118 *Russian Chemical Bulletin, International Edition, Vol. 53, No. 1, pp. 118—126, January, 2004*

Unsymmetrical dinuclear cobalt and nickel trimethylacetate complexes

I. G. Fomina,[a]* ***A. A. Sidorov,***[a] ***G. G. Aleksandrov,***[a] ***V. I. Zhilov,***[a] ***V. N. Ikorskii,***[b] ***V. M. Novotortsev,***[a]
I. L. Eremenko,[a] ***and I. I. Moiseev***[a]

[a]*N. S. Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences,*
31 Leninsky prosp., 119991 Moscow, Russian Federation.
Fax: +7 (095) 954 1279. E-mail: fomina@igic.ras.ru
[b]*A. V. Nikolaev Institute of Inorganic Chemistry, Siberian Branch of the Russian Academy of Sciences,*
3 prosp. Akad. Lavrent´eva, 630090 Novosibirsk, Russian Federation.
Fax: +7 (383 2) 34 4489

The reaction of the dinuclear complex $Co_2(\mu\text{-}OOCCMe_3)_2(\eta^2\text{-}OOCCMe_3)_2bpy_2$ (**1**) with the polymer $[Co(OH)_n(OOCCMe_3)_{2-n}]_x$ afforded the unsymmetrical dinuclear complex $bpyCo_2(\mu_2\text{-}O,\eta^2\text{-}OOCCMe_3)(\mu_2\text{-}O,O'\text{-}OOCCMe_3)_2(\eta^2\text{-}OOCCMe_3)$ (**2**). The reaction of 2,2´-dipyridylamine with $[Co(OH)_n(OOCCMe_3)_{2-n}]_x$ gave rise to the analogous complex $[(C_5H_4N)_2NH]Co_2(\mu_2\text{-}O,\eta^2\text{-}OOCCMe_3)(\mu\text{-}OOCCMe_3)_2(\eta^2\text{-}OOCCMe_3)$ (**3**). The reaction of complex **1** with $Ni_4(\mu_3\text{-}OH)_2(\mu\text{-}OOCCMe_3)_4(OOCCMe_3)_2(MeCN)_2[\eta^2\text{-}o\text{-}C_6H_4(NH_2)(NHPh)]_2$ (**4**) produced an isostructural heterometallic analog of complex **2** with composition $bpyM_2(\mu_2\text{-}O,\eta^2\text{-}OOCCMe_3)(\mu_2\text{-}O,O'\text{-}OOCCMe_3)_2(\eta^2\text{-}OOCCMe_3)$ (**5**) (M = Co, Ni; Co : Ni = 1 : 1) and the dinuclear heterometallic complex $bpy(HOOCCMe_3)M(\mu\text{-}OH_2)(\mu\text{-}OOCCMe_3)_2M(OOCCMe_3)_2[o\text{-}C_6H_4(NH_2)(NHPh)]$ (**6**) (M = Co, Ni; Co : Ni = 0.15 : 1.85). Compounds **2** and **5** exhibit ferromagnetic spin-spin exchange interactions.

Key words: cobalt and nickel complexes, trimethylacetate complexes, 2,2´-bipyridyl, 2,2´-dipyridylamine, *N*-phenyl-*o*-phenylenediamine, heterometallic complexes, X-ray diffraction analysis, magnetic properties.

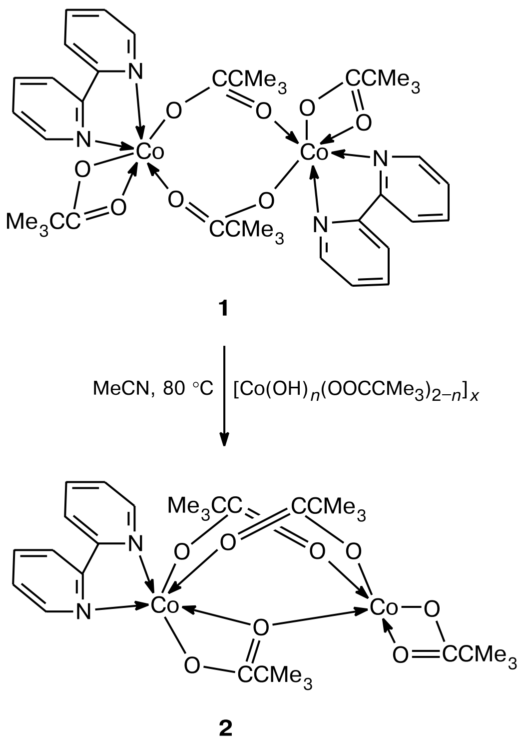
A search for ways of controlling the magnetic properties of polynuclear complexes is of interest for the directed design of structures exhibiting ferromagnetic properties, including compounds, which serve as molecular ferromagnetics and possess residual magnetization.[1—3] The magnetic characteristics of compounds can be modified both by varying the local ligand environment about the metal centers in complexes with retention of the metal core of the molecules and by partially replacing the magnetic ions of one type with those of another type (for example, with ions in another spin state). However, the solution of this complicated chemical problem calls for the development of efficient procedures for the assembly of such modified systems. For this purpose, it is convenient to use rather labile metal complexes generating coordinatively unsaturated metal-containing species, which can serve as "magnetic" ligands with respect to another metal-containing reagent. In the present study, we applied this approach to the synthesis of homo- and heterometallic trimethylacetate dinuclear complexes with Co and Ni atoms and compared the magnetic behavior of the starting compounds and final products.

Results and Discussion

Recently,[4] we have reported the synthesis of the dinuclear antiferromagnetic complex $Co_2(\mu\text{-}OOCCMe_3)_2(\eta^2\text{-}OOCCMe_3)_2bpy_2$ (**1**) with two carboxylate bridges. In this complex, the Co atoms bear one excess electron compared to the saturated 18-electron shell, which, apparently, leads to a noticeable weakening of the bonds between the Co atoms and the carboxylate anions. This is evidenced by the nonequivalence of the Co—O bonds in the chelate-coordinated carboxylate anion. As a result, the molecule is rather labile and can eliminate the mononuclear $bpyCo(OOCR)_2$ fragment in the presence of donors. We used the cobalt carboxylate fragments of the polymeric $[Co(OH)_n(OOCCMe_3)_{2-n}]_x$ complex, which can interact with the metal center through electron pairs of the O atoms of the carboxylate groups, as new donor ligands with respect to the Co^{II} atom in molecule **1**. In this case, the reaction with the use of the reagent ratio of 1 : 1 (with respect to the Co atom) in MeCN or benzene afforded the unsymmetrical dinuclear complex $bpyCo_2(\mu_2\text{-}O,\eta^2\text{-}OOCCMe_3)(\mu_2\text{-}$

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 1, pp. 116—123, January, 2004.

Scheme 1



O,O′-OOCCMe$_3$)$_2$(η^2-OOCCMe$_3$) (**2**) containing the bpyCo(OOCR)$_2$ (from complex **1**) and Co(OOCR)$_2$ (from the polymer) fragments (Scheme 1).

