Dinuclear copper(II) complexes with an unsymmetrical exchange fragment

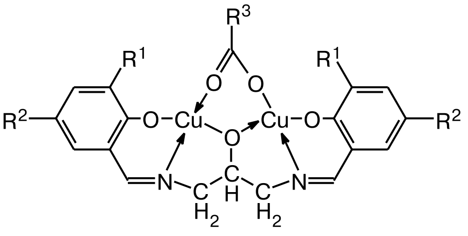
V. A. Kogan,[a]★ V. V. Lukov,[a] V. M. Novotortsev,[b] I. L. Eremenko,[b] and G. G. Aleksandrov[b]

[a]*Rostov State University,*
7 ul. Zorge, 344090 Rostov-on-Don, Russian Federation.
E-mail: kogan@chimfak.rsu.ru
[b]*N. S. Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences,*
31 Leninsky prosp., 119991 Moscow, Russian Federation.
E-mail: ilerem@igic.ras.ru

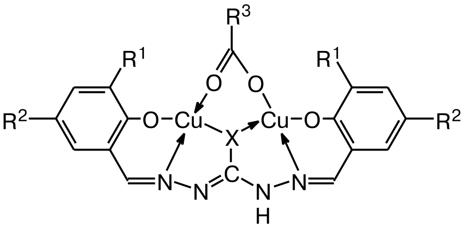
New dinuclear copper(II) complexes with azomethines and hydrazones, which were produced by condensation of substituted salicylaldehyde derivatives with 1,3-diaminopropan-2-ol or carbo(thiocarbo)hydrazide, were studied. The structures of the $[Cu_2L(\mu\text{-}CH_2ClCOO)(CH_3OH)]\cdot(CH_3OH)$ ($L = C_{17}H_{15}N_2O_3$) and $[Cu_2L^2(Cl_3CCO)(CH_3OH)]\cdot H_2O$ ($L^2 = C_{32}H_{42}N_4O_3$) complexes were established by X-ray diffraction. The magnetic properties of these complexes, including the influence of the nature of the substituents in the ligands on exchange interactions, were studied.

Key words: dinuclear complexes, copper(II), exchange interactions, unsymmetrical exchange fragment, magnetochemical correlations.

Dinuclear copper(II) compounds with azomethine ligands and their analogs with other 3d atoms have attracted particular attention because of their structural characteristics and magnetic properties.[1—19] The Cu^{II} atoms contain one unpaired electron, which substantially simplifies calculations of the energy parameters of exchange interactions. In addition, complexes with the azomethine ligand contain the stable dinuclear $Cu(\mu\text{-}X)(\mu\text{-}X^1)Cu$ fragment, whose geometric parameters depend only slightly on the nature of the substituents at the periphery of the molecule. This fact allows one to rather correctly estimate the exchange parameters for series of complexes and predict the existence of new compounds possessing the desired magnetic properties. In this respect, compounds containing various types of X and X^1 bridges (for example, containing one- and three-atom bridges) are of most interest. Among these compounds are copper complexes, in which the carboxylate group serves as one of the bridging ligands (structures **A** and **B**).



A



B

Investigations of such complexes containing various substituents in chelate-bridging ligands and the carboxylate group provide estimates of the influence of the electronic and steric factors on the energetics of the spin-spin exchange. However, it is important to know not only the magnetic properties but also the detailed geometry of the complexes, which requires the use of X-ray diffraction. In the present study, we analyzed the magnetic data for a series of compounds of types **A** and **B** and established the structures of the key complexes.

Results and Discussion

Recently,[20,21] we have developed convenient procedures for the synthesis of a series of complexes **A** and **B**. The structure of the **A**-type copper complex ($R^1 = R^2 = H$, $R^3 = Me$) has been established by X-ray diffraction analysis.[21] Magnetic measurements and calculations of the exchange parameters (Table 1) revealed a wide range of the $-2J$ values for the systems under study. For complexes **A**,

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 3, pp. 592—596, March, 2005.

