H, 3.7	N, 8.8	F, 11.5

IV: prismatic brown crystals (82% yield).

For $C_{31}H_{31}N_6O_{10}F_6CsNi$

Anal. calcd., %	C, 39.1	H, 3.3	N, 8.8	F, 11.9
Found, %	C, 39.2	H, 3.2	N, 8.7	F, 12.3

Synthesis of $K[Co(Hfac)L_2] \cdot 2.5Me_2CO$ (V). At room temperature, a solution of HL (0.055 g, 0.2 mmol) in acetone (3 mL) and then a solution of KOH (0.011 g, 0.2 mmol) in MeOH (0.5 mL) were added to a solution of $[Co(H_2O)_2(Hfac)_2]$ (0.05 g, 0.1 mmol) in acetone (1 mL). The reaction mixture was colored black. After 2 days, crystal concretions precipitated, which were recrystallized from an acetone–heptane mixture (5 : 2) to give dark brown prismatic crystals of **V**, which were collected on a filter and washed with heptane. The yield was 0.049 g (50%).

For $C_{32.5}H_{34}N_6O_{10.5}F_6KCo$ (partly desolvated)

Anal. calcd., %	C, 43.9	H, 3.9	N, 9.5	F, 12.8
Found, %	C, 43.8	H, 3.8	N, 9.1	F, 12.9

X-ray diffraction. The sets of reflections from single crystals were collected on Bruker AXS-Smart Apex II and Apex Duo diffractometers (the absorption corrections were applied by the SADABS program, version 2.10) [19]. The structures were solved by direct methods and refined by the full-matrix least-squares method in the anisotropic approximation for all nonhydrogen atoms. The positions of H atoms were calculated geometrically and refined in the riding model. All calculations for structure solution and refinement were carried out using the SHELX program package. The crystallographic characteristics of compounds and X-ray experiment details are summarized in Table 1; selected bond lengths and interatomic distances are listed in Table 2.

Full data on the structures of **I**–**V** are deposited with the Cambridge Crystallographic Data Centre (CCDC nos. 1974139–1974143; deposit@ccdc.cam.ac.uk; http://www.ccdc.cam.ac.uk/data_request/cif).

The magnetic susceptibility (χ) of polycrystalline samples was measured on a MPMS XL SQUID magnetometer (Quantum Design) in a 2–310 K range in a 5 kOe magnetic field. The paramagnetic components χ were determined with allowance for the diamagnetic contribution estimated from the Pascal constants. The efficient magnetic moment (μ_{eff}) was calculated by the formula $\mu_{eff} = [3k\chi T/(N_A\mu_B^2)]^{1/2}$, where

Table 1. Crystallographic data and structure refinement parameters for **I–V**

Parameter	Value				
	I	**II**	**III**	**IV**	**V**
Molecular formula	$C_{34}H_{37}N_6O_{11}F_6KNi$	$C_{34}H_{37}N_6O_{11}F_6NaNi$	$C_{38.50}H_{46}N_6O_{12.50}F_6RbNi$	$C_{31}H_{31}N_6O_{10}F_6CsNi$	$C_{38.50}H_{46}N_6O_{12.50}F_6KCo$
M	917.50	901.39	1050.99	953.24	1004.84
T, K	240	295	240	296	240
System; Z	$P2_1/c$; 8	$P2_12_12_1$; 8	$P2_1/c$; 8	$P\bar{1}$; 4	$P2_1/c$; 8
a, Å	19.7547(9)	11.0707(13)	20.196(3)	11.7373(8)	20.0833(12)
b, Å	24.7678(12)	21.790(2)	27.815(5)	17.2803(12)	27.830(2)
c, Å	19.8038(10)	34.756(3)	18.824(3)	20.1143(14)	18.9399(14)
α, deg	90	90	90	98.870(4)	90
β, deg	117.461(3)	90	115.913(7)	101.264(3)	116.796(4)
γ, deg	90	90	90	102.339(3)	90
V, Å^3	8597.8(7)	8384.3(15)	9511(3)	3826.0(5)	9449.2(12)
ρ(calcd.), g cm^{-3}	1.418	1.428	1.468	1.655	1.413
θ Range, deg	67.234	28.278	68.229	28.173	67.768
Ranges of hkl indices, min/max	$-22 \le h \le 23$, $-29 \le k \le 29$, $-23 \le l \le 22$	$-14 \le h \le 11$, $-27 \le k \le 26$, $-40 \le l \le 45$	$-24 \le h \le 24$, $-33 \le k \le 33$, $-22 \le l \le 22$	$-15 \le h \le 15$, $-22 \le k \le 22$, $-26 \le l \le 26$	$-23 \le h \le 23$, $-33 \le k \le 33$, $-21 \le l \le 22$
Number of measured/ unique reflections	104203/15167	45894/19330	131996/16581	64338/18624	133941/16914
R_{int}	0.1694	0.0711	0.0586	0.0616	0.1012
Number of reflections with $I > 2\sigma(I)$	6328	9282	12172	10922	9748
Number of parameters	1063	1152	1273	1148	1345
GOOF	0.865	0.805	1.127	0.851	1.012
R_1/wR_2 ($I > 2\sigma(I)$)	0.0601/0.1449	0.0456/0.0773	0.0755/0.1642	0.0343/0.0663	0.0823/0.2233
R_1/wR_2 (all data)	0.1443/0.1850	0.1188/0.0919	0.1013/0.1807	0.0739/0.0760	0.1346/0.2774
$\Delta\rho_{max}/\Delta\rho_{min}$, e/Å^3	0.423/−0.607	0.277/−0.292	0.759/−0.693	0.645/−0.431	0.680/−0.532

