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Complexes of Cu^{II}, Ni^{II}, and Co^{II} with 2-cyano-2-(1-oxyl-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazol-2-yl)-1-R-ethylenolates

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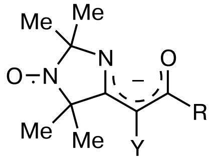
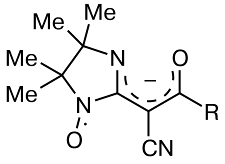
Copper(II), nickel(II), and cobalt(II) complexes with deprotonated enaminoketone derivatives of 2-imidazoline nitroxide were synthesized. Their crystal structures were established by X-ray diffraction analysis, and their magnetic properties were investigated. All complexes exhibit strong (40—110 cm^{-1}) intramolecular ferromagnetic exchange interactions.

Key words: nitroxide radicals, copper, nickel, cobalt, X-ray diffraction analysis, exchange interactions.

Earlier, a series of molecular magnetics have been prepared based on coordination compounds of paramagnetic transition metal ions with deprotonated enaminoketone derivatives of 3-imidazoline nitroxide (L').[1] Magnetic ordering in these systems is favored by the occurrence of ferromagnetic intramolecular exchange interactions between unpaired electrons of the paramagnetic centers in the complexes with 3-imidazoline nitroxides, which is confirmed by both experimental studies and quantum-chemical calculations.[2—6] However, the energy of these interactions is at most 15—25 cm^{-1} due to breaking of the conjugation chain in the intramolecular $M...N\dot{-}O$ exchange channel (M is metal). This is the reason for unsuccessful attempts to use complexes with 3-imidazoline nitroxides for the preparation of magnetics, which undergo the magnetic phase transition to a magnetically ordered state at a temperature above 10—20 K.[1] In continuation of these studies, it seemed reasonable to develop a procedure for the synthesis and perform systematic investigation of coordination compounds with deprotonated enaminoketone derivatives of 2-imidazoline (L^R), whose structures are favorable for the occurrence of strong (high-energy) intramolecular exchange interactions. Earlier,[7] we have reported the synthesis and spectroscopic characteristics of HL^R compounds containing the nitrile substituent in the side chain. In the present study, we describe the synthesis, structures, and magnetic properties of the heterospin Cu^{II}, Ni^{II}, and Co^{II} complexes with L^R (**1—11**). The compositions and characteristics of these complexes are given in the Experimental section.



L'



L^R

R = Ph, CF_3

Results and Discussion

In the absence of reducing agents and moisture, nitroxides HL^R (R = CF_3 or Ph) are rather stable in solution, from which they can be isolated as individual solids. However, HL^R are gradually transformed into the corresponding diamagnetic derivatives in the course of storage or purification. Hence, HL^{Ph} derived from the corresponding hydroxylamine[7] was immediately neutralized with KOH and introduced into the reaction with metal ions, after which the reaction mixture was rapidly concentrated to dryness to remove MeOH (like other alcohols, it can gradually reduces nitroxide). Subsequent operations were carried out in MeCN, which does not oxidize L^R. In the synthesis of complexes with L^{CF_3}, stable

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potassium salt KL^{CF_3} proved to be the reagent of choice. The mixed-ligand $CuL^R(hfac)$ complexes were prepared by the reaction

$$CuL^R{}_2 + Cu(hfac)_2 \rightarrow 2\ CuL^R(hfac),$$

hfac is hexafluoroacetylacetonate.

Apparently, bis-chelates $ML^{CF_3}{}_2$ (M = Ni or Co) have polymer structures, because they are soluble only in strongly coordinating organic solvents (DMF or DMSO) or mixtures containing these solvents. We expected that the introduction of additional ligands, such as 1,10-phenanthroline (Phen) or 2,2´-bipyridyl (bpy), into the reaction system would hinder the polymer formation and allow us to isolate mixed-ligand complexes in the crystalline state. Actually, we succeeded in preparing single crystals of complexes **1**—**5** suitable for X-ray diffraction analysis. Besides, we synthesized mixed-ligand complexes **6** and **7** with DMSO. All these compounds have molecular structures.

A distorted octahedral environment about the metal atoms is formed by the O and N atoms of two deprotonated bidentate L^R ligands and two N atoms (in the case of bpy and Phen ligands) or two O atoms (in the case of DMSO ligands) (Fig. 1). The M—O and M—N bond lengths (Table 1) are typical of these metal ions in an octahedral environment.[8] The nitrile and nitroxide groups of the L^R ligand are not involved in coordination but form weak hydrogen bonds with solvent molecules if the latter are present in the crystal structure (complexes **6** and **7**). The mixed-ligand Ni^{II} and Co^{II} complexes with L^{Ph} and bpy or Phen are kinetically much less stable than the complexes with L^{CF_3}. That is why we managed to grow single crystals and investigate the structure of only one compound of this type, *viz.*, complex **5**.

The bis-chelate Cu^{II} complexes with deprotonated enaminoketones of the 2-imidazoline series are substantially better soluble than the Ni^{II} and Co^{II} complexes. For Cu^{II}, we prepared compounds with composition $CuL^R{}_2$. The $CuL^{Ph}{}_2$ complex (**8**) has a molecular structure. The coordination polyhedron of the Cu atom is a distorted tetrahedron (Fig. 2, Table 2) formed by the electron-donating O and N atoms of the deprotonated enaminoketone fragments L^R. The nitrile groups of the L^{Ph} ligand are not involved in coordination.

