Formation of cobalt- and lithium-containing heterometallic pyridonate carboxylate coordination polymers

N. V. Zauzolkova,[a] M. E. Nikiforova,[a] M. A. Kiskin,[a] A. S. Bogomyakov,[b] A. A. Sidorov,[a] and I. L. Eremenko[a]*

[a]N. S. Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, 31 Leninsky prosp., 119991 Moscow, Russian Federation. Fax +7 (495) 952 1279. E-mail: sidorov@igic.ras.ru

[b]International Tomography Center, Siberian Branch of the Russian Academy of Sciences, 3a ul. Institutskaya, 630090 Novosibirsk, Russian Federation. Fax: +7 (383 2) 33 1399. E-mail: bus@tomo.nsc.ru

The reaction of cobalt(II) chloride with 2-hydroxypyridine (Hhp) and lithium pivalate in acetonitrile affords the 1D polymer $[Li_3CoCl(\mu\text{-Piv})(\mu_3\text{-Piv})_2(\mu_3,\eta^2\text{-Piv})(\mu\text{-Hhp})_2(\eta^1\text{-HPiv})]_n$, in which the repeating units are linked by bridging pyridone molecules. The reaction of cobalt nitrate hexahydrate with 2-hydroxy-6-methylpyridine (Hmhp) in the presence of the deprotonating agent (Et_3N) resulted in the crystallization of the 1D polymer of the composition $[Li_2Co_7(\mu_3\text{-OH})_2(\mu_3\text{-Piv})_3(\mu\text{-Piv})_2(\mu_3,\eta^2\text{-mhp})_5(\mu,\eta^2\text{-mhp})_2(\mu_3\text{-mhp})(\mu,\eta^2\text{-NO}_3)\cdot 2MeCN]_n$, in which the bulky metal fragments $\{Li_2Co_7(OH)_2(Piv)_5)(mhp)_8\}$ are linked together through the lithium atoms by chelate bridging nitrate anions. The resulting 1D polymers were characterized by X-ray diffraction, and their magnetic properties were investigated.

Key words: 2-hydroxy-6-methylpyridine, heterometallic complexes, coordination polymers, X-ray diffraction analysis.

It is known that the reactions of transition metal trimethylacetates with alkali metal pivalates afford polynuclear heterometallic complexes with different structures and composition.[1—4] Other polydentate donor ligands containing various functional moieties are used to increase the nuclearity of such heteroatomic structures.[5,6] Depending on the geometric arrangement of the donor centers and their electronic characteristics, both discrete polynuclear molecules[7—9] and coordination polymers[8,10,11] can be prepared. In the present study, we used 2-hydroxypyridine and 2-hydroxy-6-methylpyridine as additional ligands, which can act as bridging or terminal O-donor ligands in the pyridone form and can lead to the chelate bridging or bridging coordination through the nitrogen atoms and the deprotonated oxygen atom in the form of pyridonate anions. This diversity provides interesting possibilities for the synthesis of different-nuclearity molecular heterometallic complexes and coordination polymers.[7—13]