Table 2. Selected bond lengths and interatomic distances for **I**–**V**

Bond	*d*, Å				
	I	**II**	**III**	**IV**	**V**
M(II)–O	2.009(3)–2.071(4)	2.019(3)–2.075(3)	2.009(3)–2.083(4)	2.003(2)–2.070(2)	2.022(4)–2.124(5)
M(II)–N	2.101(3)–2.115(4)	2.097(4)–2.120(4)	2.082(4)–2.111(4)	2.115(2)–2.128(2)	2.127(4)–2.150(4)
M(I)–O	2.679(3)–3.069(4)	2.287(5)–2.813(6)	2.805(3)–3.179(5)	3.002(2)–3.362(2)	2.692(4)–3.268(5)
Cs–F				3.341(15)–3.443(14)	
N–O	1.258(5)–1.267(5)	1.265(6)–1.272(6)	1.259(6)–1.269(7)	1.262(3)–1.270(4)	1.255(6)–1.273(7)
M(II)···M(I)	3.684(2), 3.700(1)	3.331(2), 3.353(2)	3.857(1), 3.871(1)	4.0127(6), 4.0751(6)	3.703(2), 3.708(2)

N_A, μ_B, and k are the Avogadro number, Bohr magneton, and Boltzmann constant, respectively. The experimental temperature dependence of the magnetic susceptibility was analyzed using the isotropic spin Hamiltonian $H = -2\sum J_{ij} S_i S_j$.

RESULTS AND DISCUSSION

The studies demonstrated that the reaction of $[Ni(H_2O)_2(Hfac)_2]$ with HL in an acetone–methanol mixture takes place only in the presence of KOH. The reaction results in crystallization of complex **I**. The complexes **II**, **III**, and **IV** containing the $\{Ni(Hfac)L_2\}$ moieties were prepared under similar conditions using NaOH, RbOH, and CsOH (Fig. 1). In the solid phase, these compounds are combined into polymer structures by alkali metal cations. In addition, the crystal structure may incorporate acetone molecules bound to the alkali metal cation. The Ni environment in all compounds is a slightly distorted octahedron formed by two O_{Hfac} atoms and the O_L and N_L donor atoms with the Ni–O distances of 2.009(3)–2.083(4) Å and Ni–N distances of 2.082(4)–2.128(4) Å (Table 2). The N–O bond lengths in the nitroxide group of L are typical of imino nitroxides: 1.255(6)–1.273(7) Å [20].

The environments of alkali metal atoms are different (Fig. 2). In compound **I**, the K atom environment is a seven-vertex polyhedron formed by four O_{NO_2} atoms of the nitro groups of two L, two bridging O_L atoms of two other L, and the O atom of the acetone molecule (K–O 2.679(3)–3.069(4) Å). All these bonds form polymer chains in the structure (Fig. 2a).

Compound **II** has the same composition as **I**, with a similar environment of alkali metal atoms (Na–O 2.287(5)–3.032(5) Å), but layers are formed in the structure instead of chains (Fig. 2b).

Structure **III** is also composed of polymer chains (Fig. 2c). The environment of Rb atoms is an eight-vertex polyhedron formed by O_{NO_2}, and O_L oxygen atoms and two acetone molecules (Rb–O 2.805(3)–3.179(5) Å). In addition, acetone solvate molecules reside between the chain. Compound **V** has the same structure.

The cesium environment in **IV** includes O atoms (3.002(2)–3.362(2) Å) and F atoms (3.341(15)–3.443(14) Å), which form an irregular nine-vertex polyhedron (Fig. 3c). Considering all these contacts, the structure can be defined as a framework (Fig. 3).

