Heterospin complexes based on dinuclear Cu^{II} triketonate and nitroxides*

V. I. Ovcharenko,[a]★ S. V. Fokin,[a] G. V. Romanenko,[a] V. N. Ikorskii,[a] R. Z. Sagdeev,[a] D. S. Yachevskii,[b] D. L. Chizhov,[b] and V. N. Charushin[b]★

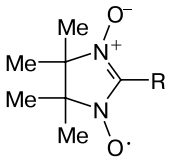
[a] *International Tomography Center, Siberian Branch of the Russian Academy of Sciences, 3a ul. Institutskaya, 630090 Novosibirsk, Russian Federation Fax: +7 (383) 333 1399. E-mail: Victor.Ovcharenko@tomo.nsc.ru*

[b] *I. Ya. Postovsky Institute of Organic Synthesis, Ural Branch of the Russian Academy of Sciences, 22 ul. S. Kovalevskoi, 620219 Ekaterinburg, Russian Federation. Fax: +7 (343) 374 1189. E-mail: charushin@prm.uran.ru*

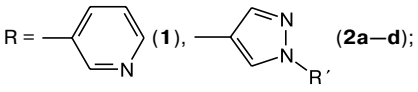
Heterospin complexes of bis(μ_2-1,1,2,2,8,8,9,9-octafluorononane-3,5,7-trionato)dicopper(II) ($[Cu_2L_2]$) with nitronyl nitroxides 2-(1-methyl-1*H*-pyrazol-4-yl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazole-1-oxyl 3-oxide (**2**) and 4,4,5,5-tetramethyl-2-(3-pyridinyl)-4,5-dihydro-1*H*-imidazole-1-oxyl 3-oxide (**1**) were synthesized and structurally characterized. Crystals of the complexes are formed by the discrete bis[1-methyl-4-(4,4,5,5-tetramethyl-3-oxide-1-oxyl-4,5-dihydro-1*H*-imidazol-2-yl)-1*H*-pyrazole]-bis(μ_2-1,1,2,2,8,8,9,9-octafluorononane-3,5,7-trionato)dicopper(II) etherate (**3**) and bis[3-(4,4,5,5-tetramethyl-3-oxide-1-oxyl-4,5-dihydro-1*H*-imidazol-2-yl)pyridine]-bis(μ_2-1,1,2,2,8,8,9,9-octafluorononane-3,5,7-trionato)dicopper(II) (**4**) molecules. Each Cu atom of the dinuclear chelate fragment coordinates one paramagnetic ligand through the N atom of the pyrazole or pyridine fragment, respectively. In complex **3**, the paramagnetic ligands are located on one side of the plane of the chelate fragment, whereas the ligands in complex **4** are located above and below the plane of the chelate fragment. The magnetic properties of complexes **3** and **4** are determined by dominant antiferromagnetic exchange interactions between the unpaired electrons of the Cu^{II} atoms in the dinuclear Cu_2L_2 moiety.

Key words: copper(II), metal triketonates, nitroxides, X-ray diffraction study, magnetic properties.

Coordinatively unsaturated metal chelate compounds are widely used as acceptor matrices in the synthesis of heterospin systems containing stable nitroxides.[1] Among these compounds, fluorine-containing matrices, which increase the electron-withdrawing properties of the central atom and are stereochemically nonrigid, have attracted considerable attention. High electron-withdrawing ability of the metal atom is favorable for coordination of weak donors, such as >N—O groups of nitroxides; due to stereochemical nonrigidity of metal-containing matrices, structurally different compounds can be prepared by reactions with polyfunctional nitroxides, and detailed magnetic-structural correlations can be revealed.[2—4] For example, the reactions of copper(II) hexafluoroacetylacetonate $[Cu(hfac)_2]$ with stable nitronyl nitroxides **1** and **2** produced a family of heterospin complexes exhibiting thermally induced magnetic effects, which are characterized by the temperature dependences of the effective magnetic moment analogous to those for a spin-crossover.[3—10]



1, **2**



R′ = Me (**a**), Et (**b**), Pr (**c**), Bu (**d**)

The discovery of these new magnetically active systems called for a detailed investigation of the structures and magnetic properties of this type of heterospin complexes, which necessitates the development of new synthetic approaches and methods for the controlled chemi-

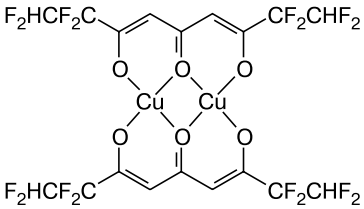
* Dedicated to Academician O. M. Nefedov on the occasion of his 75th birthday.