Table 1. Magnetic properties of dinuclear metal chelates **A** and **B**

Complex	Type	R^1	R^2	R^3	X	T /K	μ_{eff}* /μ_B	$-2J$ /cm^{-1}
1	**A**	H	H	Me	O	82	0.75	173.4
						284	1.59	
2	**A**	H	H	CH_2Cl	O	82.2	0.97	134
						288	1.61	
3	**A**	H	H	CCl_3	O	82	1.17	116
						293	1.74	
4	**A**	Bu^t	Bu^t	Me	O	82.2	0.92	143
						285.4	1.61	
5	**A**	Cl	Cl	Me	O	82	1.20	111.8
						284	1.75	
6	**A**	H	NO_2	Me	O	81.9	1.25	96.4
						285.6	1.68	
7	**A**	H	H	CH_2Ph	O	82	1.00	132
						296	1.62	
8	**B**	H	H	Me	O	82.3	0.95	183.8
						286.7	1.53	
9	**B**	Bu^t	Bu^t	Me	O	82.3	0.84	196
						279.4	1.64	
10	**B**	Cl	Cl	Me	O	82.3	1.23	102.8
						286.7	1.62	
11	**B**	H	NO_2	Me	O	82.3	1.07	129.9
						286.7	1.71	
12	**B**	H	H	CH_2Cl	O	82.2	0.81	165
						290.0	1.65	
13	**B**	H	H	CCl_3	O	82	1.21	93.6
						286	1.62	
14	**B**	H	H	CH_2Ph	O	82	1.15	135.8
						293	1.62	
15	**B**	Bu^t	Bu^t	CH_2Cl	O	82	1.05	127
						287	1.65	
16	**B**	Bu^t	Bu^t	CCl_3	O	82	1.17	113.8
						289	1.72	
17	**B**	Bu^t	Bu^t	CH_2Ph	O	84	0.99	147.2
						291	1.60	
18	**B**	Cl	Cl	CH_2Cl	O	82	1.30	79.8
						282	1.64	
19	**B**	Cl	Cl	CCl_3	O	82	1.45	65
						290	1.75	
20	**B**	H	NO_2	CH_2Cl	O	82	1.17	99.8
						283	1.61	
21	**B**	H	NO_2	CCl_3	O	82	1.35	77.1
						285	1.67	
22	**B**	H	H	Me	S	296	—**	—
23	**B**	H	NO_2	Me	S	82	0.42	450
						294	1.13	
24	**B**	I	I	Me	S	82	0.57	372
						294	1.26	

* The magnetic moment μ_{eff} was calculated per copper atom in the dinuclear molecule.

** Diamagnetic.

the exchange parameter was found to depend on the nature of the substituent R^3 in the carboxylate bridge ($-2J$ varies from 173.4 cm^{-1} in the compound containing the acetate group to 116 cm^{-1} in trichloroacetate). This is an unusual fact, because such a strong influence of the peripheral substituent was not observed even in copper dimers, which have a Chinese-lantern structure and contain four bridging carboxylate groups.[4,5] To elucidate the possible causes of this effect, we studied the structure of the "intermediate" member of the acetate—chloroacetate—trichloroacetate series using complex **2** as an example.

Complex **2** (R = CH_2Cl) crystallizes with two methanol molecules, $[Cu_2L(\mu\text{-}CH_2ClCOO)(MeOH)]\cdot(MeOH)$ (L = $C_{17}H_{15}N_2O_3$). In the crystal, one of the methanol molecules is coordinated to the metal atom, whereas the second molecule is linked to the molecule of the complex only by hydrogen bonds. The main structural fragment in the crystal structure is the dinuclear complex (Fig. 1) consisting of two Cu atoms coordinated by the pentadentate bridging ligand L (Cu...Cu, 3.514(1) Å) and the bridging chloro-substituted acetate ligand (Cu—O, 1.924(3) and 1.946(3) Å).