According to the X-ray diffraction data (Fig. 1, Table 1), molecule **2** contains two Co atoms located at a nonbonded distance (3.272(1) Å), which is noticeably shorter than that in the starting complex **1** (Co...Co, 4.383(1) Å[4]). The Co$_2$(μ-OOCCMe$_3$)$_2$(μ-O$_{\rm OOCR}$) dinuclear fragment in complex **2** contains two carboxylate bridges with the unsymmetrical Co—O bonds (Co(1)—O, 1.962(2) and 2.014(2) Å; Co(2)—O, 2.017(2) and 2.035(2) Å; C—O, 1.252(4)—1.258(4) Å; O—C—O, 125.7(3) and 124.8(3)°; the dihedral angle between the Co$_2$O—C—O planes is 95.5°). The bridging O atom in complex **2** (Co(1)—O, 1.987(2) Å; Co(2)—O, 2.259(2) Å; Co—O—Co, 100.59(6)°) belongs to the carboxylate group chelated at the Co atom (Co(2)—O, 2.141(2) Å; O—C—O, 119.0(3)°). The same metal atom is coordinated by the bipyridyl ligand (Co(2)—N, 2.075(3) and 2.100(3) Å), whereas the second metal center bears the chelate-coordinated carboxylate group (Co(1)—O, 1.993(2) and 2.270(2) Å; O—C—O, 118.4(3)°).

As a result, one of the metal atoms is in a distorted octahedral environment and possesses a 19-electron shell, whereas another metal atom has a nearly trigonal-bipyramidal environment and bears 17 electrons. The formation of compound **2** in the above-described process gives promise that this scheme of transformations with the use of various metal-containing carboxylates, which possess the M(OOCR)$_2$ fragment, as a source of new donor ligands may offer a way of preparing analogs of complex **2** with various combinations of d elements.

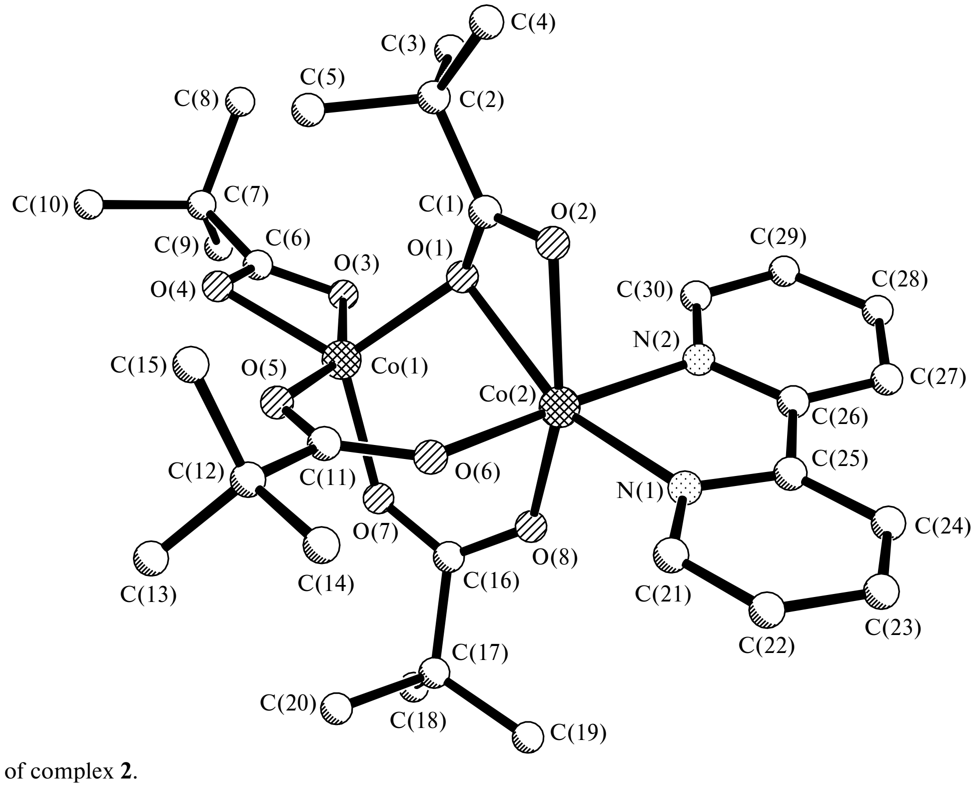


Fig. 1. Structure of complex **2**.

Table 1. Selected distances (*d*) in the dinuclear complexes $LM(\mu_2\text{-}O,\eta^2\text{-OOCCMe}_3)(\mu\text{-OOCCMe}_3)_2Co(\eta^2\text{-OOCCMe}_3)$

Distance	*d*/Å		
	LM = bpyCo (**2**)	LM = $[(C_5H_4N)_2NH]Co$ (**3**)	LM = bpyNi (**5**)
M...Co	3.272(1)	3.321(1)	3.222(1)
M—N	2.075(3), 2.100(3)	2.084(9), 2.087(8)	2.042(2), 2.047(2)
M—O($OOCR_{bridge}$)	2.016(2), 2.035(2)	2.001(8), 2.078(8)	2.008(2), 2.013(2)
M—O($OOCR_{chel-bridge}$)	2.141(2), 2.259(2)	2.129(9), 2.362(10)	2.128(2), 2.153(2)
Co—O($OOCR_{bridge}$)	1.961(2), 2.014(2)	1.972(8), 1.982(9)	1.956(2), 2.009(2)
Co—O($OOCR_{chel-bridge}$)	1.987(2)	1.977(8)	1.995(2)
Co—O($OOCR_{chel}$)	1.993(2), 2.270(2)	1.996(8), 2.400(10)	1.986(2), 2.279(2)

A complex analogous to complex **2** but containing the coordinated 2,2´-dipyridylamine ligand was prepared directly by the reaction of the amine with the polymeric Co complex with the use of the Co : L ratio of 2 : 1. The $[(C_5H_4N)_2NH]Co_2(\mu_2\text{-}O,\eta^2\text{-OOCCMe}_3)(\mu\text{-OOCCMe}_3)_2(\eta^2\text{-OOCCMe}_3)$ compound (**3**) (Fig. 2, see Table 1) also contains the nonequivalent metal atoms in distorted octahedral and trigonal-bipyramidal environments. These atoms are located at a nonbonded distance of 3.321(1) Å.

In spite of expansion of the metallocycle through chelate coordination of dipyridylamine (Co—N, 2.084(9) and 2.087(8) Å; N—Co—N, 87.0(3)°), compound **3** retains the number and type of carboxylate bridges ((Co(1)—O)(μ_2-*O,O´*-OOCCMe$_3$), 2.001(8) and 2.078(8) Å; (Co(2)—O)(μ_2-*O,O´*-OOCCMe$_3$), 1.972(8) and 1.982(9) Å). The chelate-bridging OCO group is located at a substantially longer distance from the metal atom having an octahedral environment (Co(1)—O, 2.129(9) and 2.362(10) Å), which, in turn, leads to a decrease in the O—Co—O chelate angle (57.2(3)°) compared to those observed in compounds **2** (60.17(5) and 61.48(6)°) and **1** (60.66(8)°). However, these distortions exert only a slight effect on the coordination sphere of the second Co atom, which has a smaller coordination number (5) and the unsaturated 17-electron shell.