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 11, pp. 1836—1840, November, 2006.

1066-5285/06/5511-1904

cal influence on their physical characteristics. Systematic studies of this class of compounds are based primarily on successive variations of the nature of substituents at position 2 of the imidazoline ring, changes in the structure of the paramagnetic organic fragment, and the preparation of solid solutions of heterospin complexes containing either different paramagnetic organic ligands or different metals in the $M(hfac)_2$ matrix.[3,4]

In the present study, we examined the possibility of synthesizing heterospin complexes based on nitroxides and the dinuclear fluorinated matrix bis(μ_2-1,1,2,2,8,8,9,9-octafluorononane-3,5,7-trionato)dicopper(II) (**Cu_2L_2**). We used nitroxides **1** and **2a**, which form complexes with $[Cu(hfac)_2]$ showing thermally induced magnetic anomalies.[3]



Cu_2L_2

Results and Discussion

The heterospin complexes $[Cu_2L_2(\mathbf{2a})_2] \cdot Et_2O$ (**3**) and $[Cu_2L_2(\mathbf{1})_2]$ (**4**) were synthesized in good yields as high-quality single crystals suitable for X-ray diffraction according to the procedures described in the Experimental section. The solvent used in the synthesis is the main factor determining the possibility of preparing solid phases of the complexes. For example, when the reaction of Cu_2L_2 with **2a** was performed in benzene, toluene, or an acetone—heptane mixture, only the starting reagents poorly soluble in these solvents were obtained as the solid phase upon cooling of the reaction mixture or gradual removal of the solvent. When the reaction was performed in diethyl ether, the solvate of dinuclear complex **3** least soluble in this solvent was obtained as the solid phase.

A single-crystal X-ray diffraction study demonstrated that complex **3** has a molecular structure (Fig. 1, *a*). In the dinuclear fragment $\{Cu_2L_2\}$ ($d_{Cu...Cu}$ = 3.0423(9) Å), the deprotonated ligands L are tridentate-bridging (Fig. 1, *a*). The Cu—O distances involving the bridging O(2) atom (1.947(2) and 1.956(2) Å) are substantially longer than the distances to the O(1) and O(3) atoms (1.897(2) and 1.913(2) Å, respectively). These O atoms form a base of a distorted square pyramid of each Cu atom, whose apex is occupied by the imine N atom of the pyrazole ring of paramagnetic ligand **2a** (d_{Cu-N} = 2.343(3) Å). The overall symmetry of the molecule is C_2 (symmetry axis is perpendicular to the parallelo-