A study of the magnetic properties of the prepared different-metal and different-ligand complexes

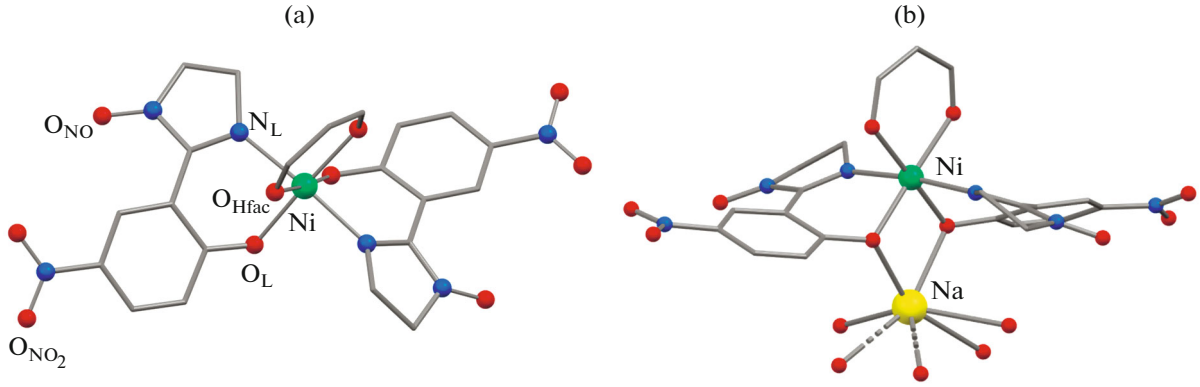


Fig. 1. (a) Structure of the coordination anion $[Ni(Hfac)L_2]^-$ and (b) fragment of structure **II**. Here and below: ● are N atoms and ● are O atoms; CF_3 and CH_3 groups and H atoms are omitted; the dashed lines indicate the bonds participating in the formation of the polymeric structure.

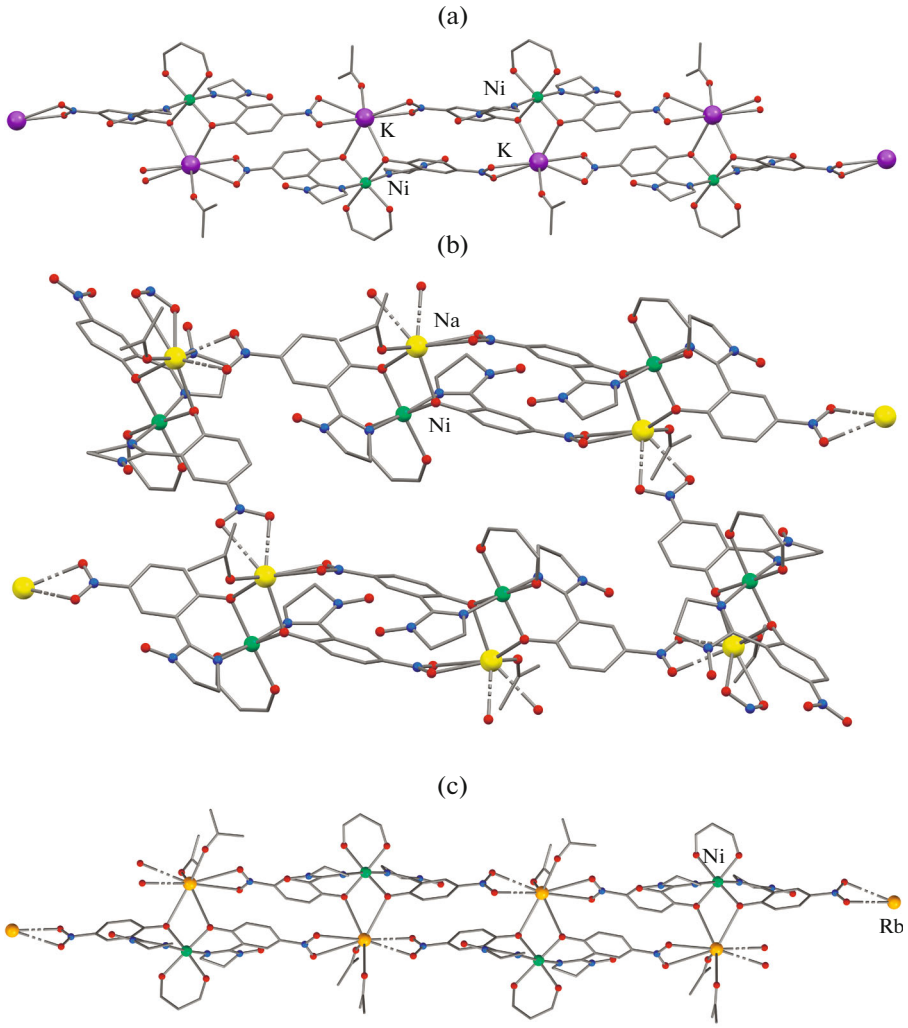


Fig. 2. Structure of the layer in (a) **I** and (b) **II** and (c) chains in **III**.