The distorted square-planar coordination about the Cu(1) atom is supplemented by one methanol molecule (Cu(1)—O(6), 2.398(5) Å) to form the square-pyramidal coordination. The coordination environment of the second Cu(2) atom is also a square pyramid due to the involvement of the O atom of the adjacent molecule of the complex (Cu(2)...O(3)($1 - x$, $1 - y$, $-z$), 2.661(3) Å), resulting in the formation of centrosymmetric dimers in the crystal (Fig. 2).

These dimers are, in turn, linked to each other ($1 - x$, $1 - y$, $-z$) by the O(6)—H...O(1) hydrogen bonds ($1 - x$, $1 - y$, $1 - z$) (O...O, 2.793(5) Å; H...O, 2.02 Å; O—H...O, 140°) involving the proton of the methanol molecule (C(20)—O(6)) coordinated to the Cu(1) atom and form H-bonded chains extended along the *c* axis. In the crystal, the second disordered methanol molecule (O atom occupies two equivalent positions, O(1s) and O(2s), with occupancies of ~0.5) is bound to the chlorine and oxygen atoms of one chelate fragment of complex **2** only by the O(1s)...Cl(x, y, z) (3.206 Å) and O(2s)...O(3)($1 - x$, $2 - y$, $-z$) (2.777 Å) hydrogen bonds. The main geometric parameters of the central moiety of **2** are virtually identical to those found for nonsolvated Me-substituted derivative **1** (R = Me)[21] (Table 2). The only difference in the structure of the dinuclear fragments in the methyl and chloromethyl derivatives is that the carbon atom (C(9)) bound to the bridging O(2) atom is randomly disordered. Analysis of the disorder of the C(9) atom showed that the crystal consists of two structural isomers. In one of them (*cis* isomer), the H(9a) atom and the methanol molecule coordinated to the copper atom are located on one side of the plane of the five-membered metallocycle Cu(1)N(1)C(8)C(9a)O(2). In another (*trans*) isomer, the H(9b) atom and the methanol molecule coordinated to the copper atom are located on the opposite sides of the plane of the five-membered metallocycle. The C(9a) atom (occupancy is 0.7) deviates from the Cu(1)Cu(2)O(1)

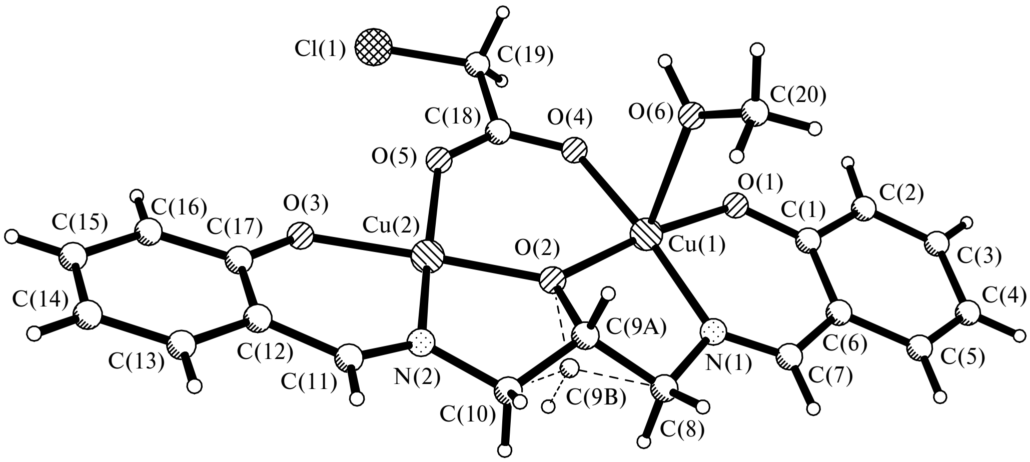


Fig. 1. Structure of the $[Cu_2L(\mu\text{-}CH_2ClCOO)(CH_3OH)]$ complex (**2**) taking into consideration of disorder of the C(9) atom.