Upon the replacement of Ph with CF_3, the acceptor properties of the central metal atom become more pronounced, due to which the coordination number of the Cu atom in $CuL^{CF_3}{}_2 \cdot MeCN$ (**9**) increases to six. In complex **9**, the central metal atom in a square environment is additionally coordinated by the N atom of the nitrile group of the adjacent $CuL^{CF_3}{}_2$ fragment to form a polymer chain (Fig. 3, *a*). The N atom of the MeCN molecule occupies the sixth coordination site at the Cu atom. It should be noted that the Cu—N_{MeCN} distance in **9** is large (2.774(14) Å). Apparently, this weak binding of the MeCN molecules is responsible for gradual decomposition of crystals of **9** on storage. Mixed-ligand complex **10** with

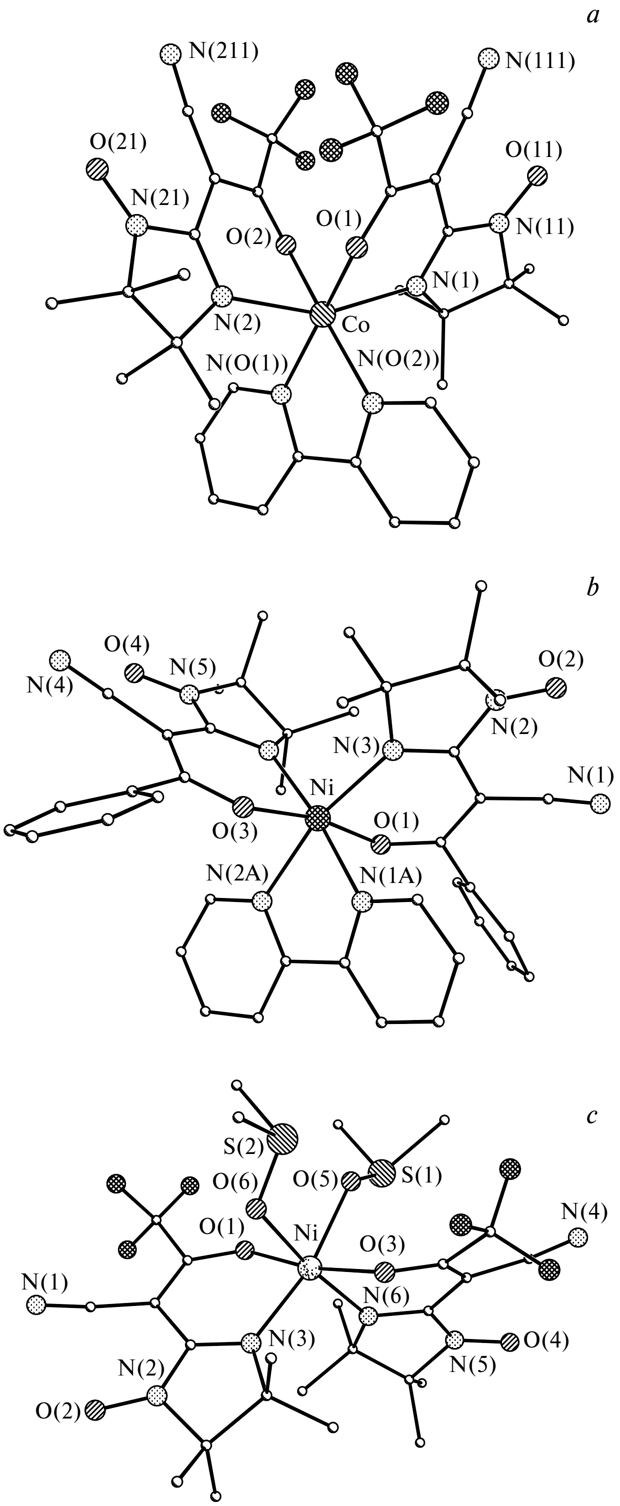

Fig. 1. Molecular structures of mixed-ligand complexes **4** (*a*), **5** (*b*), and **6** (*c*).

Table 1. Selected bond length (*d*) and bond angles (ω) in complexes **1**, **2**, and **4**—**7** (M = Ni^{II}, Co^{II})

Parameter	NiL$^{CF_3}{}_2$(Phen) **(1)**	CoL$^{CF_3}{}_2$(Phen) **(2)**	CoL$^{CF_3}{}_2$(bpy) **(4)**	NiL$^{Ph}{}_2$(bpy)· ·MeCN **(5)**	NiL$^{CF_3}{}_2$(DMSO)$_2$· ·2DMSO·0.25H$_2$O **(6)**	CoL$^{CF_3}{}_2$(DMSO)$_2$· ·2DMSO·0.25H$_2$O **(7)**
Bond			*d*/Å			
M—O$_L$	2.030(4), 2.031(5)	2.0678(11), 2.0647(11)	2.074(2), 2.066(2)	2.015(3), 2.002(3)	1.997(7), 2.044(6)	2.062(6), 2.053(6)
M—O	—	—	—	—	2.107(6), 2.136(6)	2.131(6), 2.184(6)
M—N$_L$	2.148(5), 2.139(5)	2.1815(12), 2.1985(13)	2.186(3), 2.195(3)	2.126(4), 2.098(4)	2.080(8), 2.081(7)	2.126(8), 2.125(7)
M—N	2.060(5), 2.081(6)	2.1271(12), 2.1527(13)	2.132(3), 2.134(3)	2.120(4), 2.149(4)	—	—
N$\overset{\cdot}{-}$O	1.257(6), 1.254(7)	1.265(2), 1.263(2)	1.252(4), 1.263(4)	1.260(5), 1.269(5)	1.282(10), 1.265(9)	1.259(9), 1.269(8)
Angle			ω/deg			
O$_L$—M—N$_L$	83.1(2), 84.5(2)	82.97(4), 81.20(5)	83.08(10), 81.62(9)	88.04(13), 88.03(13)	87.7(3), 87.4(3)	85.7(3), 85.1(3)
O—M—O	—	—	—	—	84.7(3)	84.0(2)
N—M—N	79.8(2)	77.38(5)	76.74(11)	76.45(15)	—	—
O$_L$—M—O$_L$	101.2(2)	102.71(5)	98.8(1)	169.8(1)	171.2(3)	172.6(3)

stoichiometry CuL^{CF_3}(hfac), like complex **9**, has a chain-polymer structure (Fig. 3, *b*) due to coordination of the Cu atom by the nitrile group of the adjacent CuL^{CF_3}(hfac) fragment.