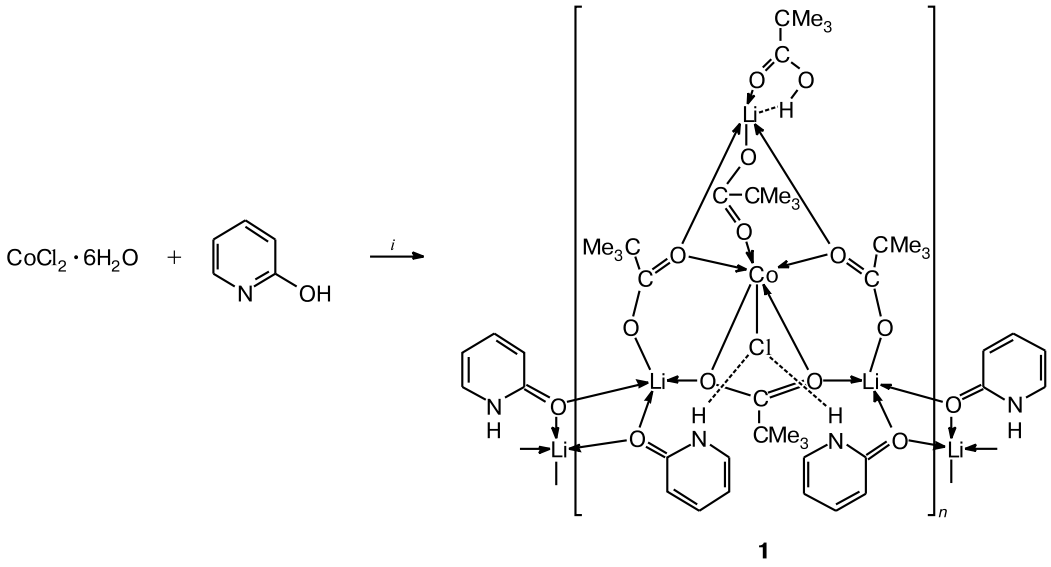
Results and Discussion

Earlier,[14] we have reported on the synthesis of polynuclear cobalt complexes containing the coordinated 6-methyl-2-pyridonate anion, as well as neutral 2-pyridone, as the ligands by the reaction of 2-hydroxy-6-methylpyridine with polymeric cobalt pivalate. Heteronuclear structures containing cobalt and alkali metal (lithium) atoms were synthesized by the direct reaction of $CoCl_2\cdot 6H_2O$ with 2-hydroxypyridine (Hhp) and lithium pivalate ($Co_{at} : Hhp : Li_{at} = 1 : 2 : 4$) in MeCN upon heating to 60 °C. It appeared that under these conditions the 1D coordination polymer $[Li_3CoCl(\mu\text{-Piv})(\mu_3\text{-Piv})_2(\mu_3,\eta^2\text{-Piv})(\mu\text{-Hhp})_2(\eta^1\text{-HPiv})]_n$ (**1**) was formed (Scheme 1, Fig. 1). The latter polymer was isolated as violet crystals. The repeating unit of the polymer chain of **1** contains the metal fragment consisting of three lithium atoms and one cobalt atom $\{Li_3Co\}$. The cobalt atom is in a distorted octahedral environment formed by the oxygen atoms of one chelate bridging and three bridging pivalate anions. In the chain, the cobalt atom is linked to lithium atoms by the bridging pivalate anions (Table 1), the lithium atoms forming a virtually equilateral triangle around the cobalt atom (Li...Li, 5.246(6), 5.349(6), and 5.710(6) Å). The coordination polyhedron of the cobalt atom involves also the Co—Cl bond. The chloride anion forms a hydrogen bond with the NH group of the 2-pyridone ligand. The oxygen atoms of two 2-pyridone molecules are bridging and link the lithium atoms of adjacent repeating units. The environment of the lithium atom lying in the vertex of the equilateral triangle $\{Li_3\}$ involves also the pivalic acid molecule, which forms a hydrogen bond with the oxygen atom of the bridging pivalate anion. Selected geometric characteristics of complex **1** are given in Table 1.

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 2, pp. 267—273, February, 2011.

1066-5285/11/6002-273

Scheme 1



1

i. LiPiv, MeCN, 60 °C, 30 min

According to magnetochemical measurements, the effective magnetic moment of compound **1** at room temperature is 5.20 μ_B per formula unit $\{Li_3Co\}$ (Fig. 2), which is consistent with the known experimental values[15] observed for high-spin ($S = 3/2$) cobalt(II) ions taking into account the spin-orbit interaction (4.4—5.2 μ_B). A decrease in the temperature leads to a decrease in μ_{eff} to 4.03 μ_B (5 K), which is characteristic of systems containing the high-spin cobalt(II) ion and can be attributed to the spin-orbit effects.

The reaction of 2-hydroxy-6-methylpyridine (Hmhp) with cobalt nitrate instead of cobalt chloride with an equimolar cobalt to lithium ion ratio in the presence of triethylamine afforded the unusual 1D coordination