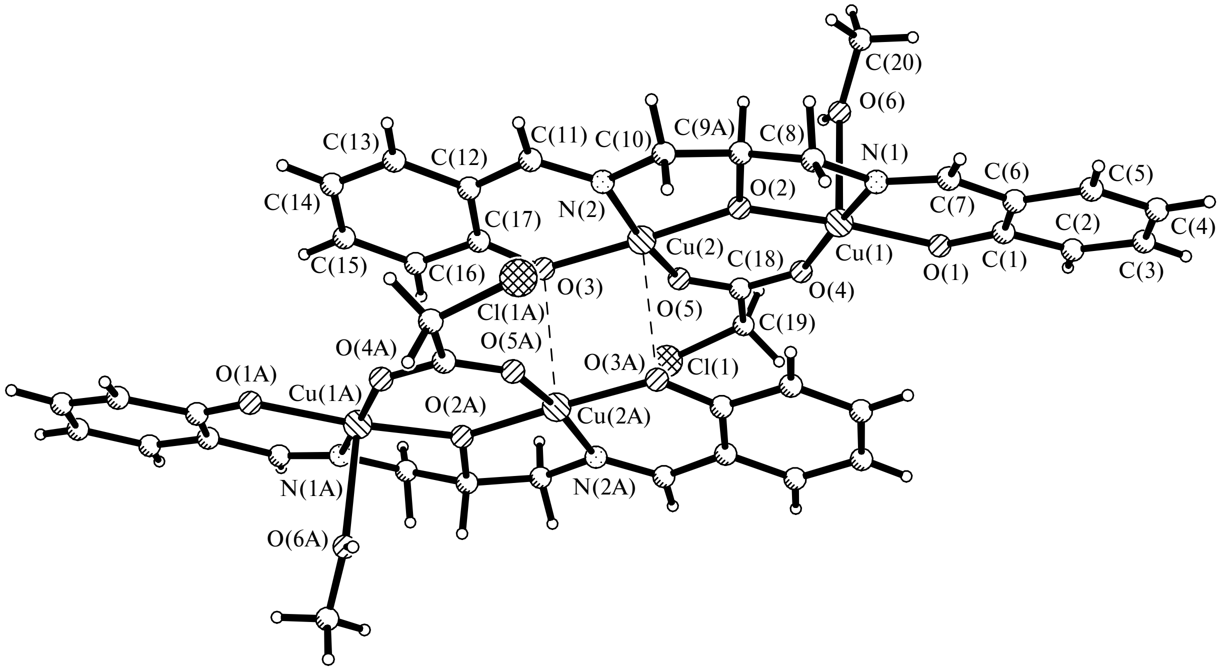


Fig. 2. Centrosymmetric dimer consisting of two molecules **2**.

plane by 0.43 Å toward the coordinated methanol molecule. In another isomer, the C(9b) atom deviates from this plane by 0.32 Å in the opposite direction.

The Cu—O—Cu angle is an important geometric parameter of the similar structures of dinuclear complexes **1** and **2**. Both compounds are characterized by the almost equal values of this angle (132.8(2)° for **1** and 132.7(2)° for **2**). On the one hand, this angle suggests that such compounds are unlikely to possess ferromagnetic exchange interactions, which are generally observed in oxygen-bridged compounds with the M—O—M angle close to 90°.[22—26] On the other hand, a sharp difference in the exchange parameters of compounds **1** and **2** suggests that the exchange makes a considerable contribution through the "carboxylate channel." The latter fact is somewhat unexpected, because it was assumed that the main exchange interactions in known oxo- and hydroxy-bridged polynuclear carboxylates make a contribution through the bridging oxygen atoms.[5,22]

However, the "oxygen channel" for compounds **A** also plays a considerable role. For example, the exchange parameter $-2J$ depends substantially on the peripheral perturbations in the salicylaldehyde fragment of the ligands, and the insertion of electron-withdrawing groups leads to a noticeable decrease in $-2J$ (see Table 2).