The magnetic behavior of dinuclear complex **2** differs sharply from that of the starting antiferromagnetic symmetrical dinuclear complex **1** (Fig. 3). It appeared that compound **2** exhibits ferromagnetic spin-spin exchange interactions. Its effective magnetic moment (μ_{eff}) increases from 6.51 to 7.62 μ_B (per overall formula) in the temperature range of 300—6 K and then decreases to 7.06 μ_B at 2 K. Therefore, the formal removal of one bipyridyl

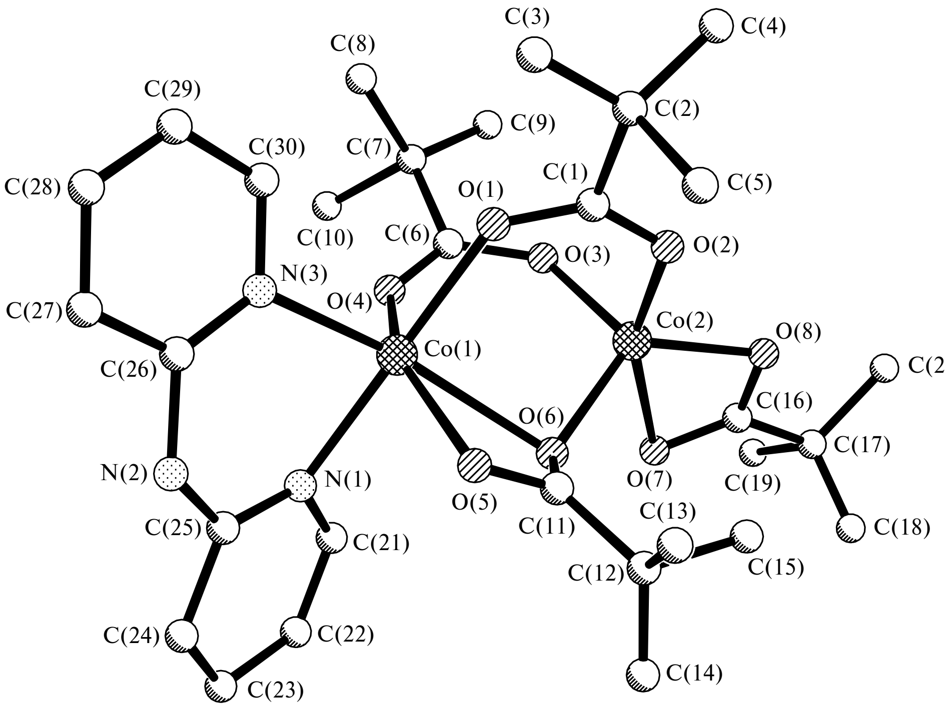


Fig. 2. Structure of complex **3**.

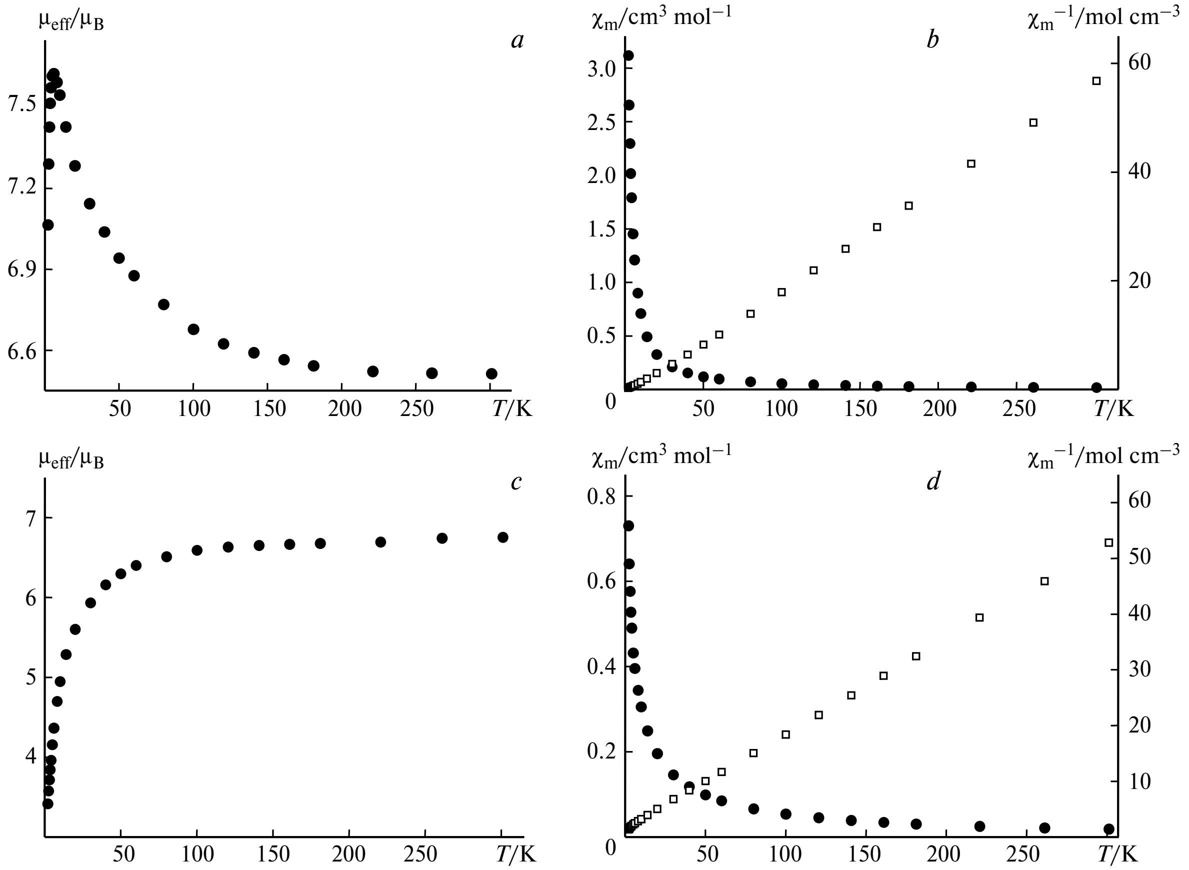


Fig. 3. Magnetic properties of dinuclear complexes **2** (*a*, *b*) and **1** (*c*, *d*) (μ_{eff} is the effective magnetic moment, χ_m is the static magnetic susceptibility).