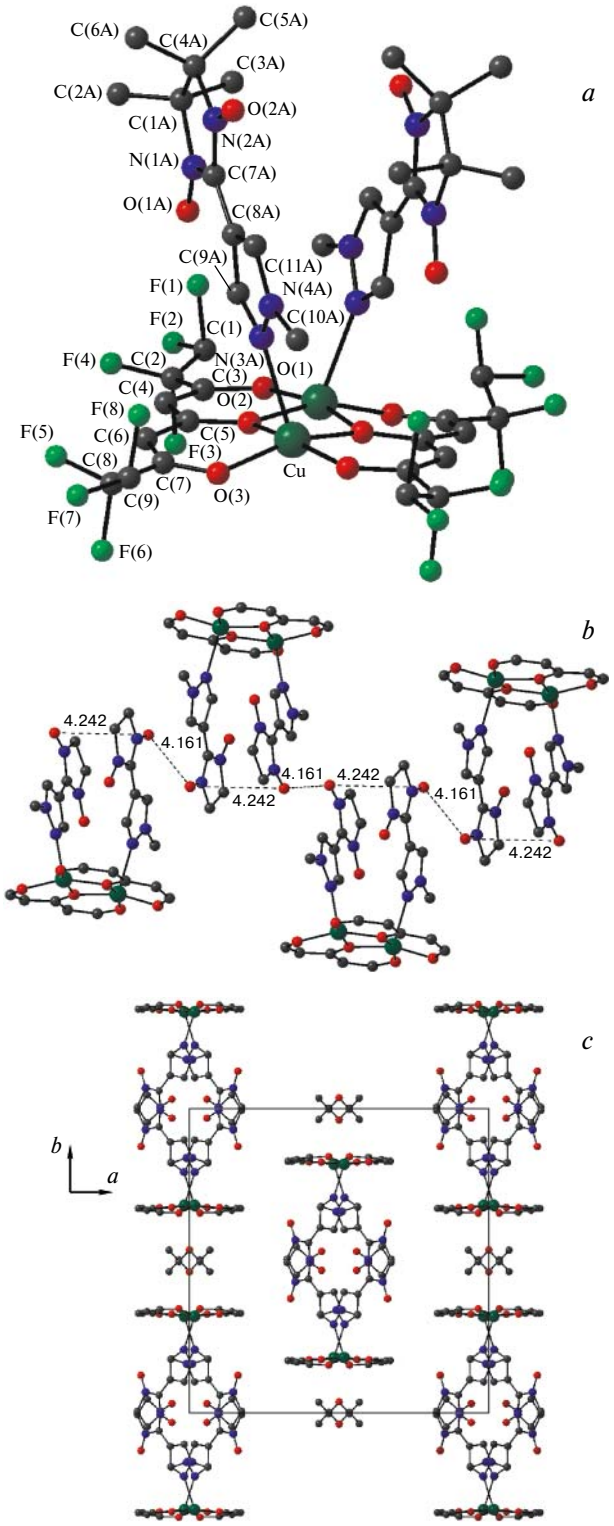
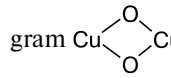


Fig. 1. *a*. Molecular structure of complex **3** (H atoms are omitted). *b*. The shortest distances between the O atoms of the >N—O groups in the structure of complex **3** (diethyl ether molecules of crystallization, the HCF_2CF_2 substituents, the Me groups of the 2-imidazoline rings, and the H atoms are omitted). *c*. The crystal structure projected onto the (001) plane (Me and HCF_2CF_2 substituents and the H atoms are omitted). (See Note to Fig. 2.)

gram  and passes through the intersection point of its diagonals) is responsible for the arrangement of both ligands **2a** on one side of the $\{Cu_2L_2\}$ fragment. It should be noted that this is a rare case of coordination of ligands by the dinuclear Cu^{II} triketonate matrix. A search of the Cambridge Structural Database[11] revealed eight mixed-ligand complexes based on dinuclear Cu^{II} triketonates, among which only one compound, *viz.*, bis[2,5-bis(trifluoroacetyl)cyclopentanoato]diaquadicopper(II) monohydrate, contains both coordinated water molecules on one side of the coordination plane.[12] The N—O distances in the nitronyl nitroxide fragments are similar to each other and are typical of free nitronyl nitroxides (1.275(4) and 1.282(4) Å). In the crystal of complex **3**, the heterocyclic fragments of molecules **2a** are virtually coplanar; the angle between the planes of the pyrazole ring and the CN_2 fragment of the imidazoline ring is 5.5(1)°. The shortest distance between the O atoms of the >N—O groups in the molecule of complex **3** is 4.242(4) Å, and the corresponding distance between the adjacent molecules is 4.161(4) Å (Fig. 1, *b*). Such short distances are attributed to the fact that the coordinated nitroxide ligands of the alternating $[Cu_2L_2(\mathbf{2a})_2]$ molecules in the crystal structure face each other (Fig. 1, *c*). The arrangement of the diethyl ether molecules of crystallization in the crystal structure is shown in the projection onto the (001) plane (Fig. 1, *c*).

Molecule **4** is centrosymmetric (Fig. 2, *a*). The geometric parameters of the dinuclear fragment $\{O_2Cu(\mu\text{-}O)_2CuO_2\}$ are virtually identical to those in molecules **3** (Cu—O distances are 1.920(2) and 1.921(2) Å; the distance to the bridging O atom is 1.955(2) Å). The apex of the distorted square pyramid of each Cu atom is occupied by the N atom of the pyridine ring of **1** (d_{Cu-N} = 2.415(2) Å). The molecules of the nitroxides are coordinated on the opposite sides of the dinuclear fragment $\{Cu_2L_2\}$. The 2-imidazoline ring in complex **4**, unlike that in complex **3**, is nonplanar. The C(01) and C(04) atoms are located above and below the plane passing through the O(01), N(1), C(07), N(2), and O(02) atoms of the nitronyl nitroxide fragment (Fig. 2, *a*). The angle between the planes of the pyridine ring and the CN_2 fragment of the imidazoline ring is 38.1(1)°.