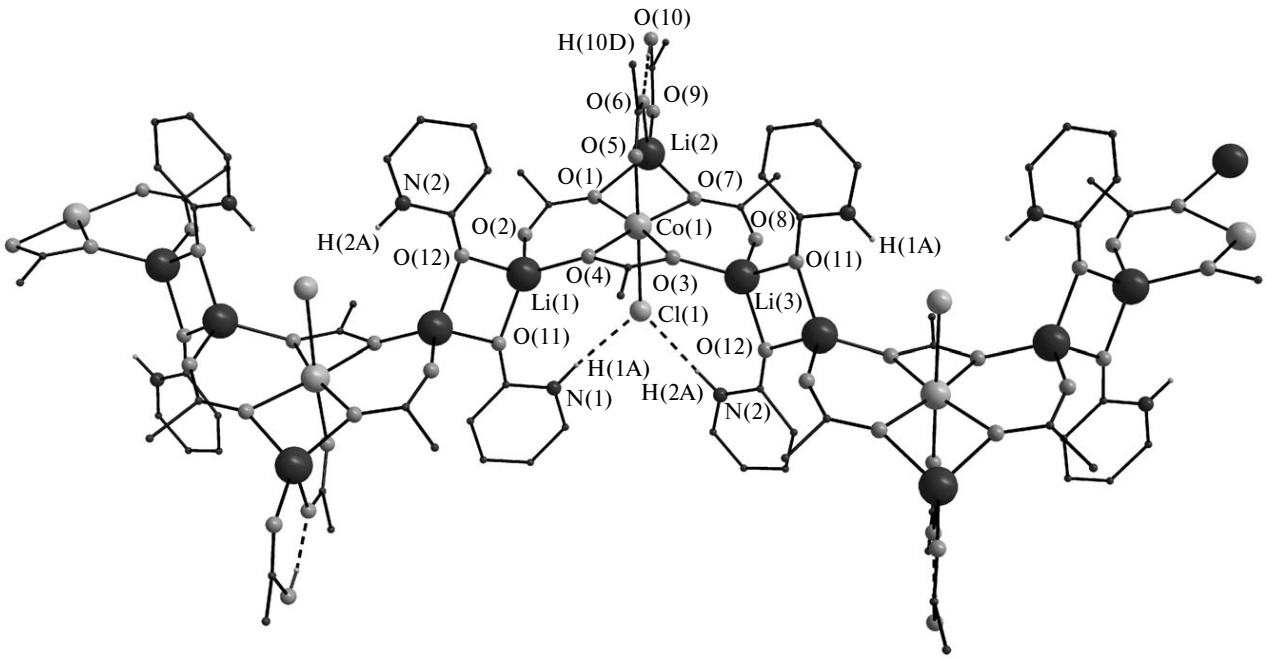


Fig. 1. Polymer chain in the crystal structure of complex **1** (hydrogen atoms of the pyridine moiety and the methyl groups of the trimethylacetate anions are not shown).

Table 1. Selected geometric characteristics of complexes **1** and **2**

Bond	*d*/Å	
	1	**2**
Co—O (μ_3-OH)	—	2.0022(18)—2.1469(18)
Co—O (μ_3-Piv)	2.079(4)	2.0425(19)—2.0852(19)
Co—O (Piv(bridge))	2.071(5)—2.178(16)	1.981(2)—2.018(2)
Co—O (Piv(complex))	2.156(4)—2.175(4)	—
Co—O (μ_3,η-L)*	—	2.0861(18)—2.4022(18)
Co—O (μ_3-L)*	—	2.0542(19)—2.0646(19)
Co—O (μ,η-L)*	—	2.0259(19)—2.3176(19)
Co—N	—	2.039(2)—2.207(2)
Co—Cl	2.4816(6)	—
Co...Li	2.779(4)	2.664(6)—2.819(5)
Li...Li	2.819(6)	10.779
Li—N	—	2.450(6)—2.695(6)
Li—O (Piv(complex))	1.920(11)—1.943(12)	—
Li—O (μ_3-Piv)	1.853(11)—1.922(12)	2.015(6)—2.300(7)
Li—O (Piv(bridge))	1.937(5)	1.914(6)
Li—O (Piv(terminal))	1.909(4)	—
Li—O (HL)**	1.932(12)—1.936(10)	—
Li—O (L)*	—	1.899(6)—1.931(6)
Li—O (NO_3^-)	—	2.083(6)—2.467(6)
N—H...Cl	2.31—2.36	—
C—H...O	1.71	—

* L is 2-pyridone (**1**), 6-methyl-2-pyridone (**2**).
** HL is 2-hydroxypyridine (**1**), 2-hydroxy-6-methylpyridine (**2**).

polymer $[Li_2Co_7(\mu_3\text{-}OH)_2(\mu_3\text{-}Piv)_3(\mu\text{-}Piv)_2(\mu_3,\eta^2\text{-}mhp)_5(\mu,\eta^2\text{-}mhp)_2(\mu_3\text{-}mhp)(\mu,\eta^2\text{-}NO_3)\cdot 2MeCN]_n$ (**2**) (Scheme 2). The repeating unit of the polymer chain of **2** has a twofold axis passing through the lithium atoms (Fig. 3). The reaction leads to the deprotonation of all 2-hydroxy-6-methylpyridine molecules and their incorporation into the coordination polymer. Unlike compound **1**, the cobalt atoms in complex **2** are linked together by both the trimethylacetate bridges and 6-methyl-2-pyridonate anions.