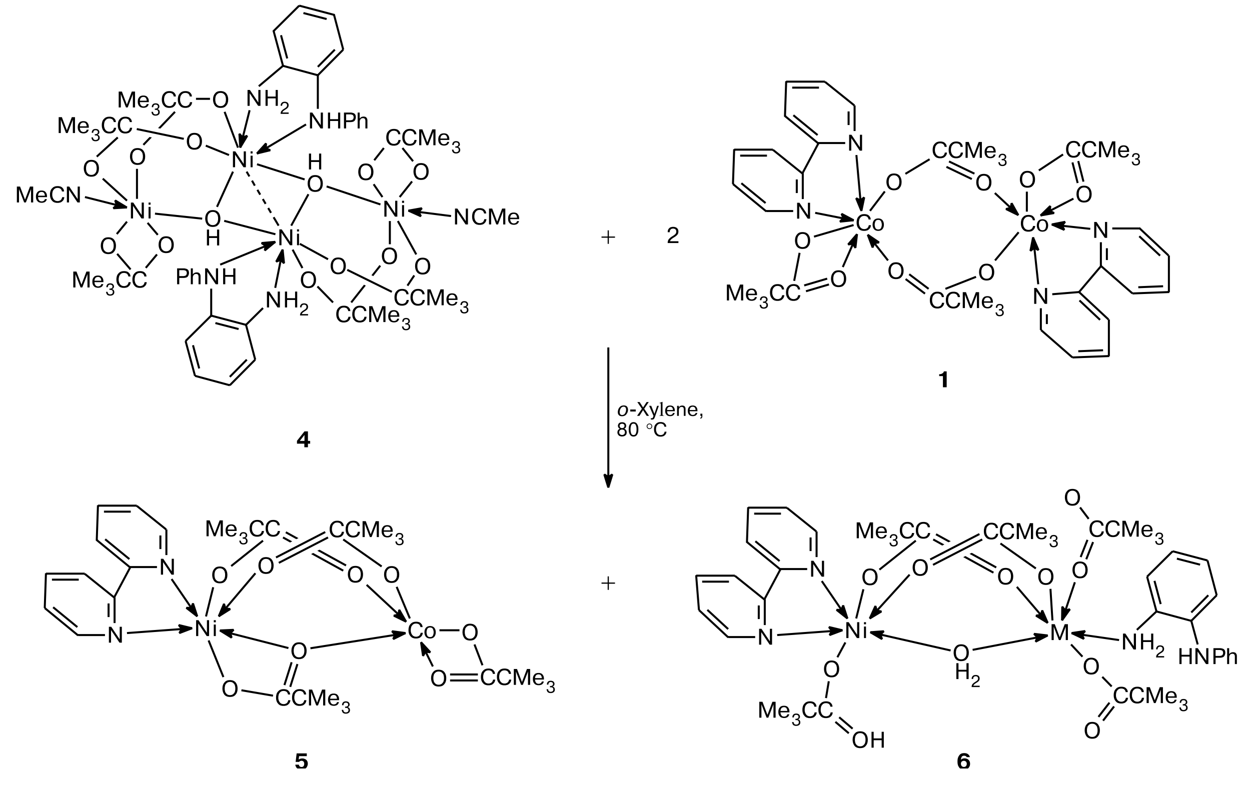
ligand from dimer **1** leads not only to a substantial rearrangement of the metal carboxylate core in **2** but also to a qualitative change in the magnetic properties of the new compound.

We also attempted to prepare heteronuclear analogs of dinuclear ferromagnetic complex **2** using sources of $M(OOCCMe_3)_2$ other than $[Co(OH)_n(OOCCMe_3)_{2-n}]_x$. For this purpose, we employed a procedure analogous to that described for the synthesis of **2** but with the use of the tetranuclear nickel complex $Ni_4(\mu_3\text{-}OH)_2(\mu\text{-}OOCCMe_3)_4(OOCCMe_3)_2(MeCN)_2[\eta^2\text{-}o\text{-}C_6H_4(NH_2)(NHPh)]_2$ (**4**) as a source of a donor metal-containing agent (Scheme 2).

The reaction was carried out in *o*-xylene at 80 °C (starting ratio Ni : Co = 1 : 1). Two dinuclear complexes were isolated in approximately equal yields (40—45%). According to the results of inductively coupled plasma atomic emission spectrometry (ICP-AES), one of these complexes contains Co and Ni atoms in a ratio of 1 : 1. X-ray diffraction study demonstrated that this compound is a structural analog of complex **2**. Although it is difficult to distinguish between the Ni and Co atoms, the best results of refinement were obtained for the structure in which the metal position with the coordinated bipyridyl ligand is occupied by the Ni atom, whereas the metal position in a trigonal-bipyramidal oxygen environment is occupied by the Co atom. This model is consistent with the known structural data, which provide evidence that the octahedral environment of the nickel atom is most favorable in polynuclear trimethylacetates.[5—9] However, the trigonal-bipyramidal ligand environment of the metal atom was observed for cobalt in structural analogs of complex **5** as well as in complexes **2** and **3** and the dinuclear anion $[Co_2(\mu_2,\eta^2\text{-}OOCCMe_3)(\mu_2\text{-}OOCCMe_3)_2(\eta^2\text{-}OOCCMe_3)_2]^-$.[10] Therefore, the structure of this heterometallic compound can be, apparently, represented as the $bpyNi(\mu_2,\eta^2\text{-}OOCCMe_3)(\mu_2\text{-}OOCCMe_3)_2Co(\eta^2\text{-}OOCCMe_3)$ complex (**5**) (Fig. 4, see Table 1). In this case, the bipyridyl molecule should be transferred from the Co atom to the Ni atom in the course of the reaction.

Compound **5**, like its homonulcear analog **2**, exhibits ferromagnetic properties (Fig. 5). However, the plot of μ_{eff} *vs.* T for complex **5** is somewhat different from that observed for compound **2**. The magnetic moment of the heteronuclear complex is substantially smaller in accordance with a change in the spin state of one of the metal centers ($S_{Ni} = 1$ instead of $S_{Co} = 3/2$).

Scheme 2



R = CMe$_3$

The second reaction product, *viz.*, the dinuclear complex bpy(HOOCCMe$_3$)M(μ-OH$_2$)(μ-OOCCMe$_3$)$_2$M′(OOCCMe$_3$)$_2$[*o*-C$_6$H$_4$(NH$_2$)(NHPh)] (**6**), was isolated as a solvate containing one-half of the *o*-xylene molecule per molecule of the complex. According to the ICP-AES data, compound **6** has predominantly