In CuL^{Ph}(hfac) (**11**), the deprotonated enaminoketone fragment also serves as a bridge. However, this crystal structure consists of the tetranuclear [CuL^{Ph}(hfac)]$_4$ molecules rather than of chains (Fig. 4). Presumably, the formation of the tetramers is favored by stacking interactions between the Ph rings (distance between the parallel Ph rings is ~3.6 Å).

In complexes **10** and **11**, the coordination environment of the Cu atoms is a square pyramid, whose bases are formed by the electron-donating O and N atoms of the deprotonated enaminoketone group L^R and the O$_{hfac}$ atoms, and the axial position is occupied by the N atom of the nitrile group of the adjacent CuL^R(hfac) fragment. The axial Cu—N$_{CN}$ distances are noticeably longer (2.241(4)—2.288(9) Å). The Cu—O and Cu—N distances in the base of the pyramid are in the ranges of 1.897(6)—1.937(6) and 1.963(6)—1.982(8) Å, respectively. The C≡N—Cu angles in the complexes with

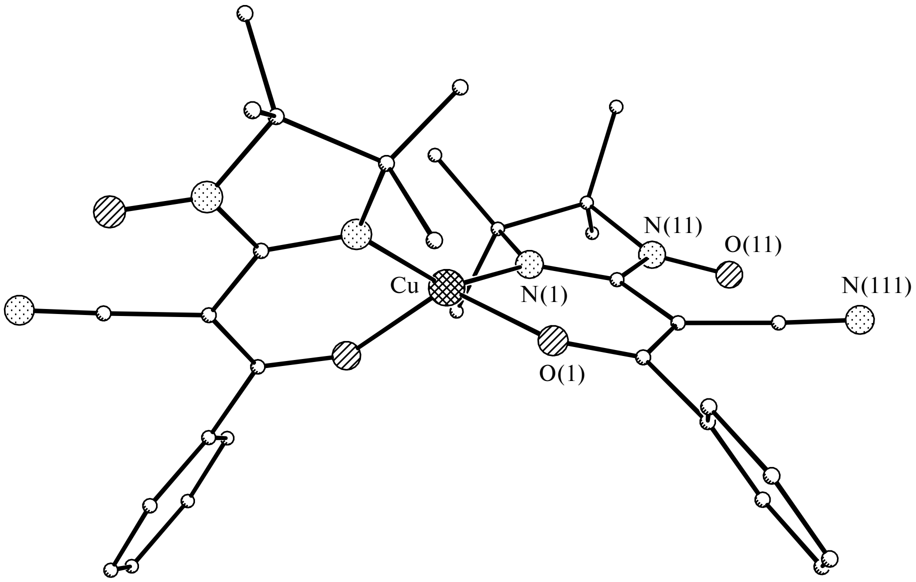

Fig. 2. Molecular structure of compound **8**.

Table 2. Selected bond length (*d*) and bond angles (ω) in Cu^{II} complexes **8**—**11**

Parameter	CuL^{Ph}$_2$ (**8**)	CuL^{CF_3}$_2$ · MeCN (**9**)	CuL^{CF_3}(hfac) (**10**)	[CuL^{Ph}(hfac)]$_4$ (**11**)
Bond			*d*/Å	
Cu—O$_L$	1.897(5)	1.963(6), 1.953(7)	1.929(6), 1.937(6), 1.897(6)	1.919(3)
Cu—N$_L$	1.937(5)	2.024(6), 2.033(6)	1.982(8), 1.966(8), 1.963(9)	1.967(4)
Cu—N$_{CN}$	—	2.299(9), 2.774(14)	2.284(9), 2.266(11), 2.288(9)	2.241(4)
Cu—O$_{hfac}$	—	—	1.952(6), 1.999(7), 1.949(8), 1.962(6), 1.962(7), 1.881(8)	1.942(3), 1.986(3)
N$\overset{\cdot}{-}$O	1.264(10)	1.269(10), 1.264(10)	1.26(1), 1.23(1), 1.25(1)	1.239(6)
Angle			ω/deg	
O$_L$—Cu—N$_L$	92.6(2)	88.50(1), 87.88(1)	91.4(3), 91.7(3), 91.6(3)	91.2(1)
O—Cu—O	—	—	88.3(3), 89.0(3)	87.9(1)
N—Cu—N	—	178.0(4)	88.7(3)	—
C≡N—Cu	—	144.2(9), 139.8(13)*	154.0(9), 165.1(10), 160.7(9)	155.3(5)

* For MeCN.

the coordinated nitrile group vary from 139.76(1) to 165.13(2)°.

In most of the compounds under study, the imidazoline ring is nonplanar and adopts an envelope conformation. The exception is the [CuL^{Ph}(hfac)]$_4$ complex in which the paramagnetic ligand (except for the Ph ring and the Me groups) is virtually planar (within 0.08 Å). The average deviation of the atoms of the imidazoline ring from the plane passing through the atoms of the heterocycle is 0.002 Å. An analogous planar structure of the imidazoline ring has been observed earlier in 2-cyano-4,4,5,5-tetramethyl-2-imidazoline-1-oxyl 3-oxide[9,10] and the Cu(hfac)$_2$ complex with pyrazole-substituted 2-imidazoline nitronyl nitroxide.[11] However, the long axis of the anisotropic displacement ellipsoid of the C(4) atom in the [CuL^{Ph}(hfac)]$_4$ complex is virtually perpendicular