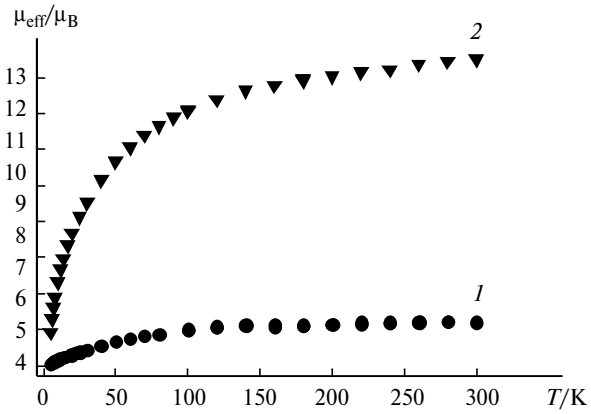
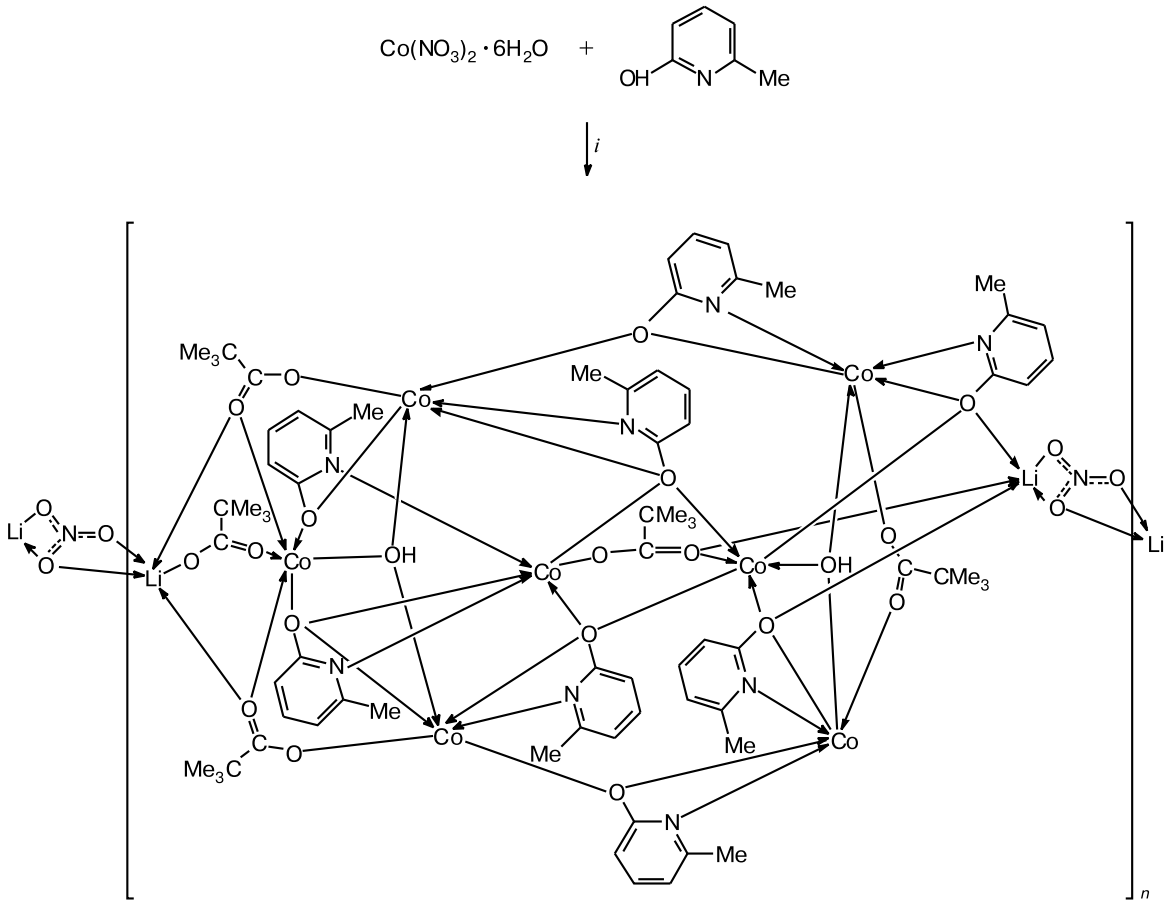


Fig. 2. Temperature dependences of the effective magnetic moment for complexes **1** (*1*) and **2** (*2*).

The metal core of the repeating unit consists of seven cobalt atoms and two lithium atoms. Seven cobalt atoms of this fragment form two pyramids, *viz.*, the tetragonal and trigonal pyramids containing cobalt atoms in the vertices. These two pyramids share an edge of the bases (Fig. 4). The geometry of the cobalt-containing fragment in complex **2** is similar to that in the complex $[Co_7(OH)_2(OOCPh)_4(chp)_8(MeCN)]$ (**3**, where $PhCOO^-$ is the benzoate anion and chp is the anion of 6-chloro-2-hydroxypyridine) described in the studies.[10,16] In compound **2**, like in molecule **3**, one of two μ_3-OH groups links the cobalt atom in the vertex of the tetragonal pyramid (Co—O, 2.0633(18) Å) to two cobalt atoms located at the base of this pyramid (Co—O, 2.0060(18) and 2.0022(18) Å). The second hydroxy group links two other cobalt atoms lying at the base of this pyramid (Co—O, 2.0909(18) and 2.0735(18) Å) to the cobalt atom at the base of the adjacent pyramid (Co—O, 2.1469(18) Å). Two μ_3,η^2-chelate bridging pyridonate anions form bonds between two cobalt atoms, which lie at the base of the pyramids and belong to the common face, and the vertices of the pyramids (Co—O, 2.0861(18)—2.4022(18) Å; Co—N, 2.090(2) and 2.125(2) Å). Two μ,η^2-pyridonate anions link together transition metal atoms lying at the base of the tetragonal pyramid (Co—O, 2.0259(18)—2.3890(18) Å; Co—N, 2.053(2) and 2.066(2) Å). The other two pyridonate anions (μ_3,η^2 and μ_3) are in-

Scheme 2



2

i. LiPiv, Et_3N, MeCN, 60 °C, 30 min.