showed the presence of ferromagnetic exchange interactions between the spins of paramagnetic centers. The μ_{eff} values at 300 K are somewhat higher than the theoretical purely spin values (3.74 and 4.58 μ_B for Ni(II) and Co(II) complexes, respectively) and increase with decreasing temperature (Fig. 4). This result is in agreement with the results of quantum chemical calculations, which demonstrated that the iminonitroxide coordination via the N atom of the paramagnetic moiety is favorable for ferromagnetic type exchange interactions [21–33]. The experimental dependences of $\mu_{eff}(T)$ for the complexes were analyzed using the exchange coupled trimer model (spin Hamiltonian $H = -2J(S_{L1}S_M + S_MS_{L2})$) for the {M(Hfac)$L_2$} groups. The decrease in the μ_{eff} value at low temperatures is due to weaker cluster–cluster antiferromagnetic type exchange interactions and/or zero-field splitting, which were considered in the molecular field approximation. The optimal *g*-factors of the metal ion (g_M) and exchange interaction parameters (J and zJ') derived from analysis of experimental dependences $\mu_{eff}(T)$ are listed in Table 3; the nitroxide *g*-factor was taken to be 2.

Thus, the study demonstrated that Ni(II) and Co(II) hexafluoroacetonates react with the spin-labeled Schiff base HL in organic media in the pres-

Table 3. Optimal *g*-factors of the metal ion (g_M) and exchange interaction parameters (J and zJ') derived from analysis of experimental dependences $\mu_{eff}(T)$

Compound	g_M	J, cm^{-1}	zJ', K
I	2.24	72	–0.17
II	2.26	70	–0.34
III	2.18	58	–0.51
IV	2.32	56	–0.10
V	2.17	60	–0.54