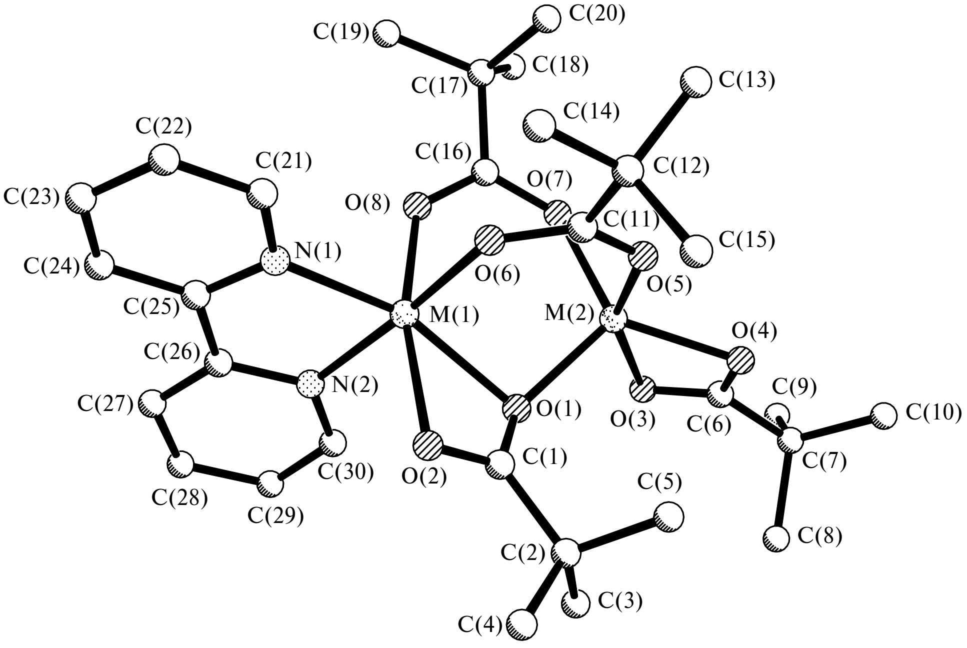


Fig. 4. Structure of heteronuclear complex **5**.

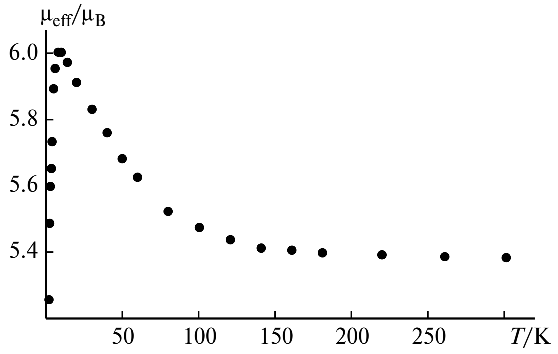


Fig. 5. Magnetic properties of complex **5**.

Ni atoms (Ni : Co = 1.85 : 0.15). X-ray diffraction analysis (Fig. 6, Table 2) demonstrated that molecule **6** contains the aqua-bridged M(μ-OH$_2$)(μ-OOCR)$_2$M′ fragment (M(1)...M(2) and M(1)—O(H$_2$O), 2.023(4) Å; M(2)—O(H$_2$O), 2.076(4) Å) typical of compounds modeling the active sites of carboxylate-containing metalloenzymes.[11—14]

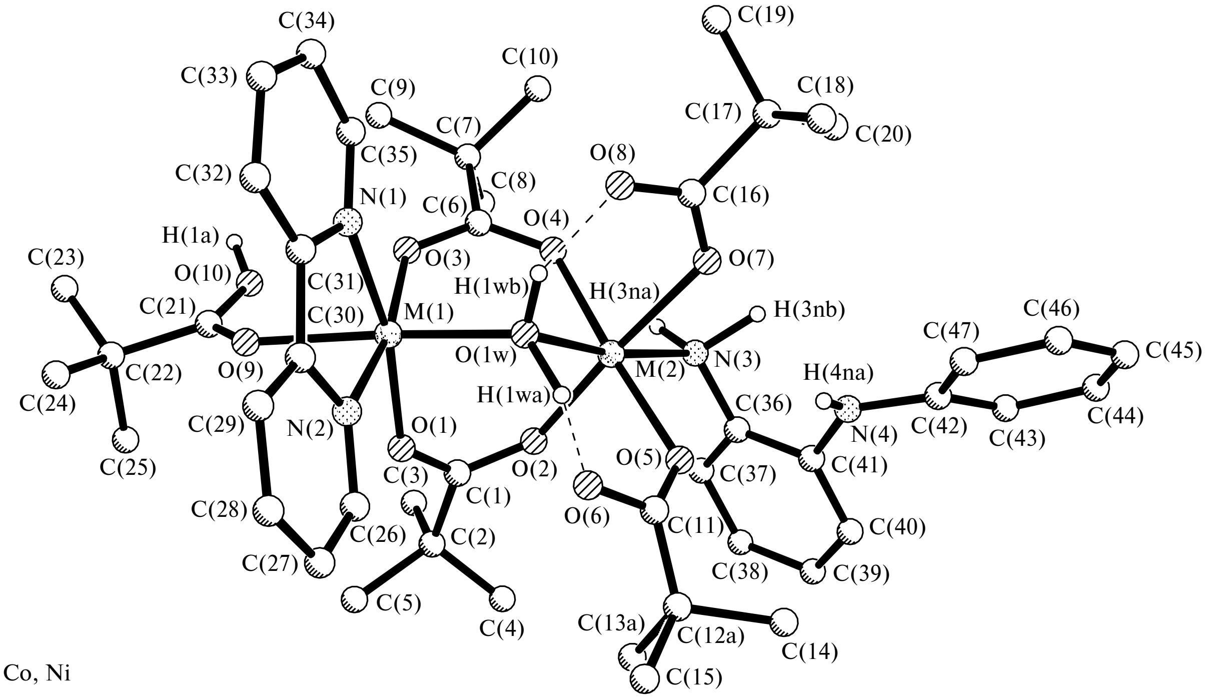
However, the metal atoms in complex **6** are coordinated by different N-donor ligands, *viz.*, bipyridyl (M(1)—N, 2.053(5) and 2.071(5) Å) and *N*-phenyl-*o*-phenylenediamine, which is bound to the metal center through the NH$_2$ groups (M(2)—N, 2.134(5) Å). The pivalic acid molecule (H atom of the OH group was revealed from the difference Fourier synthesis) serves as the second ligand coordinated to the M(1) atom, whereas the M(2) atom bears the coordinated diamine ligand along with two trimethylacetate anions, which form hydrogen bonds with the bridging water molecule (1.45—1.60 Å).

Since both metal centers in complex **6** are in a distorted octahedral environment, it is practically impossible to distinguish the positions partially occupied by the Co atoms. The best results of refinement correspond to the formula bpy(HOOCCMe$_3$)Ni(μ-OH$_2$)(μ-OOCCMe$_3$)$_2$Ni$_{0.85}$Co$_{0.15}$(OOCCMe$_3$)$_2$[*o*-C$_6$H$_4$(NH$_2$)(NHPh)] (**6**).

The results of the present study demonstrated the efficiency of the procedure for the synthesis of heterometallic compounds with the use of labile cobalt trimethylacetate complexes (for example, compound **1**) as a source of coordinatively unsaturated species, which can add other metal fragments involved in polynuclear counter agents. Deeper transformations involving the formal exchange of N-donor ligands (for example, bipyridyl) between the metal centers can also proceed. We observed such transformations in the case of complexes **5** and **6**.