volved in the binding of two cobalt atoms at the base of the trigonal pyramid to the vertex of the pyramid (Co—O, 2.1015(18)—2.2157(18) Å; Co—N, 2.207(2) Å). Two μ_3,η^2-chelate bridging pyridonate anions link two transition metal atoms at the base of the tetragonal pyramid (Co—N, 2.039(2) and 2.056(2) Å) to its vertex (Co—O, 2.1082(18) and 2.1279(18) Å) and the lithium atom. Five carboxylate anions link together seven cobalt atoms and two lithium atoms. One of the carboxylate anions acts as a bridge between two cobalt atoms lying at the base of the tetragonal pyramid. Two other carboxylate anions link the other two metal atoms belonging to the common face to the cobalt atom at the base of the trigonal pyramid and the lithium atom (Li—O, 2.015(6) and 2.040(6) Å). The fourth carboxylate anion links together the vertices of the pyramids. The lithium atoms are linked to the heptanuclear metal core by the fifth bridging carboxylate group, as well as by the oxygen atoms of the pyridonate anion and the trimethylacetate anion. The repeating units form a polymer chain as a result of the formation of the complex with the nitrate ion. The terminal lithium atoms of the adjacent mononuclear fragments coordinate one nitrate ion, resulting in the binding of the repeating units.

The magnetic measurements of compound **2** showed that the magnetic moment μ_{eff} per the $\{Co_7\}$ moiety is 12.50 μ_B at room temperature (see Fig. 2). This value is smaller than the calculated maximum possible value (13.75 μ_B) for seven non-interacting cobalt(II) ions (taking into account the spin-orbit contribution).[15] A decrease in the temperature leads to the monotonic fall of the curve $\mu_{eff}(T)$ to 4.92 μ_B at 5 K, which is attributed to spin-orbit interactions between the cobalt(II) ions and indicates that antiferromagnetic exchange interactions between the cobalt(II) atoms in the heptanuclear fragment prevail.

To sum up, we synthesized two 1D coordination polymers containing cobalt and lithium atoms using different reaction conditions. A chain consisting of alternating metal atoms (one cobalt atom and two lithium atoms) is formed

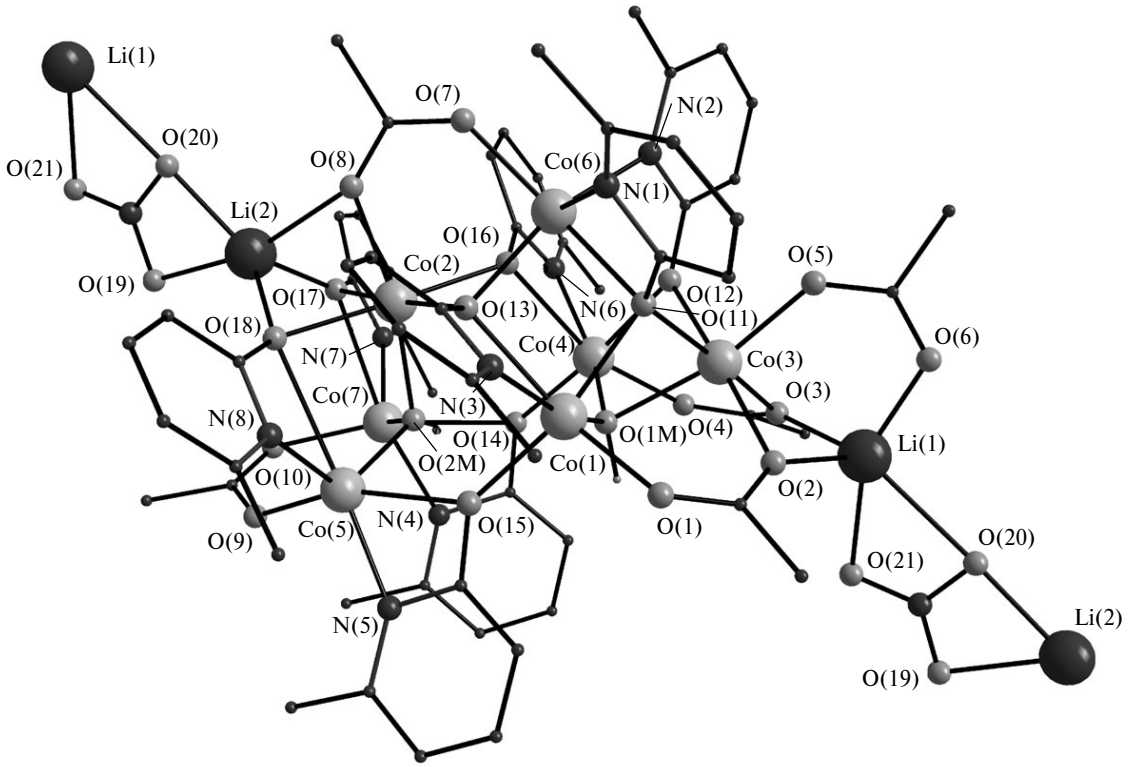


Fig. 3. Elementary fragment in the crystal structure of polymer **2** (hydrogen atoms of the pyridonate anions and the methyl groups of the trimethylacetate anions are not shown).

with the involvement of the bridging pyridone molecules. The deprotonation of pyridone results in different modes of the chelate bridging coordination of the pyridonate anions, which form the bulky metal core of the monomeric unit in the chain of compound **2**.