Such dependences (decrease in the exchange parameter upon the insertion of electron-withdrawing substituents into the carboxylate group and in the presence of

Table 2. Bond lengths (*d*) and bond angles (ω) in the exchange fragment of compounds **1** (R = Me) and **2** (R = CH_2Cl)

Parameter	**1**	**2**
Bond	*d*/Å	
Cu(1)—O(2)	1.910(2)	1.934(3)
Cu(2)—O(2)	1.912(2)	1.905(3)
Cu(1)—O(4)	1.929(2)	1.953(4)
Cu(2)—O(5)	1.944(2)	1.946(3)
O(4)—C(18)	1.248(4)	1.241(7)
O(5)—C(18)	1.237(4)	1.253(6)
Angle	ω/deg	
Cu(1)—O(2)—Cu(1)	132.8(2)	132.7(2)
O(2)—Cu(1)—O(4)	94.3(1)	94.6(2)
Cu(1)—O(4)—C(18)	135.9(2)	133.7(3)
O(2)—Cu(2)—O(5)	94.3(1)	94.3(2)
Cu(2)—O(5)—C(18)	135.4(2)	134.7(3)
O(5)—C(18)—O(4)	127.1(3)	129.3(5)

electron-withdrawing groups in the ligands) are also observed for complexes **B** (see Table 1). The replacement of the bridging oxygen atom by the sulfur atom leads to a sharp increase in the spin-spin exchange. In the case of complex **22**, this replacement gives rise to diamagnetism ($-2J \gg 1000$ cm^{-1}). This effect is, presumably, attributable to an increase in the degree of covalency of the Cu—X bonds (X = S) compared to that in oxygen analogs and, as a consequence, to an increase in electron density delocalization in the Cu—X—Cu fragment, resulting in enhancement of antiferromagnetic exchange interactions.[4,22,26] However, compounds **B** are less stable and are gradually transformed even in the solid state, which is reflected in the magnetic behavior of the complexes (for these complexes, the magnetic moments μ_{eff} are in the range of 1.75—1.80 μ_B and they are virtually independent of the temperature). To explain this unusual transformation, it was necessary to perform structural investigations. We studied compound **16** ($R^1 = R^2 = Bu^t$, $R^3 = CCl_3$) by X-ray diffraction. Upon storage in air for one month, crystals were found to contain molecules of the complex whose formal composition corresponds to molecule **B**. In addition, the crystals contain water solvate molecules. It should be noted that the structure of complex **16a** obtained after storage in air sharply differs from the structure of the starting product (Fig. 3).

The $[Cu_2L^2(Cl_3CCO)(CH_3OH)]$ complex ($L^2 = C_{32}H_{42}N_4O_3$) (**16a**) crystallizes as the monohydrate **16a**$\cdot H_2O$. In the crystal, the water molecule is linked to the N(2) atom of complex **16a** through the N(2)—H...O(1w) hydrogen bond (N...O, 2.856(7) Å; H...O, 1.98 Å; N—H...O, 174.3°). Two copper atoms are linked to each other by the hexadentate bridging ligand L^2. The Cu^{II} atoms are in the square-planar ligand environment. One copper atom is additionally coordinated by the monodentate carboxylate group (Cu(1)—O(3), 1.964(8) Å), and another copper atom is coordinated by the methanol molecule (Cu(2)—O(5), 1.963(8) Å). However, the complex contains no carboxylate or oxygen bridges, and the bis-chelate fragment of the L^2 ligand serves as a bridge. Presumably, this is attributable to adsorption of water molecules by the crystal of the starting complex **16**, resulting in the formation of new hydrogen bonds with the ligands and the Cu—O(bridge) bond cleavage followed by the rearrangement of the complex. This