In the crystals, the molecules are packed so that the O atoms of the >N—O groups of the adjacent molecules are located below the base of the Cu pyramid, thus transforming the latter into a bipyramid. Hence, the crystals of **4** can be formally described as consisting of infinite ribbons (Fig. 2, *b*). However, taking into account that the additional distances are long ($d_{Cu...O}$ = 2.681(2) Å), the structure **4** should be considered as molecular. This is also evidenced by the virtually equal N—O distances in the nitronyl nitroxide fragments (1.283(3) and 1.275(3) Å)

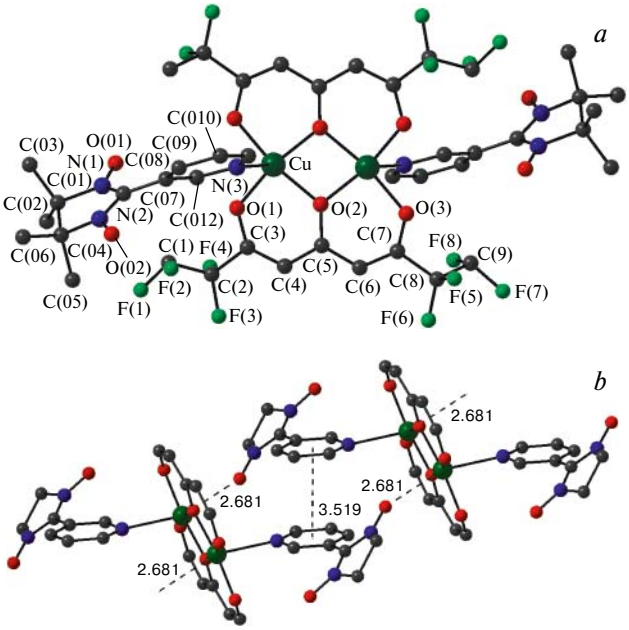


Fig. 2. *a*. Molecular structure of complex **4** (H atoms are omitted). *b*. The molecular packing in the crystal structure (Me and HCF_2CF_2 substituents and the H atoms are omitted).
Note. Figures 1 and 2 are available in full color in the on-line version of the journal (http://www.springerlink.com/issn/1573-9171/current) and on the web-site of the journal (http://russchembull.ru).

identical to those observed in the crystals of **3**, in which the Cu atoms and the nitronyl nitroxide fragments are located at large distances (Fig. 1). The ribbon-like packing of molecules **4** in the crystal structure (see Fig. 2, *b*) is most likely attributed to the tendency of the aromatic pyridine rings to form stacking interactions. In the solid state, these rings are located parallel (dihedral angle between the planes of the ring is 0° within experimental error) one above another at rather short distances between the eclipsed atoms (~3.5 Å).

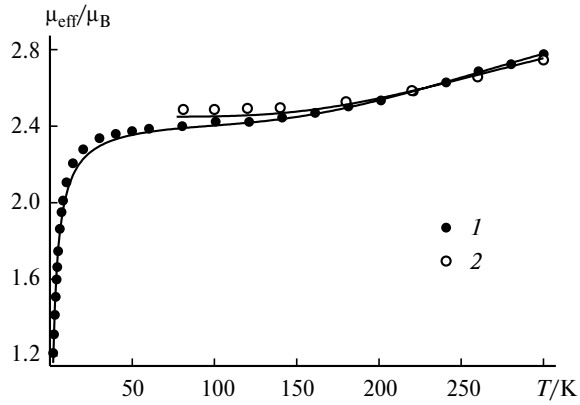
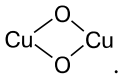


Fig. 3. Temperature dependences of the effective magnetic moments for complexes **3** (*1*) and **4** (*2*). The theoretical curves are shown by solid line curves.