Experimental

The complexes were synthesized in air with the use of commercial solvents, which were purified according to standard procedures. The new complexes were synthesized with the use of $Co(NO_3)_2 \cdot 6H_2O$ (analytical grade), $CoCl_2 \cdot 6H_2O$ (analytical grade), 2-hydroxypyridine, 2-hydroxy-6-methylpyridine, and triethylamine (Acros). Lithium pivalate was prepared by the neutralization of trimethylacetic acid (Acros) with lithium hydroxide (reagent grade). The IR spectra of the complexes were recorded on a Specord M-80 instrument in KBr pellets. The elemental analysis was carried out on a Carlo Erba microanalyzer. The static magnetic susceptibility χ'_M was measured on a MPMS-5S Quantum Design SQUID magnetometer in the temperature range of 5—300 K. The effective magnetic moments

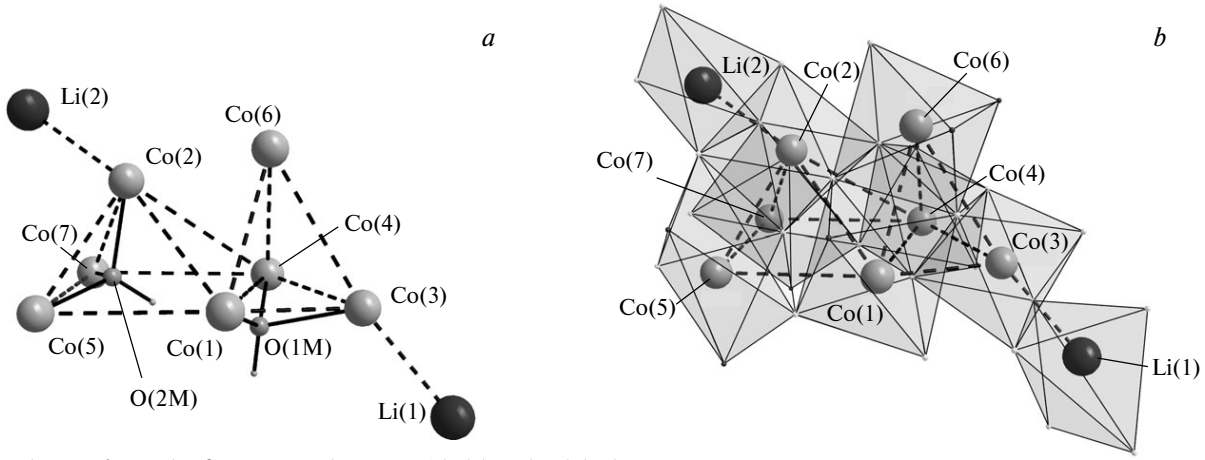


Fig. 4. Metal core of complex **2** represented as pyramids (*a*) and polyhedra (*b*).

were calculated by the equation $\mu_{eff} = (8\chi'_M T)^{1/2}$ (see Ref. 15). The purity of bulk samples of **1** and **2** was confirmed by X-ray powder diffraction analysis with a G670 Guinier camera (HUBER) (Cu-Kα_1 radiation). The unit cell parameters of polymer **1** calculated from the experimental X-ray powder diffraction patterns are as follows: monoclinic *C*, *a* = 18.857(14) Å, *b* = = 15.530(14) Å, *c* = 14.914(8) Å, β = 95.10(4)°, *V* = 4350.2(68) Å^3; polymer **2**: monoclinic *P*, *a* = 14.97(3) Å, *b* = 24.309(21) Å, *c* = 25.20(3) Å, β = 101.02(9)°, *V* = 8998.7(296) Å^3.

Poly(μ$_3$,η^2-trimethylacetato-*O*,*O*,*O*′)bis(μ$_3$-trimethylacetato-*O*,*O*,*O*′)(μ-trimethylacetato-*O*,*O*′)(η^1-chloro)bis(μ-2-pyridone)(η^1-trimethylacetic acid)cobalt(II)trilithium, [Li$_3$CoCl(μ-Piv)(μ$_3$-Piv)$_2$(μ$_3$,η^2-Piv)(μ-Hhp)$_2$(η^1-HPiv)]$_n$ (1). A mixture of $CoCl_2 \cdot 6H_2O$ (0.300 g, 1.262 mmol) and 2-hydroxypyridine (0.240 g, 2.524 mmol) was dissolved in acetonitrile (30 mL) at 60 °C, and then lithium pivalate (0.545 g, 5.049 mmol) was added. The reaction mixture was stirred at 60 °C for 30 min, slowly cooled to room temperature, and kept for 24 h. The violet crystals suitable for X-ray diffraction were filtered off, washed with cold MeCN (*T* = –5 °C), and dried in air at 20 °C. Compound **1** was obtained in a yield of 0.125 g (12.21% based on cobalt). Found (%): C, 51.46; H, 7.03; N, 3.55. $C_{35}ClCoH_{56}Li_3N_2O_{12}$. Calculated (%): C, 51.78; H, 6.95; N, 3.45. IR, ν/cm^{-1}: 3124 w, 3092 w, 3020 w, 2976 m, 2964 m, 2868 w, 2364 m, 2308 w, 1692 m, 1650 s, 1568 m, 1548 w, 1480 s, 1460 m, 1444 w, 1432 m, 1408 s, 1356 s, 1316 w, 1272 s, 1228 s, 1204 m, 1160 m, 1100 m, 996 m, 936 w, 900 w, 880 w, 784 s, 732 m, 604 m, 576 m, 512 w, 448 m, 392 m.