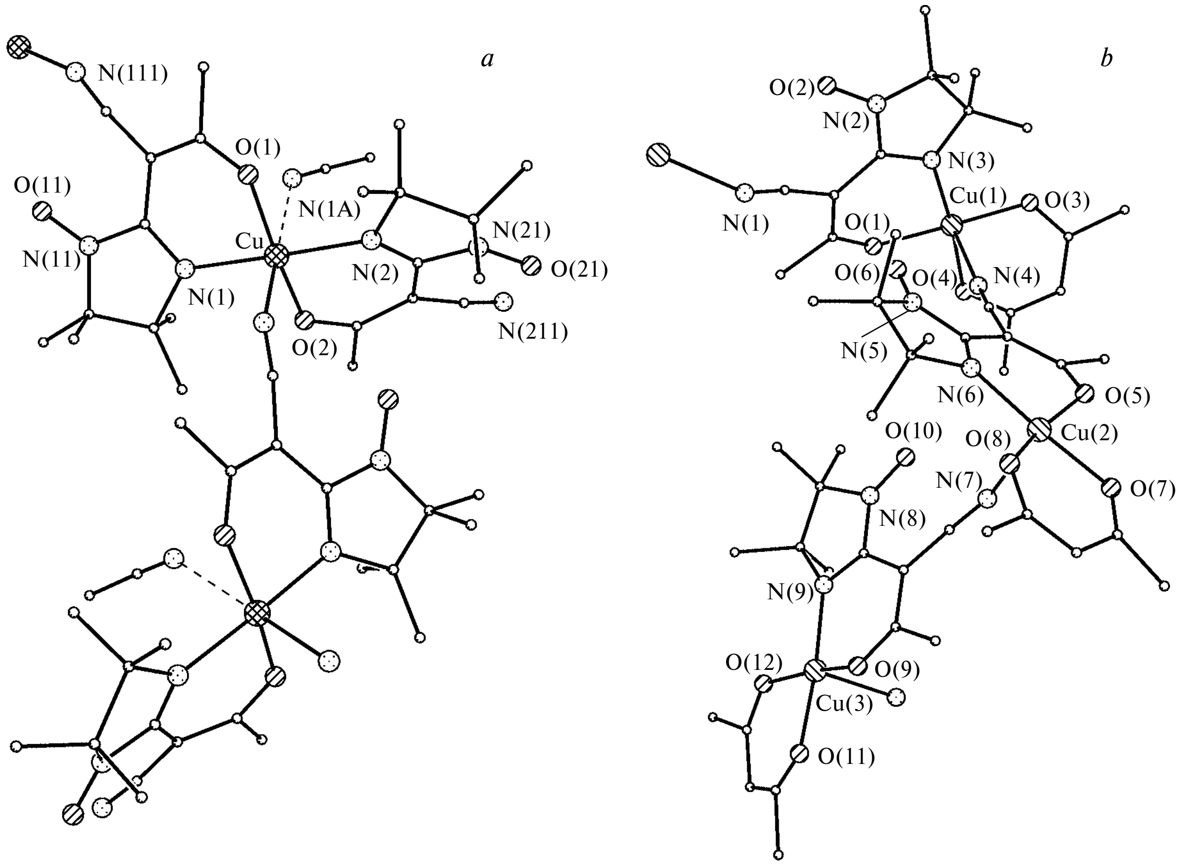

Fig. 3. Polymer chains in the structures of **9** (*a*) and **10** (*b*).

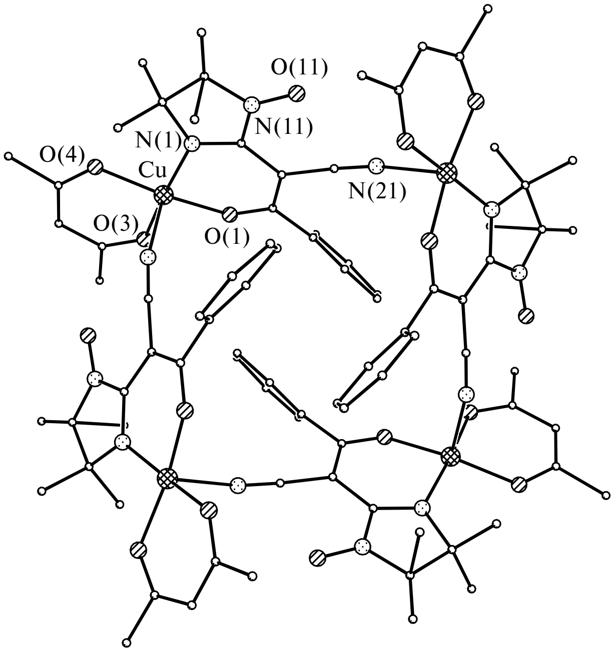

Fig. 4. Molecular structure of compound **11**.

to the plane of the heterocycle, which indicates that the observed planar structure of the heterocycle is actually a superposition of two envelope conformations with the C(4) atoms locating above and below the plane of the ring.

The most interesting result was obtained in the study of complexes **9**—**11** with the coordinated nitrile group. Analysis of the geometric parameters of these compounds demonstrated that the nitroxide group is not involved in coordination to the metal ion due to competitive coordination of the CN group and the resulting steric hindrance. This can be accounted for by the fact that the nitrile and nitroxide groups are virtually in a single plane. Hence, polymerization through coordination of the >N$\overset{\cdot}{-}$O group in the presence of the nitrile substituent (which was observed in complexes with deprotonated enaminoketones of 3-imidazoline[12,13]) giving rise to high-dimensionality heterospin structures is very hindered in complexes with 2-imidazoline analogs.