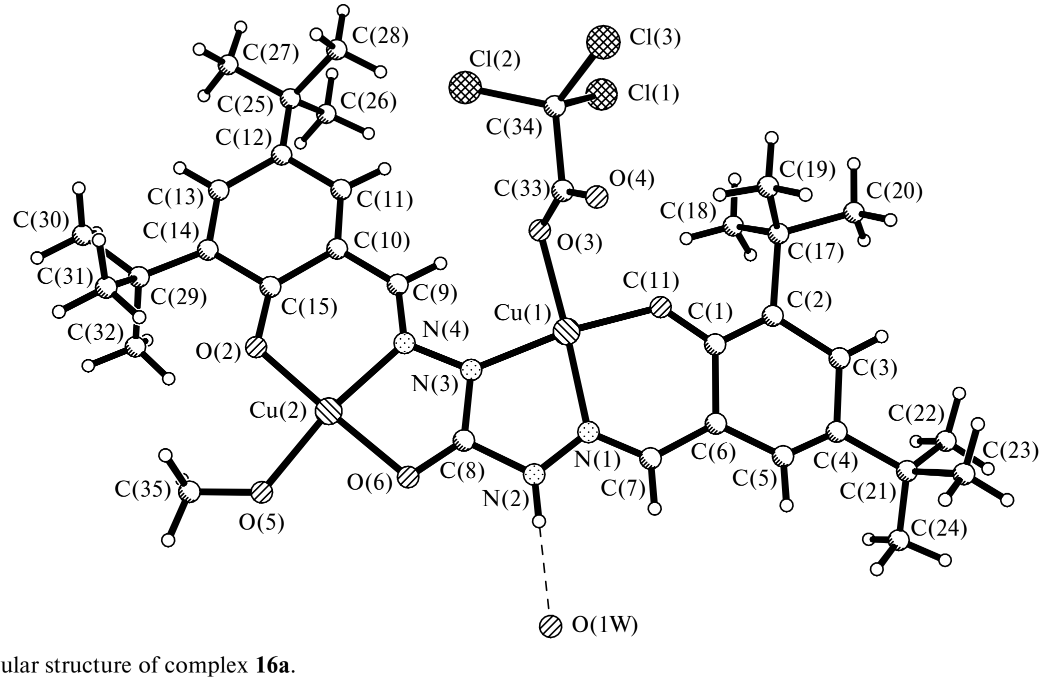


Fig. 3. Molecular structure of complex **16a**.

gives rise to a radically new structure, in which exchange interactions have different mechanisms. This transformation of the dinuclear magnetic structure in the crystal was observed for the first time and can serve as a warning for chemists concerned with molecular magnetism.

Experimental

The synthesis and physicochemical study of the ligands and complexes by elemental analysis and IR and ^{1}H NMR spectroscopy have been described earlier.[20,21]

The magnetic susceptibility was determined by the relative Faraday method in the temperature range 78—300 K on an instrument designed at the Chair of Physical and Colloidal Chemistry of the Rostov State University with the use of $Hg[Co(CNS)_4]$ as the calibration standard. The exchange interaction parameters were calculated from the temperature dependence of the magnetic susceptibility in terms of the Heisenberg—Dirac—Van Vleck (HDVV) dinuclear model with the use of the modified Bleaney—Bowers equation[25] using the program, which minimizes the rms error r

$$r = \left[\frac{1}{n}\sum_{1}^{n}(\chi_i - \chi_i^0)\chi_i^{-2}\right]^{\frac{1}{2}}.$$

Here χ_i and $\chi_i{}^0$ are the experimental and theoretical molar magnetic susceptibilities, respectively, at the ith point, and n is the number of the points.

X-ray diffraction study of complex 2. Crystals of compound **2** were grown as the solvate with methanol of composition $\mathbf{2}\cdot CH_3OH$ by slow evaporation of a solution in methanol at room temperature. The crystals of $\mathbf{2}\cdot CH_3OH$ are triclinic, a = 8.261(5) Å, b = 10.792(5) Å, c = 13.024(6) Å, α = 80.87(4)°, β = 88.09(4)°, γ = 75.77(4)°, Z = 2, d_{calc} = 1.727 g cm^{-3}, μ = 2.081 mm^{-1}, V = 1111(1) Å^3, space group $P\bar{1}$. The structure was solved by direct methods and refined anisotropically by the full-matrix least-squares method using the SHELXS97 [27] and SHELXL97 [28] program packages (positions of the H atoms were refined using a riding model) to R_1 = 0.070 (wR_2 = 0.217) for 3403 reflections with $I > 2\sigma(I)$; GOOF was 1.001. The X-ray diffraction data were collected on an automated Enraf-Nonius CAD-4 diffractometer (λ(Mo-Kα), graphite monochromator, ω scanning technique, $2\theta_{max}$ = 54°, 5883 independent reflections). A semiempirical absorption correction was applied.[29]