Poly[bis(μ^3-hydroxo)(μ,η^2-nitro)tris(μ$_3$-trimethylacetato-*O*,*O*,*O*′)bis(μ-trimethylacetato-*O*,*O*′)pentakis(μ$_3$,η^2-6-methyl-2-pyridonato)bis(μ,η^2-6-methyl-2-pyridonato)(μ$_3$-6-methyl-2-pyridonato)heptacobalt(II)dilithium acetonitrile solvate], [Li$_2$Co$_7$(μ$_3$-OH)$_2$(μ$_3$-Piv)$_3$(μ-Piv)$_2$(μ$_3$,η^2-mhp)$_5$(μ,η^2-mhp)$_2$(μ$_3$-mhp)(μ,η^2-NO$_3$)·2MeCN]$_n$ (2). A mixture of $Co(NO_3)_2 \cdot 6H_2O$ (0.300 g, 1.031 mmol) and 2-hydroxy-6-methylpyridine (0.225 g, 2.063 mmol) was dissolved in MeCN (30 mL) at 60 °C, and then lithium pivalate (0.111 g, 1.031 mmol) was added with stirring. The reaction mixture was stirred at 60 °C until dissolution, and then triethylamine (0.209 g, 2.063 mmol) was added. The solution was stirred at 60 °C for 30 min, slowly cooled to room temperature, and kept for 24 h. The violet crystals that formed were filtered off, washed with cold MeCN (*T* = –5 °C), and dried in air. Compound **2** was obtained in a yield of 0.204 g (70% based on cobalt). Found (%): C, 46.63; H, 4.97; N, 7.62. $C_{77}Co_7H_{101}Li_2N_{11}O_{23}$. Calculated (%): C, 46.83; H, 5.16; N, 7.80. IR, ν/cm^{-1}: 3904 w, 3750 w, 3676 w, 2956 w, 2363 m, 2336 w, 2314 w, 1605 s, 1556 s, 1520 w, 1463 s, 1412 w, 1360 m, 1224 w, 1156 w, 1040 w, 1012 w, 952 w, 896 w, 860 w, 792 m, 748 w, 668 w, 608 w, 512 w, 468 w, 420 w, 376 w.

X-ray diffraction study. X-ray diffraction data sets for complexes **1** and **2** were collected according to a standard procedure[17] on a Bruker SMART APEX II automated diffractometer equipped with a CCD detector and a monochromatic radiation source (Mo-Kα radiation, λ = 0.71073 Å). For both complexes, semiempirical absorption corrections were applied.[18] The structures of the complexes were solved by direct methods and refined by the full-matrix least-squares method with anisotropic displacement parameters for all nonhydrogen atoms. The hydrogen atoms of the *tert*-butyl substituents of the pivalate ligands, OH groups (for **2**), and NH groups of the pyridonate ligands (for **1**) were positioned geometrically and refined using a riding model. All calculations were carried out with the use of the SHELX-97 program package.[19] Crystallographic parameters and the X-ray diffraction data collection and structure refinement statistics are given in Tables 1 and 2.

Table 2. Crystallographic characteristics and the X-ray data collection and structure refinement statistics for complexes **1** and **2**

Parameter	**1**	**2**
Molecular formula	$C_{35}H_{56}ClCoLi_3N_2O_{12}$	$C_{77}H_{101}C_7Li_2N_{11}O_{23}$
Molecular weight	812.02	1975.08
Crystal system	Monoclinic	Monoclinic
Space group	C_2	$P2_1/n$
a/Å	18.8573(8)	14.9761(10)
b/Å	15.5310(6)	24.2529(16)
c/Å	14.9122(6)	25.2135(18)
α/deg	90.00	90.00
β/deg	95.1110(10)	100.9390(10)
γ/deg	90.00	90.00
V/Å	4350.0(3)	8991.5(11)
Z	4	4
d_{calc}/g cm^{-3}	1.240	1.459
μ/cm^{-1}	0.511	1.334
Radiation	Mo-Kα (λ = 0.71073 Å)	
θ-Scan range/deg	1.37—29.88	1.62—26.40
Number of measured reflections	16218	54223
Number of reflections with $I > 2\sigma(I)$	10770	18441
R_1[a] ($I > 2\sigma(I)$)	0.0436	0.0374
wR_2[b] ($I > 2\sigma(I)$)	0.1279	0.1083

[a] $R_1 = \Sigma\|F_o| - |F_c\|/\Sigma|F_o|$.
[b] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

We thank Yu. A. Velikodnyi for performing X-ray powder diffraction studies.