Table 1. Optimal parameters of the theoretical curves $\mu_{eff}(T)$

Complex	g	J_1	J_2	zJ_3
		cm^{-1}		
3	2.15	−279	31	−2.1
4	2.10	−273	−0.5	—

The temperature dependences of the effective magnetic moment (μ_{eff}) for **3** and **4** are shown in Fig. 3. For both complexes, μ_{eff} decreases with decreasing temperature and approaches ~2.4 μ_B at a temperature below 150 K, which corresponds to the contribution of two weakly interacting spins with $S = 1/2$. We modelled these dependences (see Fig. 3) with the use of the isotropic Hamiltonian including the exchange interaction J_1(Cu—O—Cu) in the dinuclear fragments and two indirect exchange interactions J_2(Cu...N—O$^{\bullet}$). For complex **3**, for which measurements were carried out down to lower temperatures, weak intermolecular exchange interactions (zJ_3) were also taken into account by the molecular field method. The program for calculations of the heterospin exchange clusters under consideration has been described earlier.[13] The optimized parameters (Table 1) clearly indicate that strong exchange interactions in complexes **3** and **4** are present in the two-center exchange clusters  .

Due to the antiferromagnetic character of the complexes, the spins of the copper ions at $T < 150$ K already virtually completely compensate each other, and only the unpaired electrons of the nitronyl nitroxide fragments make the contribution to the magnetic moments of both complexes.

To conclude, we synthesized and structurally characterized heterospin complexes based on the fluorinated Cu^{II} triketonate matrix and nitronyl nitroxides. The compounds obtained in the solid phase consist of discrete molecules **3** and **4**, in which each Cu atom in the dinuclear chelate matrix coordinates one paramagnetic ligand through the N atom of the pyrazole or pyridine fragment, respectively. In molecules **3**, the paramagnetic ligands are located on one side of the chelate matrix, whereas these ligands in molecules **4** are on the opposite sides. The magnetic properties of these compounds are determined by the dominant antiferromagnetic exchange interactions between the unpaired electrons of the Cu^{II} ions in the dinuclear matrix Cu_2L_2.

Based on a comparison of the results of the present study with the data for the Cu(hfac)$_2$ complexes with the same nitronyl nitroxides studied earlier,[3] it can be hypothesized that the fluorinated dinuclear Cu^{II} triketonate matrices under study are apparently stereochemically more rigid compared to Cu(hfac)$_2$. This hinders the formation of numerous forms of heterospin complexes, which fact has been observed earlier for the products of the reactions of **2a** and **1** with Cu(hfac)$_2$. The reactions of Cu_2L_2 with nitroxides **2a** and **1** produced the only compound regardless of the reagent ratio, and the solvent used in the synthesis is the key factor determining the possibility of preparing the solid phase of heterospin complexes.

The investigation of the crystal structure of complex **4** demonstrated that dinuclear fluorine-containing transition metal triketonates can be considered as valuable matrices for the development of procedures for the synthesis of heterospin ribbon-like (or ladder-like) structures.

Experimental

Nitronyl nitroxides **1** and **2** were synthesized according to known procedures.[2,9] 1,1,2,2,8,8,9,9-Octafluorononane-3,5,7-trione was prepared by modified Claisen condensation, *i.e.*, by diacylation of acetone with ethyl tetrafluoropropionate in the presence of LiH.[14,15]

Bis(μ_2-1,1,2,2,8,8,9,9-octafluorononane-3,5,7-trionato)dicopper(II) [Cu_2L_2]. 1,1,2,2,8,8,9,9-Octafluorononane-3,5,7-trione (1.57 g, 5.0 mmol), $Cu(CH_3COO)_2 \cdot 1H_2O$ (2.10 g, 10.5 mmol), and CH_3COOH (1 mL) were stirred in methanol (20 mL) at room temperature for 3 h. Then water (100 mL) was added, and the reaction mixture was stirred for 1 h. The green precipitate that formed was filtered off, washed with water (5×20 mL), twice precipitated from methanol, and dried at 100 °C. The yield was 77%. Decomp. t. > 250 °C. Found (%): C, 28.6; H, 1.2; F, 40.3. $Cu_2C_{18}H_8O_6F_{16}$. Calculated (%): C, 28.8; H, 1.1; F, 40.5.