X-ray diffraction study of complex 16a. Crystals of compound **16a** were grown as the monohydrate of composition $\mathbf{16a}\cdot H_2O$. The crystals of $\mathbf{16a}\cdot H_2O$ are monoclinic, at 120 K a = 13.532(5) Å, b = 27.827(9) Å, c = 11.708(4) Å, β = 114.83(2)°, Z = 4, d_{calc} = 1.425 g cm^{-3}, μ = 1.312 mm^{-1}, V = 4001(2) Å^3, space group $P2_1/c$. The X-ray diffraction data were collected on a Bruker AXS SMART 1000 diffractometer equipped with a CCD detector (λ(Mo-Kα), graphite monochromator, 120 K, ω scanning technique, the scan step was 0.3°, the counting time was 30 s per frame, $2\theta_{max}$ = 50.2°) using a standard procedure.[29] A total of 15957 reflections were measured, of which 6259 reflections were independent. A semiempirical absorption correction was applied.[29,30] The structure was solved by direct methods using the SHELXS97 program package[27] and refined anisotropically by the full-matrix least-squares method using the SHELXL97 program package[28] (positions of the H atoms were refined using a riding model) to R_1 = 0.088, $R_w(F_o{}^2)$ = 0.221 for 2372 reflections with $I > 2\sigma(I)$; GOOF was 1.012.

This study was financially supported by the Russian Academy of Sciences (Program of Basic Research of the Presidium of the Russian Academy of Sciences "Directed Synthesis of Compounds with Desired Properties and Design of Functional Materials on Their Basis," the Section "Molecular Design of Magnetically Active Compounds and Materials," Project TsB-1.6).

References

1. V. A. Kogan, V. V. Zelentsov, O. A. Osipov, and A. S. Burlov, *Usp. Khim.*, 1979, **48**, 1208 [*Russ. Chem. Rev.*, 1979, **48** (Engl. Transl.)].
2. V. A. Kogan and V. V. Lukov, *Koord. Khim.,* 1997, **23**, 13 [*Russ. J. Coord. Chem.*, 1997, **23** (Engl. Transl.)].
3. V. A. Kogan and V. V. Lukov, *Koord. Khim.,* 2004, **30**, 219 [*Russ. J. Coord. Chem.*, 2004, **30** (Engl. Transl.)].
4. V. T. Kalinnikov, Yu. V. Rakitin, and V. M. Novotortsev, *Usp. Khim.*, 2003, **72**, 1123 [*Russ. Chem. Rev.*, 2003, **72** (Engl. Transl.)].
5. Yu. V. Rakitin and V. T. Kalinnikov, *Sovremennaya magnetokhimiya* [*Modern Magnetochemistry*], Nauka, St.-Petersburg, 1994, 272 pp. (in Russian).
6. M. Verdaguer, *Polyhedron*, 2001, **70**, 1115.
7. E. Ruiz, P. Alemany, S. Alvarez, and J. Cano, *Inorg. Chem.*, 1997, **36**, 3683.
8. Sh. Emori, G. Hirofumi, and M. Hiroshi, *Bull. Chem. Soc. Jpn*, 1996, 1921.
9. R. Ando, M. Nagai, T. Yagyu, and M. Maeda, *Inorg. Chim. Acta*, 2003, **351**, 107.
10. E. Ruiz, P. Alemany, and S. Alvarez, *J. Am. Chem. Soc.*, 1997, **119**, 1297.
11. A. Asokan, B. Varghese, and P. T. Monoharan, *Inorg. Chem.*, 1999, **38**, 4393.
12. S. Mukherjee, T. Weyhermiiller, and E. Bothe, *Eur. J. Inorg. Chem.*, 2003, 863.
13. Yu. P. Tupolova, V. V. Lukov, V. A. Kogan, L. D. Popov, V. V. Tkachev, and A. N. Chekhlov, *Zh. Neorg. Khim.,* 2003, **48**, 1780 [*Russ. J. Inorg. Chem.*, 2003, **48** (Engl. Transl.)].
14. E. V. Dontsova, V. V. Lukov, V. A. Kogan, L. D. Popov, V. V. Tkachev, G. V. Shilov, and D. D. Makitova, *Zh. Neorg. Khim.,* 2003, **48**, 2063 [*Russ. J. Inorg. Chem.*, 2003, **48** (Engl. Transl.)].
15. V. A. Kogan, V. V. Lukov, and S. I. Levchenkov, *Mendeleev Commun.*,1998, **4**, 145.
16. Y. Nishida and S. Kida, *Inorg. Chem.*, 1988, **27**, 447.
17. Y. Mikariya, T. Sasaki, and A. Anjiki, *Bull. Chem. Soc. Jpn*, 1992, **62**, 334.
18. D. S. Dash, A. K. Panda, and A. Mahapatra, *J. Indian Chem. Soc.*, 2002, **79**, 642.
19. 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].