Magnetic properties. The temperature dependences of the effective magnetic moment (μ_{eff}) for compounds **1**—**11** are shown in Fig. 5. For the Cu^{II}, Ni^{II}, and Co^{II} complexes with organic radicals, the dependences $\mu_{eff}(T)$ are virtually identical in character. As the temperature decreases, μ_{eff} increases (see Fig. 5, *a*—*e*), which is indicative of the dominant role of ferromagnetic exchange interactions between the spins of the metal atom and the radical in the bis-chelate fragments. Hence, at room temperature, μ_{eff} for all complexes are larger than the limiting value for noninteracting spins. A decrease in μ_{eff} at low temperatures is caused by intermolecular antiferromagnetic exchange interactions. The exception is complex **6** for which μ_{eff} increases at helium temperatures, which is indicative of the occurrence of ferromagnetic intermolecular interactions.

The structural data showed that intramolecular exchange interactions between unpaired electrons through the shortest M—N=C—N$\overset{\cdot}{-}$O channel play the major role in complexes **1**—**11**. The dominant role of ferromagnetic exchange interactions between spins in molecules **1**—**11** implies that the main mechanism responsible for exchange involves the transfer of the spin density from the d electrons of the metal atoms in the M—N=C—N$\overset{\cdot}{-}$O channel through the system of the σ orbitals to the N$\overset{\cdot}{-}$O group, whose unpaired electron is located on the orthogonal π* orbital.[2,14] In complexes **9**—**11**, there is also the Cu...N$\overset{\cdot}{-}$O exchange interaction through the nitrile group (in addition to the above-described exchange channel). However, it was demonstrated[11,12] that the efficiency of exchange interactions through the nitrile group at the α position of the side chain of the ligand is negligibly small compared to intramolecular exchange interactions. For this reason, theoretical analysis of the magnetic properties of the complexes was carried out within the framework of isolated exchange clusters including weak intercluster interactions.[15] The dependences $\mu_{eff}(T)$ were calculated using the isotropic exchange spin-Hamiltonian $\hat{H} = -2J\hat{S}_i\hat{S}_j$ ($\hat{S}_i$ and $\hat{S}_j$ are the spin operators). The optimum parameters of the effective g factor of metal, the energies of exchange interaction in the exchange cluster (J), and the energies of intermolecular interaction (nJ') are given in Table 3. The theoretical curves are shown by solid lines in Fig. 5, *a*—*e*.

Therefore, the energy of intramolecular exchange interactions substantially increases (by a factor of 5—10) on going from metal complexes with deprotonated enaminoketone derivatives of 3-imidazoline nitroxide to metal complexes with isomeric derivatives of 2-imidazoline nitroxide. However, we succeeded in preparing kineti-

Table 3. Optimum parameters of the spin-Hamiltonian for complexes **1**, **3**, **5**, **6**, and **8**—**11**

Compound	g	J/cm^{-1}	nJ'/cm^{-1}
NiL$^{CF_3}{}_2$(Phen) (**1**)	2.17±0.04	49±5	−0.16±0.02
NiL$^{CF_3}{}_2$(bpy) (**3**)	2.2±0.1	37±5	−0.33±0.03
NiL$^{Ph}{}_2$(bpy)·MeCN (**5**)	2.2±0.1	60±1	−2.5±0.5
NiL$^{CF_3}{}_2$(DMSO)$_2$· ·2DMSO·0.25H$_2$O (**6**)	2.0±0.2	50±2	0.07±0.01
CuL$^{Ph}{}_2$ (**8**)	2.0±0.2	43±2	−2.4±0.2
CuL$^{CF_3}{}_2$·MeCN (**9**)	2.1±0.1	72±3	−0.8±0.1
CuL^{CF_3}(hfac) (**10**)	2.1±0.1	110±30	−4±1
[CuL^{Ph}(hfac)]$_4$ (**11**)	2.08±0.03	45.9±0.7	−0.06±0.02

Note. g is the effective g factor of metal, J is the energy of exchange interactions in the exchange cluster, nJ' is the energy of intermolecular interactions of the complexes.