This study was financially supported by the Russian Foundation for Basic Research (Project Nos 08-03-00343, 09-03-12228, and 09-03-90446), the Council on Grants of the President of the Russian Federation (Program for State Support of Young Scientists and Leading Scientific Schools of the Russian Federation, Grants MK-444.2009.3 and NSh-3672.2010.3), the Ministry of Education and Science of the Russian Federation (Federal Contracts GK-14.740.11.0363), the Russian Academy of Sciences, the Siberian Branch of the Russian Academy of Sciences, and the Division of Chemistry and Materials Science of the Russian Academy of Sciences.

References

1. E. Yu. Fursova, O. V. Kuznetsova, G. V. Romanenko, V. I. Ovcharenko, *Izv. Akad. Nauk, Ser. Khim.*, 2006, 1863 [*Russ. Chem. Bull., Int. Ed.*, 2006, **55**, 1933].
2. E. Yu. Fursova, O. V. Kuznetsova, G. V. Romanenko, V. I. Ovcharenko, A. S. Bogomyakov, *Izv. Akad. Nauk, Ser. Khim.*, 2008, 1175 [*Russ. Chem. Bull., Int. Ed.*, 2008, **57**, 1198].
3. E. Fursova, O. Kuznetsova, G. Romanenko, Y. Schvedenkov, V. I. Ovcharenko, *J. Cluster Sci.*, 2005, **16**, 319.
4. A. C. Warden, M. T. W. Hearn, L. Spiccia, *Inorg. Chem.*, 2003, **42**, 7037.
5. G. Aromi, A. R. Bell, M. Helliwell, J. Raftery, S. J. Teat, G. A. Timco, Roubeau, R. E. P. Winpenny, *Chem.-Eur. J.*, 2003, **9**, 3024.
6. A. Ferguson, J. McGregor, A. Parkin, M. Murrie, *J. Chem. Soc., Dalton Trans.*, 2001, 504.
7. E. K. Brechin, R. O. Gould, S. G. Harris, S. Parsons, R. E. P. Winpenny, *J. Am. Chem. Soc.*, 1996, **118**, 11293.
8. E. K. Brechin, L. M. Gilby, R. O. Gould, S. G. Harris, S. Parsons, R. E. P. Winpenny, *J. Chem. Soc., Dalton Trans.*, 1998, 2657.
9. S. McConnell, M. Motevalli, P. Thornton, *Polyhedron*, 1995, **14**, 459.
10. E. K. Brechin, A. Graham, A. Parkin, S. Parsons, A. M. Seddon, R. E. P. Winpenny, *J. Chem. Soc., Dalton Trans.*, 2000, 3242.
11. E. K. Brechin, A. Graham, S. G. Harris, S. Parsons, R. E. P. Winpenny, *J. Chem. Soc., Dalton Trans.*, 1997, 3405.
12. S. Langley, M. Helliwell, J. Raftery, E. I. Tolis, R. E. P. Winpenny, *Chem. Commun.*, 2004, 142.
13. C. Cadiou, R. A. Coxall, A. Graham, A. Harrison, M. Helliwell, S. Parsons, R. E. P. Winpenny, *Chem. Commun.*, 2002, 1106.
14. A. A. Sidorov, M. E. Nikiforova, E. V. Pakhmutova, G. G. Aleksandrov, V. N. Ikorskii, V. M. Novotortsev, I. L. Eremenko, I. I. Moiseev, *Izv. Akad. Nauk, Ser. Khim.*, 2006, 1851 [*Russ. Chem. Bull., Int. Ed.*, 2006, **55**, 1920].
15. Yu. V. Rakitin, V. T. Kalinnikov, *Sovremennaya magnetokhimiya* [*Modern Magnetochemistry*], Nauka, St-Petersburg, 1994, 272 pp. (in Russian).
16. E. K. Brechin, S. G. Harris, S. Parsons, R. E. P. Winpenny, *Chem. Commun.*, 1996, 1439.
17. *SMART (Control) and SAINT (Integration) Sofware*, *Version 5.0*, Bruker AXS, Inc., Madison (WI), 1997.
18. G. M. Sheldrik, *SADABS, Program for Scanning and Correction of Area Detector Data*, Götinngen University, Götinngen, Germany, 1997.
19. G. M. Sheldrick, *SHELXL97, Program for the Refinement of Crystal Structures*, University of Göttingen, Göttingen, Germany, 1997.

Received May 12, 2010;
in revised form October 14, 2010