20. V. A. Kogan, V. V. Lukov, and V. M. Novotortsev, *Koord. Khim.,* 2005, **31**, No. 5 [*Russ. J. Coord. Chem.*, 2005, **31** (Engl. Transl.)].
21. Yu. P. Tupolova, V. V. Lukov, V. A. Kogan, L. D. Popov, I. E. Gevorkyan, V. V. Tkachev, G. V. Shilov, and D. D. Makitova, *Zh. Neorg. Khim.,* 2004, **49**, 1993 [*Russ. J. Inorg. Chem.*, 2004, **49** (Engl. Transl.)].
22. I. B. Bersuker, *Electronic Structure and Properties of Transition Metal Compounds: Introduction to the Theory*, Wiley, New York, 1996.
23. A. J. Costa-Filho, O. R. Nascimento, L. Ghiveder, and R. Calvo, *J. Phys. Chem. B*, 2001, **105**, 5039.
24. C. Ruiz-Perez, M. Hernandez-Molina, P. Lorenzo-Luis, F. Lloret, J. Cano, and M. Julve, *Inorg. Chem.*, 2000, **39**, 3845.
25. B. Bleaney and K. O. Bowers, *Proc. Roy. Soc. London, Ser. A*, 1952, **214**, 451.
26. Yu. V. Rakitin, *Magnitnye svoistva poliyadernykh kompleksov perekhodnykh metallov* [*Magnetic Properties of Polynuclear Transition Metal Complexes*], in *Itogi nauki i tekhniki. Stroenie molekul i khimicheskaya svyaz* [*Advances in Science and Technology, Ser. Molecular Structures and Chemical Bonding*], VINITI, Moscow, 1986, p. 95.
27. G. M. Sheldrick, *SHELXS97. Program for the Solution of Crystal Structures*, University of Göttingen, Germany, 1997.
28. G. M. Sheldrick, *SHELXL97. Program for the Refinement of Crystal Structures*, University of Göttingen, Germany, 1997.
29. *SMART (Control) and SAINT (Integration) Software, Version 5.0*, Bruker AXS Inc., Madison, WI, 1997.
30. A. C. T. North, D. C. Phillips, and F. S. Mattews, *Acta Crystallogr., Sect. A*, 1968, **24**, 351; G. M. Sheldrick, *SADABS, Program for Scaling and Correction of Area Detector Data*, University of Göttingen, 1997 (based on the method of R. H. Blessing, *Acta Crystallogr., Sect. A*, 1995, **51**, 33).

Received October 5, 2004;
in revised form February 21, 2005