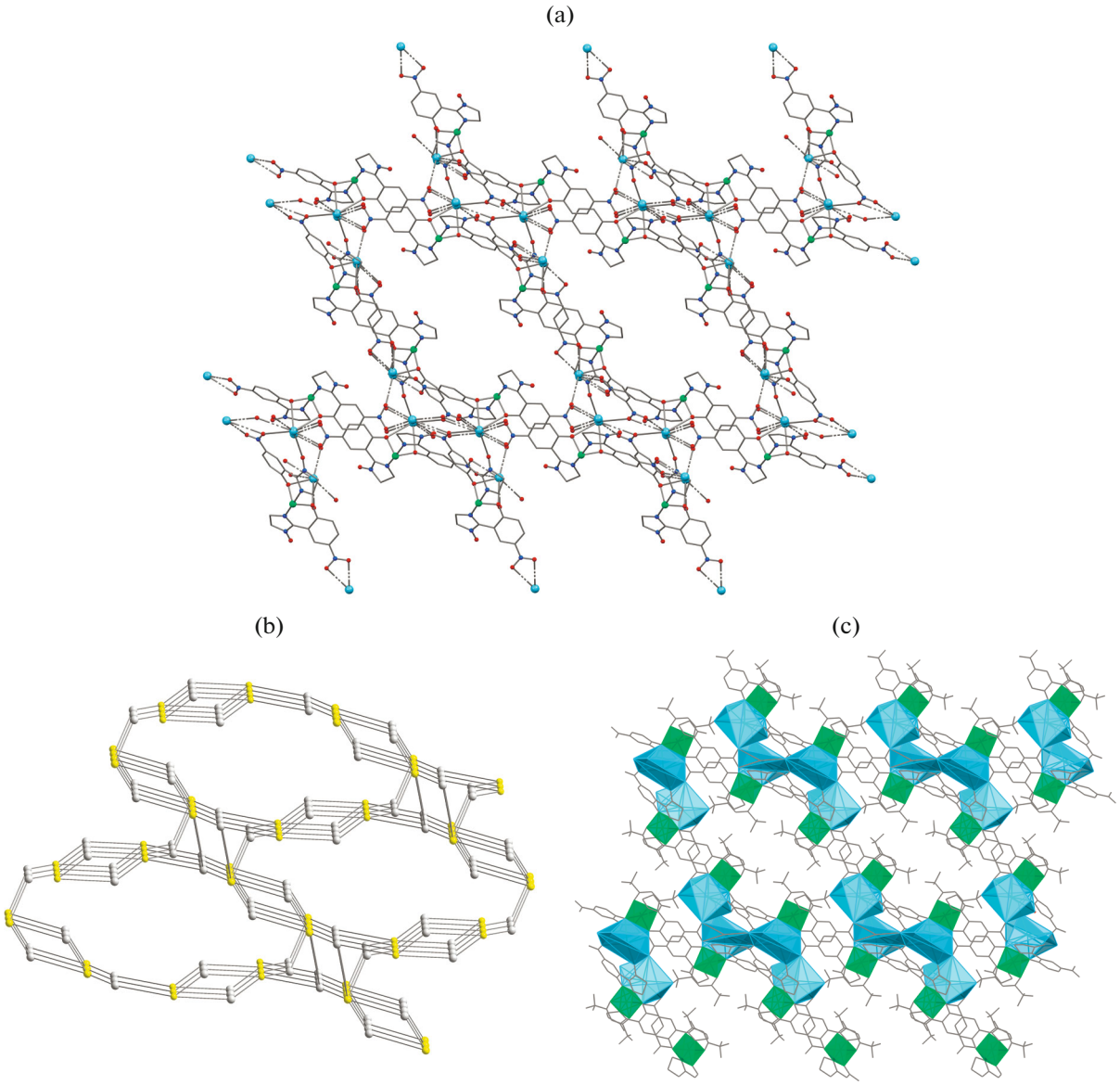


Fig. 3. (a) Framework fragment of **IV** (Hfac ligands are not shown, ● is Cs, ● is Ni); (b) schematic view of the framework: ● are the centers of paramagnetic ligands and ● are centers of binuclear {Ni···Cs} groups; (c) polyhedral view of the framework for metal atoms.

ence of alkali. The reaction results in crystallization of different-ligand heterometallic polymeric complexes from the solution. The type of the resulting polymeric structure is dictated by the alkali metal ion, particularly, layers for Na, chains for K and Rb, and framework for Cs. In the solid phase of all complexes, the ferromagnetic exchange interactions between the paramagnetic centers are mainly located in the {LML} exchange clusters. Since the ferromagnetic exchange values are rather high (Table 3), it appears expedient to replace alkali metals in these compounds by paramagnetic transition metal ions. We plan to study this issue in the future: if this is implemented, one may hope for the preparation of a new group of heterospin complexes capable of cooperative magnetic ordering.

FUNDING

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CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

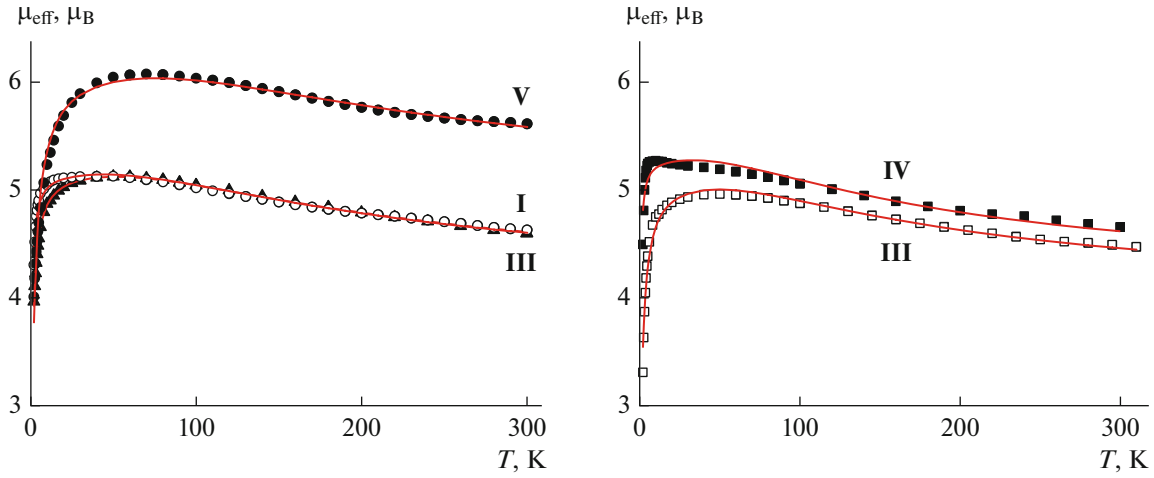

Fig. 4. Experimental dependences of $\mu_{eff}(T)$ for **I**, **II**, **III**, **IV**, and **V**. Continuous lines show the theoretical curves.

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