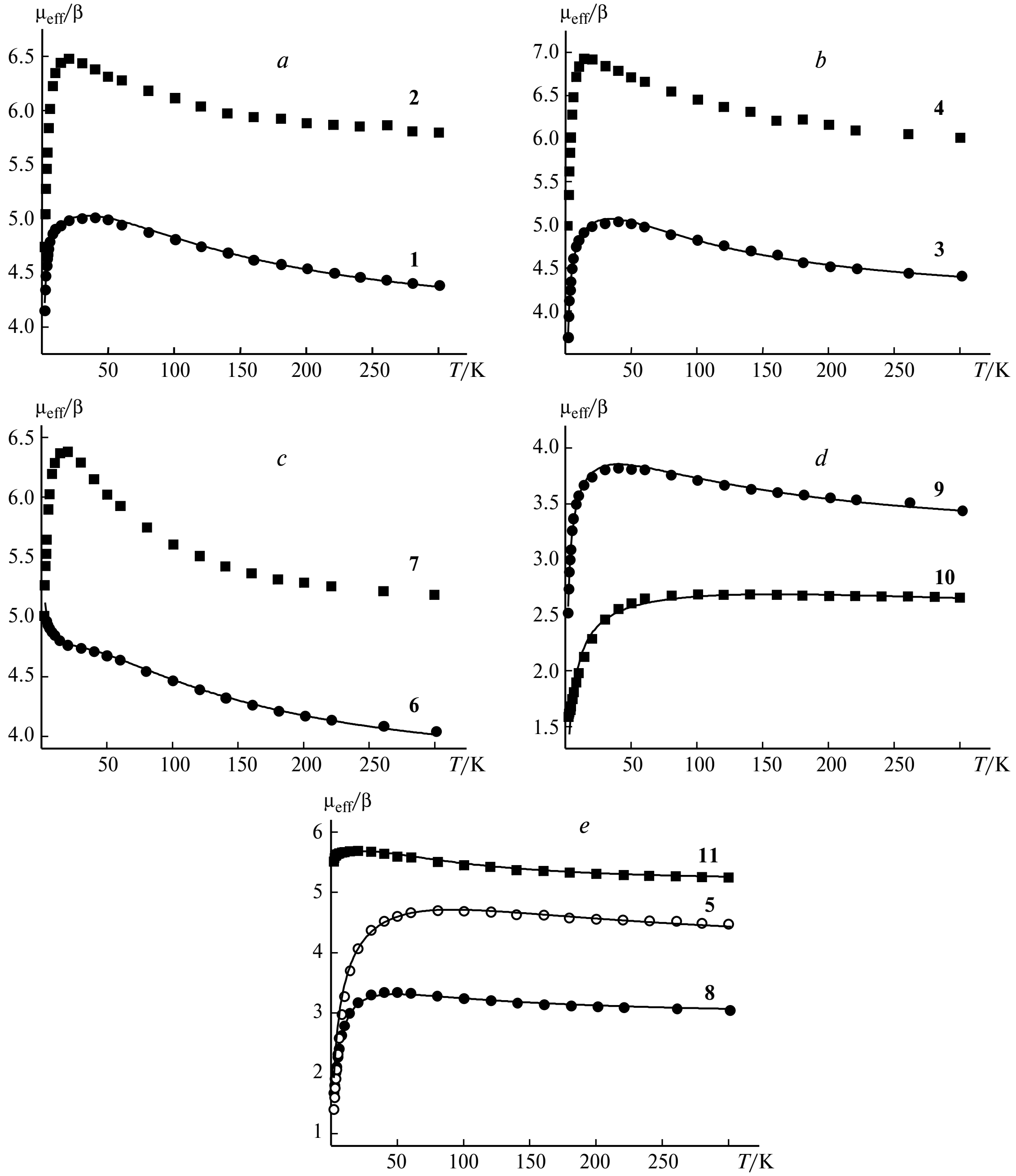

Fig. 5. Temperature dependences of the effective magnetic moment (μ_{eff}) for complexes **1** and **2** (*a*), **3** and **4** (*b*), **6** and **7** (*c*), **9** and **10** (*d*), **5**, **8**, and **11** (*e*) (β is the Bohr magneton).

cally stable enaminoketone derivatives of 2-imidazoline nitroxide only by introducing the nitrile group into the side chain of the ligand. This group in the 2-imidazoline ligands under study, unlike that in 3-imidazoline derivatives, hinders coordination of the nitroxide group to the metal ion of the adjacent bis-chelate fragment and, as a consequence, prevents the occurrence of efficient intermolecular exchange interactions. To construct high-dimensionality structures based on metal complexes with deprotonated enaminoketone derivatives of 2-imidazoline nitroxide, which can exhibit magnetic ordering at rather high temperatures, it is necessary to introduce substituents, which do not hinder coordination of the nitroxide group, instead of the nitrile group. This problem will be the subject our further investigations.

Experimental

Nitroxide HL^{Ph},[7] salt KL^{CF_3},[7] and the Cu(hfac)$_2$ complex[16] were prepared according to procedures described earlier. The mixed-ligand complexes were synthesized using Phen and bpy (Aldrich, purity ≥99%). All solvents were purified according to standard procedures.[17] The IR spectra were recorded on a Vector 22 (Bruker) spectrometer in KBr pellets in the region of 400—4000 cm^{-1}.

Bis[2-cyano-2-(1-oxyl-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazol-2-yl)-1-(trifluoromethyl)ethylenolato](1,10-phenanthroline)nickel(II), $\mathbf{NiL^{CF_3}{}_2(Phen)}$ (1). A solution of $Ni(NO_3)_2 \cdot 6H_2O$ (46 mg, 0.16 mmol) in water (10 mL) was added with stirring to a solution of KL^{CF_3} (100 mg, 0.32 mmol) in water (10 mL). The precipitate that formed was filtered off, dried *in vacuo* at 30 °C, and added to a solution of Phen (28 mg, 0.16 mmol) in MeCN (20 mL). The reaction mixture was stirred for 30 min and concentrated to dryness. The residue was recrystallized from MeCN. Dark-red single crystals suitable for X-ray diffraction analysis were grown by slow evaporation of the solution of the complex in MeCN. The yield was 45%, m.p. 240—244 °C (decomp.). Found (%): C, 51.9; H, 4.0; F, 14.4; N, 14.3. $C_{34}H_{32}F_6N_8NiO_4$. Calculated (%): C, 51.7; H, 4.1; F, 14.4; N, 14.2. IR, ν/cm^{-1}: 2987, 2937 (C—H); 2215 (C≡N); 1582, 1516 (N=C—C=C—O).

Complexes **2—4** were prepared according to an analogous procedure.

Bis[2-cyano-2-(1-oxyl-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazol-2-yl)-1-(trifluoromethyl)ethylenolato](1,10-phenanthroline)cobalt(II), $\mathbf{CoL^{CF_3}{}_2(Phen)}$ (2). The yield was 55%, m.p. 240—247 °C (decomp.). Found (%): C, 51.5; H, 3.8; F, 14.2; N, 14.2. $C_{34}H_{32}CoF_6N_8O_4$. Calculated (%): C, 51.7; H, 4.1; F, 14.4; N, 14.2. IR, ν/cm^{-1}: 2985, 2936 (C—H); 2210 (C≡N); 1583, 1519 (N=C—C=C—O).

(2,2´-Bipyridyl)bis[2-cyano-2-(1-oxyl-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazol-2-yl)-1-(trifluoromethyl)ethylenolato]nickel(II), $\mathbf{NiL^{CF_3}{}_2(bpy)}$ (3). The yield was 45%, m.p. 251—254 °C (decomp.). Found (%): C, 50.2; H, 4.1; F, 14.9; N, 14.7. $C_{32}H_{32}F_6N_8NiO_4$. Calculated (%): C, 50.2; H, 4.2; F, 14.9; N, 14.6. IR, ν/cm^{-1}: 2987 (C—H); 2211 (C≡N); 1591, 1520 (N=C—C=C—O).