Bis[1-methyl-4-(4,4,5,5-tetramethyl-3-oxide-1-oxyl-4,5-dihydro-1*H*-imidazol-2-yl)-1*H*-pyrazole]bis(μ_2-1,1,2,2,8,8,9,9-octafluorononane-3,5,7-trionato)dicopper(II) etherate (3). A mixture of powders of Cu_2L_2 (0.1000 g, 0.13 mmol) and **2a** (0.0630 g, 0.26 mmol) was dissolved in diethyl ether (5 mL) at room temperature. The resulting blue-green solution was kept in an open flask for 5 h, during which diethyl ether gradually evaporated and black crystals of the complex precipitated. The crystals were filtered off, washed with hexane, and dried in air. The yield was 55%. When stored in air, the crystals gradually lost the diethyl ether solvate molecules. Found (%): C, 39.0; H, 3.5; N, 9.0; F, 24.7. $Cu_2C_{40}H_{42}N_8O_{10}F_{16}$. Calculated (desolvated product) (%): C, 39.2; H, 3.5; N, 9.1; F, 24.8.

Bis[3-(4,4,5,5-tetramethyl-3-oxide-1-oxyl-4,5-dihydro-1*H*-imidazol-2-yl)pyridine]bis(μ_2-1,1,2,2,8,8,9,9-octafluorononane-3,5,7-trionato)dicopper(II) (4). A mixture of powders of Cu_2L_2 (0.0500 g, 0.065 mmol) and **1** (0.0312 g, 0.13 mmol) was dissolved in acetone (2 mL) at room temperature. Heptane (3 mL) was slowly and very carefully added to the resulting solution in such a way that the heptane was not mixed with the acetone solution and coated the mixture of the reagents in acetone with a layer (rapid mixing of acetone with heptane led to the formation of a finely dispersed precipitate of the complex). The resulting blue-green solution was kept for 4 h, during which the heptane slowly diffused into the acetone layer and dark blue-green crystals grew. The crystals were filtered off, washed with cold ethanol, and dried in air. The yield was 64%. Found (%): C, 41.6; H, 3.2; N, 6.8; F, 25.6. $Cu_2C_{42}H_{40}N_6O_{10}F_{16}$. Calculated (%): C, 41.4; H, 3.3; N, 6.9; F, 24.9.

X-ray diffraction study. X-ray diffraction data sets were collected from single crystals of **3** and **4** on a SMART APEX CCD (Bruker AXS) diffractometer (Mo-Kα, λ = 0.71073 Å, T = 295 K). Absorption corrections were applied using the Bruker SADABS software (version 2.10). The structures were solved by direct methods and refined by the full-matrix least-squares method with anisotropic displacement parameters for all non-hydrogen atoms. The positions of the H atoms were located in difference electron density maps. The H atoms of the methyl groups in the structure of **3** were refined isotropically in the rigid-body approximation. All calculations associated with the structure solution and refinement were carried out with the use of the Bruker SHELXTL (Version 6.14) program packages. For complex **3**: $C_{44}H_{52}Cu_2F_{16}N_8O_{11}$, M = 1300.02, crystals are monoclinic, space group $C2/c$, a = 23.691(3) Å, b = 20.368(3) Å, c = 13.4794(19) Å, β = 122.515(3)°, V = 5484.6(14) Å^3; Z = 4, ρ_{calc} = 1.574 5 g cm^{-3}, μ = 0.892 cm^{-1}, 20906 measured reflections (1.81 < θ < 23.33°), of which 3966 reflections were with $I > 2\sigma(I)$, R_1 = 0.0440, wR_2 = 0.1152. For complex **4**: $C_{42}H_{40}Cu_2F_{16}N_6O_{10}$, M = 1219.88, crystals are triclinic, space group $P\bar{1}$; a = 9.5417(14) Å, b = 10.3245(15) Å, c = 14.621(2) Å, α = 106.381(2)°, β = 95.081(2)°, γ = 114.953(2)°, V = 1216.7(3) Å^3, Z = 1, ρ_{calc} = 1.665 g cm^{-3}, μ = 0.997 cm^{-1}, 9437 measured reflections (2.28 < θ <23.27°), of which 3499 reflections were with $I > 2\sigma(I)$, R_1 = 0.0377, wR_2 = 0.1071.

Microanalysis was carried out on a Carlo-Erba 1106 analyzer at the Vorozhtsov Novosibirsk Institute of Organic Chemistry of the Siberian Branch of the Russian Academy of Sciences. The magnetic properties of the complexes were measured on a SQUID magnetometer in the temperature range of 2—300 K for complex **3** and 77—300 K for complex **4** in magnetic field of 5 kOe. The paramagnetic components of the magnetic susceptibility χ were calculated taking into account the diamagnetic contribution estimated from the Pascal constants. The effective magnetic moment was calculated by the equation

$$\mu_{eff} = [(3k/N_A\beta^2)\cdot\chi T]^{1/2} \approx (8\chi T)^{1/2},$$

where N_A is Avogadro's number, β is the Bohr magneton, and k is the Boltzmann constant.