Experimental

The complexes were synthesized in an inert atmosphere using anhydrous solvents. The starting complexes **1** and **4** were prepared according to known procedures.[4,15] The new compounds were synthesized using commercial *N*-phenyl-*o*-phenylenediamine, 2,2′-bipyridyl, and 2,2′-dipyridylamine (Fluka). The IR spectra were recorded on a Specord M-80 instrument in KBr pellets. The static magnetic susceptibilities (χ_m) was measured on a SQUID MPMS-5S (Quantuim Design) magnetom-



M = Co, Ni

Fig. 6. Structure of dinuclear complex **6**.

Table 2. Selected geometric parameters (bond lengths (*d*) and bond angles (ω)) for the unsymmetrical dinuclear complex bpy(HOOCCMe$_3$)M(μ-OH$_2$)(μ-OOCCMe$_3$)$_2$M′(OOCCMe$_3$)$_2$[*o*-C$_6$H$_4$(NH$_2$)(NHPh)] • •0.5Me$_2$C$_6$H$_4$ (**6**) (M = Ni, M′ = Co, Ni)

Bond	*d*/Å	Angle	ω/deg
M(1)—O(1)	2.007(4)	O(1)—M(1)—O(1W)	93.62(17)
M(1)—N(1)	2.071(5)	O(1W)—M(1)—N(2)	91.30(18)
M(2)—O(2)	2.023(4)	O(1W)—M(1)—N(1)	94.71(17)
M(2)—O(1W)	2.076(4)	O(1)—M(1)—O(3)	94.06(17)
O(1)—C(1)	1.238(7)	N(2)—M(1)—O(3)	170.32(17)
O(4)—C(6)	1.240(7)	O(1)—M(1)—O(9)	85.92(17)
O(7)—C(16)	1.245(7)	N(2)—M(1)—O(9)	83.92(18)
O(10)—C(21)	1.328(8)	O(3)—M(1)—O(9)	89.06(17)
N(2)—C(26)	1.329(8)	O(2)—M(2)—O(5)	90.48(19)
N(4)—C(42)	1.390(8)	O(2)—M(2)—O(1W)	97.34(17)
M(1)—O(1W)	2.023(4)	O(5)—M(2)—O(1W)	91.61(17)
M(1)—O(3)	2.089(4)	O(4)—M(2)—O(7)	87.59(19)
M(2)—O(4)	2.038(5)	O(1W)—M(2)—O(7)	91.23(16)
M(2)—O(7)	2.079(4)	O(4)—M(2)—N(3)	83.20(18)
O(2)—C(1)	1.249(7)	O(1W)—M(2)—N(3)	171.85(19)
O(5)—C(11)	1.261(7)	M(1)—O(1W)—M(2)	114.12(19)
O(8)—C(16)	1.261(7)	O(4)—C(6)—O(3)	124.1(6)
N(1)—C(35)	1.337(8)	O(7)—C(16)—O(8)	125.1(6)
N(2)—C(30)	1.375(8)	O(1)—M(1)—N(2)	92.09(19)
N(4)—C(41)	1.401(8)	O(1)—M(1)—N(1)	168.19(18)
M(1)—N(2)	2.053(5)	N(2)—M(1)—N(1)	79.4(2)
M(1)—O(9)	2.126(4)	O(1W)—M(1)—O(3)	95.76(16)
M(2)—O(5)	2.045(5)	N(1)—M(1)—O(3)	93.41(18)
M(2)—N(3)	2.134(5)	O(1W)—M(1)—O(9)	175.18(17)
O(3)—C(6)	1.293(7)	N(1)—M(1)—O(9)	85.07(18)
O(6)—C(11)	1.275(7)	O(2)—M(2)—O(4)	91.3(2)
O(9)—C(21)	1.195(7)	O(4)—M(2)—O(5)	176.61(18)
N(1)—C(31)	1.356(7)	O(4)—M(2)—O(1W)	91.05(17)
N(3)—C(36)	1.440(8)	O(2)—M(2)—O(7)	171.38(18)
		O(5)—M(2)—O(7)	90.25(18)
		O(2)—M(2)—N(3)	88.58(19)
		O(5)—M(2)—N(3)	93.94(18)
		O(7)—M(2)—N(3)	82.80(18)
		O(1)—C(1)—O(2)	125.9(6)
		O(5)—C(11)—O(6)	122.8(6)
		O(9)—C(21)—O(10)	121.7(6)

eter in the temperature range of 300—2 K. The effective magnetic moments were calculated by the equation

$$\mu_{\text{eff}} = (8\,\chi_{\text{m}}T)^{1/2}.$$

The metal contents in the complexes were determined by inductively coupled plasma atomic emission spectrometry on an IRIS Advantage instrument.

2,2′-Bipyridyl(μ-*O*,η^2-trimethylacetato)di(μ$_2$-trimethylacetato)(η^2-trimethylacetato)dicobalt(II), bpyCo$_2$(μ-*O*,η^2-OOCCMe$_3$)(μ-OOCCMe$_3$)$_2$(η^2-OOCCMe$_3$) (2). A mixture of the starting polymeric trimethylacetate [Co(OH)$_n$(OOCCMe$_3$)$_{2-n}$]$_x$ (1 g, 3.83 mmol with respect to the mononuclear fragment [Co(OH)$_{0.1}$(OOCCMe$_3$)$_{1.9}$]) and the Co$_2$(μ-OOCCMe$_3$)$_2$(η^2-OOCCMe$_3$)$_2$bpy$_2$ complex (**1**) (1.60 g, 1.915 mmol) was refluxed in MeCN (50 mL) for 2 h until the reagents were completely dissolved. The resulting solution was concentrated *in vacuo* to dryness. The solid residue was dissolved in benzene (25 mL). The solution was concentrated to 2 mL. Then hexane (5 mL) was added and the solution was kept at 5 °C for one day. The prismatic dark-violet crystals suitable for X-ray diffraction analysis were separated from the mother liquor by decantation, washed with cold hexane, and dried *in vacuo* (0.1 Torr) at 22 °C. The yield was 1.92 g (74%). Found (%): C, 53.41; H, 6.82; N, 4.32. C$_{30}$H$_{44}$Co$_2$N$_2$O$_8$. Calculated (%): C, 53.10; H, 6.49; N, 4.13. IR, ν/cm^{-1}: 3112 w, 3064 w, 2960 m, 2928 m, 2872 w, 1661 w, 1648 w, 1592 v.s, 1480 v.s, 1416 v.s, 1360 s, 1320 w, 1224 s, 1160 w, 1104 w, 1056 w, 1024 m, 936 w, 896 m, 792 s, 776 m, 768 v.s, 736 m, 680 w, 656 w, 608 s, 536 w, 424 s.