(2,2´-Bipyridyl)bis[2-cyano-2-(1-oxyl-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazol-2-yl)-1-(trifluoromethyl)ethylenolato]cobalt(II), $\mathbf{CoL^{CF_3}{}_2(bpy)}$ (4). The yield was 50%, m.p. 257—261 °C (decomp.). Found (%): C, 49.9; H, 3.9; F, 15.1; N, 14.2. $C_{32}H_{32}CoF_6N_8O_4$. Calculated (%): C, 50.2; H, 4.2; F, 14.9; N, 14.6. IR, ν/cm^{-1}: 2987 (C—H); 2211 (C≡N); 1588, 1522 (N=C—C=C—O).

(2,2´-Bipyridyl)bis[2-cyano-2-(1-oxyl-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazol-2-yl)-1-phenylethylenolato]nickel(II), solvate with MeCN (1 : 1), $\mathbf{NiL^{Ph}{}_2(bpy) \cdot MeCN}$ (5). The $Ni(NO_3)_2 \cdot 6H_2O$ complex (51 mg, 0.175 mmol) and a solution of KOH (0.35 mmol) in MeOH were added with stirring to a solution of HL^{Ph} (100 mg, 0.35 mmol) in MeCN (30 mL). The reaction mixture was rapidly concentrated to dryness, and the residue was treated with MeCN (15 mL). The resulting solution was filtered, and a solution of bpy (28 mg, 0.18 mmol) in MeCN (5 mL) was carefully applied over the surface of the former solution. After one day, dark-blue single crystals suitable for X-ray diffraction study were collected. The yield was 45%, m.p. 229—232 °C (decomp.). Found (%): C, 64.1; H, 5.6; N, 15.4. $C_{44}H_{45}N_9NiO_4$. Calculated (%): C, 64.3; H, 5.5; N, 15.3. IR, ν/cm^{-1}: 2991, 2928 (C—H); 2192 (C≡N); 1598, 1583, 1556 (N=C—C=C—O).

Bis(dimethylsulfoxide)bis[2-cyano-2-(1-oxyl-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazol-2-yl)-1-(trifluoromethyl)ethylenolato]nickel(II), solvate with DMSO and $\mathbf{H_2O}$ (4 : 8 : 1), $\mathbf{NiL^{CF_3}{}_2(DMSO)_2 \cdot 2DMSO \cdot 0.25H_2O}$ (6). A solution of $Ni(NO_3)_2 \cdot 6H_2O$ (46 mg, 0.16 mmol) in water (10 mL) was added with stirring to a solution of KL^{CF_3} (100 mg, 0.32 mmol) in water (10 mL). The precipitate that formed was filtered off and dried *in vacuo* at 30 °C. The product was dissolved in a 1 : 1 acetone—DMSO mixture (20 mL). The solution was filtered and kept at 5 °C for several days until the acetone was evaporated. Dark-red single crystals suitable for X-ray diffraction analysis were filtered off. The yield was 70%, m.p. 115—117 °C (decomp.). Found* (%): C, 40.7; H, 4.7; F, 14.5; N, 10.7. $C_{26}H_{36}F_6N_6NiO_6S_2$. Calculated (%): C, 40.8; H, 4.7; F, 14.9; N, 11.0. IR, ν/cm^{-1}: 2985 (C—H); 2207 (C≡N); 1592, 1530 (N=C—C=C—O).

Bis(dimethylsulfoxide)bis[2-cyano-2-(1-oxyl-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazol-2-yl)-1-(trifluoromethyl)ethylenolato]cobalt(II), solvate with DMSO and $\mathbf{H_2O}$ (4 : 8 : 1), $\mathbf{CoL^{CF_3}{}_2(DMSO)_2 \cdot 2DMSO \cdot 0.25H_2O}$ (7) was prepared analogously. The yield was 70%, m.p. 109—110 °C (decomp.). Found* (%): C, 40.8; H, 5.0; F, 14.9; N, 10.6. $C_{26}H_{36}CoF_6N_6O_6S_2$. Calculated (%): C, 40.8; H, 4.7; F, 14.9; N, 11.0. IR, ν/cm^{-1}: 2981, 2943 (C—H); 2207 (C≡N); 1589, 1529 (N=C—C=C—O).

Bis[2-cyano-2-(1-oxyl-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazol-2-yl)-1-phenylethylenolato]copper(II), $\mathbf{CuL^{Ph}{}_2}$ (8). The $CuCl_2 \cdot 2H_2O$ complex (30 mg, 0.175 mmol) and then a solution of KOH (0.35 mmol) in MeOH were added to a solution of HL^{Ph} (100 mg, 0.35 mmol) in MeCN (30 mL). The reaction mixture was rapidly concentrated to dryness, and the residue was extracted with a minimum amount of MeCN. The resulting solution was filtered and kept at ~20 °C. After evaporation of the major portion of the solvent, dark-violet single crystals suitable for X-ray diffraction analysis were collected. The yield was 35%, decomp. without melting >150 °C. Found (%): C, 61.5; H, 5.4; N, 13.2. $C_{32}H_{34}CuN_6O_4$. Calculated (%): C, 61.0; H, 5.4; N, 13.3. IR, ν/cm^{-1}: 2991 (C—H); 2210 (C≡N); 1581, 1562 (N=C—C=C—O).