This study was financially supported by the Russian Foundation for Basic Research (Project Nos 05-03-32305, 06-03-32157, and 06-03-04000), the US Civilian Research and Development Foundation (CRDF, Grant Y1-C-08-03), the Council on Grants of the President of the Russian Federation (Grant MK-10264.2006.3), and the Russian Academy of Sciences (Programs of the Presidium of the Russian Academy of Sciences, the Division of Chemistry and Materials Science of the Russian Academy of Sciences, the Siberian Branch of the Russian Academy of Sciences, and the Ural Branch of the Russian Academy of Sciences, integration grants).

References

1. V. I. Ovcharenko and R. Z. Sagdeev, *Usp. Khim.*, 1999, **68**, 381 [*Russ. Chem. Revs*, 1999, **68**, 345 (Engl. Transl.)].
2. A. Caneschi, D. Gatteschi, and P. Rey, *Progr. Inorg. Chem.*, 1991, **39**, 331.
3. P. Rey and V. I. Ovcharenko, *Spin transition phenomena*, in *Magnetism: Molecules to Materials IV*, Eds J. S. Miller and M. Drillon, Wiley-VCH, Weinheim, 2003, 41.
4. V. I. Ovcharenko, K. Yu. Maryunina, S. V. Fokin, E. V. Tret´yakov, G. V. Romanenko, and V. N. Ikorskii, *Izv. Akad. Nauk, Ser. Khim.*, 2004, 2304 [*Russ. Chem. Bull., Int. Ed.*, 2004, **53**, 2406].
5. F. Lanfranc de Panthou, E. Belorizky, R. Calemczuk, D. Luneau, C. Marcenat, E. Ressouche, P. Turek, and P. Rey, *J. Am. Chem. Soc.*, 1995, **117**, 11247.
6. F. Lanfranc de Panthou, D. Luneau, R. Musin, L. Öhrström, A. Grand, P. Turek, and P. Rey, *Inorg. Chem.*, 1996, **35**, 3484.
7. F. Iwahory, K. Inoue, and H. Iwamura, *Mol. Cryst. Liq. Cryst.*, 1999, **334**, 533.
8. A. Caneschi, P. Chiesi, L. David, F. Ferraro, D. Gatteschi, and R. Sessoli, *Inorg. Chem.*, 1993, **32**, 1445.
9. V. I. Ovcharenko, S. V. Fokin, G. V. Romanenko, Yu. G. Shvedenkov, V. N. Ikorskii, E. V. Tret´yakov, and S. F. Vasilevskii, *Zh. Strukt. Khim.,* 2002, **43**, 163 [*J. Struct. Chem.*, 2002, **43**, 153 (Engl. Transl.)].
10. V. I. Ovcharenko, S. V. Fokin, G. V. Romanenko, V. N. Ikorskii, E. V. Tretyakov, S. F. Vasilevsky, and R. Z. Sagdeev, *Mol. Phys.*, 2002, **100**, 1107.
11. *Cambridge Structural Database*, Version 5.27, November 2005 (Updates May 2006).
12. R. L. Lintvedt, M. D. Glick, B. K. Tomlonovic, D. P. Gavel, and J. M. Kuszaj, *Inorg. Chem.*, 1976, **15**, 1633.
13. I. V. Ovcharenko, Yu. G. Shvedenkov, R. N. Musin, and V. N. Ikorskii, *Zh. Strukt. Khim.,* 1999, **40**, 36 [*J. Struct. Chem.*, 1999, **40**, 29 (Engl. Transl.)].
14. M. V. Nikonov, D. L. Chizhov, V. G. Ratner, and K. I. Pashkevich, *J. Fluorine Chem.*, 2000, **106**, 115.
15. D. S. Yachevskii, D. L. Chizhov, V. G. Ratner, and K. I. Pashkevich, *Izv. Akad. Nauk, Ser. Khim.*, 2001, 1176 [*Russ. Chem. Bull., Int. Ed.*, 2001, **50**, 1233].

Received July 19, 2006