2,2′-Dipyridylamino(μ-*O*,η^2-trimethylacetato)di(μ$_2$-trimethylacetato)(η^2-trimethylacetato)dicobalt(II), [(C$_5$H$_4$N)$_2$NH]Co$_2$(μ$_2$-*O*,η^2-OOCCMe$_3$)(μ-OOCCMe$_3$)$_2$(η^2-OOCCMe$_3$) (3). Acetonitrile (50 mL) was added to a mixture of polymeric cobalt trimethylacetate (1 g, 3.96 mmol) and 2,2′-dipyridylamine (0.32 g, 1.98 mmol). The suspension of the starting reagents was refluxed for 15 min until the reagents were completely dissolved. The resulting violet solution was concentrated to 10 mL at 80 °C (0.1 Torr) and kept at ~20 °C for one day. Large prismatic violet crystals that precipitated were separated from the mother liquor by decantation, washed with cold benzene, and dried at ~20 °C (0.1 Torr). The yield was 1.13 g (87%). Found (%): C, 52.30; H, 6.57; N, 5.92. C$_{30}$H$_{44}$Co$_2$N$_2$O$_8$. Calculated (%): C, 52.10; H, 6.28; N, 6.08. IR, ν/cm^{-1}: 3268 w, 3140 w, 3094 w, 3030 w, 2982 s, 2914 m, 2866 m, 1604 s, 1573 w, 1558 m, 1540 w, 1480 s, 1424 m, 1350 s, 1322 s, 1256 m, 1222 s, 1150 m, 1048 v.s, 1000 m, 978 m, 894 v.s, 870 s, 794 s, 776 s, 752 v.s, 690 v.s, 650 m, 552 m, 524 m, 418 m.

2,2′-Bipyridyl(μ-*O*,η^2-trimethylacetato)di(μ$_2$-trimethylacetato)(η^2-trimethylacetato)cobalt(II)nickel(II), bpyNi(μ$_2$,η^2-OOCCMe$_3$)(μ$_2$-OOCCMe$_3$)$_2$Co(η^2-OOCCMe$_3$) (5) and 2,2′-bipyridyl(*N*-phenyl-*o*-phenylenediamino)ditrimethylacetato(μ$_2$-aquo)(trimethylacetic acid)di(μ$_2$-trimethylacetato)(η^2-trimethylacetato)cobalt(II)nickel(II), bpy(HOOCCMe$_3$)Ni(μ-OH$_2$)(μ-OOCCMe$_3$)$_2$Ni$_{0.85}$Co$_{0.15}$(OOCCMe$_3$)$_2$[*o*-C$_6$H$_4$(NH$_2$)(NHPh)] • 0.5Me$_2$C$_6$H$_4$ (6). A blue solution of [*o*-C$_6$H$_4$(NH$_2$)(NHPh)]$_2$Ni$_4$(μ$_3$-OH)$_2$(OOCCMe$_3$)$_6$(MeCN)$_2$ (**4**) (0.5 g, 0.30 mmol) and bpy$_2$Co$_2$(OOCCMe$_3$)$_4$ (**1**) (0.25 g, 0.30 mmol) in *o*-xylene (15 mL) was heated to 80 °C, concentrated to 5 mL, cooled, and kept at ~20 °C for 12 h to obtain large blue crystals suitable for X-ray diffraction study. The crystals were separated from the mother liquor by filtration and dried under a stream of argon. The yield of complex **5** was 45% (with respect to the starting dimer **1**). The mother liquor was kept at ~20 °C. After 4—8 weeks, large pale-green crystals suitable for X-ray diffraction study precipitated. The yield of solvate **6** was 45% (with respect to the starting dimer **1**).

Complex 5. Found (%): C, 53.70; H, 6.18; N, 4.73. C$_{30}$H$_{44}$CoN$_2$NiO$_8$. Calculated (%): C, 53.13; H, 6.49; N, 4.13. IR, ν/cm^{-1}: 2956 s, 2924 m, 2872 m, 1664 m, 1600 s, 1568 m, 1520 m, 1480 m, 1448 m, 1416 m, 1372 s, 1360 m, 1316 w, 1264 w, 1220 m, 1172 w, 1156 w, 1104 w, 1056 w, 1028 w, 900 w, 808 w, 792 w, 768 m, 740 w, 652 w, 612 m, 532 w, 424 w.

Solvate 6. Found (%): C, 58.70; H, 6.78; N, 5.43. C$_{51}$H$_{73}$Co$_{0.15}$N$_4$Ni$_{1.85}$O$_{11}$. Calculated (%): C, 59.13; H, 7.05; N, 5.41. IR, ν/cm^{-1}: 3452 m, 3448 m, 3430 m, 2961 s, 2930 m, 2882 m, 1784 w, 1760 w, 1684 m, 1668 m, 1608 m, 1540 w,

Table 3. Crystallographic characteristics of complexes **2**, **3**, **5**, and **6**

Parameter	**2**	**3**	**5**	**6**
Molecular formula	$C_{30}H_{44}Co_2N_2O_8$	$C_{30}H_{43}Co_2N_3O_8$	$C_{30}H_{44}CoN_2NiO_8$	$C_{47}H_{68}Co_{0.15}N_4Ni_{1.85}O_6 \cdot 0.5Me_2C_6H_4$
Space group	$P2_1/n$	$P2_12_12_1$	$P2_1/n$	$P\bar{1}$
a/Å	11.057(2)	12.087(2)	11.0343(17)	12.152(4)
b/Å	16.000(3)	16.437(3)	15.992(3)	12.986(5)
c/Å	18.805(4)	19.061(4)	18.637(3)	18.264(5)
α/deg	90	90	90	83.91(4)
β/deg	95.16(3)	90	95.611(4)	76.23(3)
γ/deg	90	90	90	77.30(3)
V/Å^3	3313.3(11)	3786.9(13)	3273.0(9)	2726.3(16)
Z	4	4	4	2
d_{calc}/g cm^{-3}	1.367	1.194	1.377	1.255
μ/mm^{-1}	1.049	0.919	1.131	0.742
Radiation	Mo-Kα (λ = 0.71073 Å)			
Number of measured reflections	6872	4080	7937	8722
Number of reflections with $I > 2\sigma$	4182	3207	6170	4913
R_1	0.0472	0.0984	0.0494	0.0791
wR_2	0.0824	0.2336	0.1072	0.1673

1520 m, 1480 m, 1416 m, 1372 m, 1352 m, 1228 w, 880 w, 744 w, 600 w, 420 w.

X-ray diffraction analysis. The experimental data sets for complexes **2**, **3**, **5**, and **6** were collected on an automated Bruker AXS SMART diffractometer equipped with a CCD detector (graphite monochromator, 110 °C, ω scanning technique, scan step was 0.3°, frames were exposed for 30 s) using a standard procedure.[16] The semiempirical absorption correction was applied.[17] The principal crystallographic characteristics and details of refinement of all structures are given in Table 3. The structures of **2**, **3**, **5**, and **6** were solved by direct methods and refined by the full-matrix least-squares method with anisotropic thermal parameters for all nonhydrogen atoms. The H atoms of the bridging water molecule, the OH group of the coordinated pivalic acid molecule, and the amino groups of the coordinated *N*-phenyl-*o*-phenylene ligand in the structure of complex **6** were located from the difference Fourier synthesis and refined isotropically. The remaining H atoms were generated geometrically and refined using the riding model. The metal atoms in heteronuclear complexes **5** and **6** were refined using both homo- (both positions are occupied by nickel atoms or both positions are occupied by cobalt atoms) and heteronuclear models. The best results of refinement were obtained for the heteronuclear model (for complex **5**, the occupancies of the positions of the Ni and Co atoms are virtually equal to unity; for complex **6**, the position in the vicinity of the coordinated bipyridyl molecule is occupied by Ni atoms with an occupancy of 1, whereas another position is occupied by Ni and Co atoms with occupancies of 0.85 and 0.15, respectively). Calculations were carried out using the SHELX97 program package.[18] The selected geometric parameters of complexes **2**, **3**, **5**, and **6** are given in Tables 1 and 2.

Unlike complexes **2**, **5**, and **6**, which crystallize as racemates in centrosymmetrical space groups, single crystals of complex **3** belonging to the asymmetrical space group $P2_12_12_1$ contain only one of two optical enantiomers. Crystallization of a racemic mixture of complex **3** formed in solution led to spontaneous resolution of optical isomers. The absolute structure of complex **3** is shown in Fig. 2; Flack's parameter[19] for the structure (for the enantiomer chosen correctly, this parameter is close to zero) is 0.03(5). In actuality, the O(1) atom (adopting a pyramidal configuration) of the chelate-bridging trimethylacetate anion serves as an asymmetric center in complex **3**. Earlier, we have observed spontaneous resolution into optically active enantiomers upon crystallization for analogous dinuclear complexes with amidine ligands.[20]

This study was financially supported by the Russian Foundation for Basic Research (Project Nos. 04-03-32880, 04-03-32883, 02-03-33075, and 00-03-40104), the Program of Basic Research of the Chemistry and Materials Science Division of the Russian Academy of Sciences ("Chemistry and Physical Chemistry of Supramolecular Systems and Atomic Clusters"), the INTAS (Grant 03-51-4532), and the Grant of the Government of Moscow ("Infrastructure and Addressed Support of Science").

References

1. V. I. Ovcharenko and R. Z. Sagdeev, *Usp. Khim.*, 1999, **68**, 381 [*Russ. Chem. Rev.*, 1999, **5**, 345 (Engl. Transl.)].
2. *Nanotechnology Research Directions: IWGN Workshop Report. Vision for Nanotechnology R&D in the Next Decade*, Eds. M. C. Roco, R. S. Williams, and P. Alivisatos, Kluwer Academic Publishers, Dordrecht—Boston—London, 2002.
3. O. Khan, *Molecular Magnetism*, VCH, New York, 1993.
4. M. O. Talismanova, A. A. Sidorov, V. M. Novotortsev, G. G. Aleksandrov, S. E. Nefedov, I. L. Eremenko, and I. I. Moiseev, *Izv. Akad. Nauk, Ser. Khim.*, 2001, 2149 [*Russ. Chem. Bull., Int. Ed.*, 2001, **50**, 2251].
5. I. L. Eremenko, S. E. Nefedov, A. A. Sidorov, and I. I. Moiseev, *Izv. Akad. Nauk, Ser. Khim.*, 1999, 409 [*Russ. Chem. Bull.*, 1999, **48**, 405 (Engl. Transl.)].

6. I. L. Eremenko, M. A. Golubnichaya, S. E. Nefedov, A. A. Sidorov, I. F. Golovaneva, V. I. Burkov, O. G. Ellert, V. M. Novotortsev, L. T. Eremenko, A. Sousa, and M. R. Bermejo, *Izv. Akad. Nauk, Ser. Khim.*, 1998, 725 [*Russ. Chem. Bull.*, 1998, **47**, 704 (Engl. Transl.)].
7. I. L. Eremenko, S. E. Nefedov, A. A. Sidorov, M. A. Golubnichaya, P. V. Danilov, V. N. Ikorskii, Yu. G. Shvedenkov, V. M. Novotortsev, and I. I. Moiseev, *Inorg. Chem.*, 1999, **38**, 3764.
8. V. M. Novotortsev, Yu. V. Rakitin, S. E. Nefedov, and I. L. Eremenko, *Izv. Akad. Nauk, Ser. Khim.*, 2000, 437 [*Russ. Chem. Bull., Int. Ed.*, 2000, **49**, 438].
9. A. A. Sidorov, P. V. Danilov, S. E. Nefedov, M. A. Golubnichaya, I. G. Fomina, O. G. Ellert, V. M. Novotortsev, and I. L. Eremenko, *Zh. Neorg. Khim.,* 1998, **43**, 930 [*Russ. J. Inorg. Chem.*, 1998, **43** (Engl. Transl.)].
10. I. G. Fomina, A. A. Sidorov, G. G. Aleksandrov, V. N. Ikorskii, V. M. Novotortsev, S. E. Nefedov, and I. L. Eremenko, *Izv. Akad. Nauk, Ser. Khim.*, 2002, 1453 [*Russ. Chem. Bull., Int. Ed.*, 2002, **51**, 1581].
11. R. H. Holm, P. Kennepohl, and E. I. Solomon, *Chem. Rev.*, 1996, **96**, 2239.
12. E. Jabri, M. B. Carr, R. P. Hausinger, and P. A. Karplus, *Science*, 1995, **268**, 998.
13. M. A. Pearson, R. A. Schaller, L. O. Michel, P. A. Karplus, and R. P. Hausinger, *Biochemistry*, 1998, **37**, 6214.
14. S. J. Lippard, *Science*, 1995, **268**, 996.
15. A. A. Sidorov, S. M. Deomidov, S. E. Nefedov, I. G. Fomina, P. V. Danilov, V. M. Novotortsev, O. G. Volkov, V. N. Ikorskii, and I. L. Eremenko, *Zh. Neorg. Khim.,* 1999, **44**, 399 [*Russ. J. Inorg. Chem.*, 1999, **44**, 336 (Engl. Transl.)].
16. *SMART (Control) and SAINT (Integration) Software, Version 5.0*, Bruker AXS Inc., Madison (WI), 1997.
17. G. M. Sheldrick, *SADABS. Program for Scanning and Correction of Area Detector Data*, Göttingen University, Götinngen (Germany), 1997.
18. G. M. Sheldrick, *SHELX97. Program for the Solution of Crystal Structures*, Göttingen University, Göttinngen (Germany), 1997.
19. H. D. Flack, *Acta Crystallogr.*, 1985, **A41**, 500.
20. T. B. Mikhailova, E. V. Pakhmutova, A. E. Malkov, I. F. Golovaneva, A. A. Sidorov, I. G. Fomina, G. G. Aleksandrov, V. N. Ikorskii, V. M. Novotortsev, I. L. Eremenko, and I. I. Moiseev, *Izv. Akad. Nauk, Ser. Khim.*, 2003, 1994 [*Russ. Chem. Bull., Int. Ed.*, 2003, **52**, 2105].

Received October 7, 2003;
in revised form December 15, 2003