Bis[2-cyano-2-(1-oxyl-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazol-2-yl)-1-(trifluoromethyl)ethylenolato]copper(II), solvate with MeCN (1 : 1), $\mathbf{CuL^{CF_3}{}_2 \cdot MeCN}$ (9). A mixture of $Cu(NO_3)_2 \cdot 3H_2O$ (39 mg, 0.16 mmol) and KL^{CF_3} (100 mg, 0.32 mmol) was dissolved in anhydrous MeCN (10 mL). The solution was kept at −10 °C for 2 days. The precipitate of KNO_3 was filtered off. After one day, dark-red crystals of the complex were filtered off. The yield was 45%, m.p. 176—179 °C (decomp.). Found (%): C, 43.6; H, 4.0; F, 17.6; N, 14.8. $C_{24}H_{27}CuF_6N_7O_4$. Calculated (%): C, 44.0; H, 4.2; F, 17.4; N, 15.0. IR, ν/cm^{-1}: 2982, 2938 (C—H); 2220 (C—N); 1588, 1523 (N=C—C=C—O).

(1,1,1,3,3,3-Hexafluoro-2,4-pentanedionato)[2-cyano-2-(1-oxyl-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazol-2-yl)-1-(trifluoromethyl)ethylenolato]copper(II), $\mathbf{CuL^{CF_3}(hfac)}$ (10). A mixture of $Cu(hfac)_2$ (73 mg, 0.15 mmol) and complex **9** (100 mg, 0.15 mmol) in MeCN (10 mL) was stirred for 30 min and then concentrated to dryness. The residue was extracted with a 1 : 1 AcOEt—heptane mixture (15 mL). The solution was

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* The sample was pre-dried *in vacuo* at 30 °C for 2 days.

filtered and kept at ~20 °C. After evaporation of the major portion of the solvent, red single crystals suitable for X-ray diffraction analysis were collected. The yield was 50%, m.p. 174—179 °C (decomp.). Found (%): C, 35.0; H, 2.2; F, 31.0; N, 7.5. $C_{16}H_{13}CuF_9N_3O_4$. Calculated (%): C, 35.2; H, 2.4; F, 31.3; N, 7.7. IR, ν/cm^{-1}: 2994 (C—H); 2236 (C≡N); 1598, 1556, 1522 (N=C—C=C—O).

Tetrakis{(1,1,1,3,3,3-hexafluoro-2,4-pentanedionato)[2-cyano-2-(1-oxyl-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazol-2-yl)-1-phenylethylenolato]copper(II)}, [CuL^{Ph}(hfac)]$_4$ (11). The $CuCl_2 \cdot 2H_2O$ complex (30 mg, 0.175 mmol) and then a solution of KOH (0.35 mmol) in MeOH were added to a solution of HL^{Ph} (100 mg, 0.35 mmol) in MeCN (30 mL). The reaction mixture was concentrated to dryness. A solution of $Cu(hfac)_2$ (84 mg, 0.175 mmol) in CH_2Cl_2 (20 mL) and then heptane (10 mL) were added to the residue. The resulting solution was filtered and kept at ~20 °C. After 12 h, dark-violet single crystals suitable for X-ray diffraction analysis were collected. The yield was 50%, m.p. 172—175 °C (decomp.). Found (%): C, 46.1; H, 3.3; F, 20.6; N, 7.7. $C_{84}H_{72}Cu_4F_{24}N_{12}O_{16}$. Calculated (%): C, 45.5; H, 3.3; F, 20.6; N, 7.6. IR, ν/cm^{-1}: 2985, 2939 (C—H); 2221 (C≡N); 1651, 1586, 1567, 1526 (N=C—C=C—O).

X-ray diffraction analysis. Dark nontransparent crystals of all compounds were grown as very thin needles or thin platelets. X-ray diffraction data sets were collected from single crystals of all compounds on an automated Bruker AXS P4 diffractometer (Mo radiation, θ/2θ scanning technique with a variable rate, V = 3 deg min^{-1}, the empirical absorption correction was applied using azimuth scanning curves) and a SMART Apex diffractometer equipped with a two-coordinate detector (Mo radiation, absorption correction was applied using the SADABS program, version 2.03). The structures were solved by direct methods and refined by the full-matrix least-squares method with anisotropic thermal parameters for nonhydrogen atoms. The positions of some H atoms (predominantly, the H atoms of the Ph rings and the Phen, bpy, and hfac ligands) were revealed from difference electron density syntheses. The positions of the remaining H atoms (virtually of all Me groups) were calculated theoretically. The H atoms of the Me groups were refined with isotropic thermal parameters in the rigid-body approximation (only thermal parameters were refined, except for compounds **2**, **4**, and **5**). For the H atoms of the Ph rings and the Phen, bpy, and hfac ligands, both the positional and thermal parameters were refined. In the structures of **6** and **7**, the positions of all H atoms were calculated geometrically and refined in the rigid-body approximation. All calculations associated with the structure solution and refinement were carried out using the SHELX-97 [18] and SHELXTL (Version 6.12) program packages.

Table 4. Crystallographic characteristics of Ni^{II} and Co^{II} complexes **1**, **2**, and **4**—**7**

Parameter	NiL$^{CF_3}{}_2$(Phen) (**1**)	CoL$^{CF_3}{}_2$(Phen) (**2**)	CoL$^{CF_3}{}_2$(bpy) (**4**)	NiL$^{Ph}{}_2$(bpy) • • MeCN (**5**)	NiL$^{CF_3}{}_2$(DMSO)$_2$ • • 2DMSO • 0.25H$_2$O (**6**)	CoL$^{CF_3}{}_2$(DMSO)$_2$ • • 2DMSO • 0.25H$_2$O (**7**)
Molecular weight	789.39	789.61	765.59	822.60	925.69	925.93
Diffractometer	«Bruker AXS P4»	«Bruker AXS P4»	«Bruker AXS P4»	«Bruker AXS P4»	«SMART Apex»	«SMART Apex»
T/K	293	293	293	293	293	293
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P\bar{1}$	$P2/n$	$P2/n$
a/Å	12.666(2)	12.741(3)	11.9315(8)	12.796(2)	13.021(3)	13.106(9)
b/Å	17.601(2)	17.620(4)	19.259(1)	13.268(2)	14.082(3)	14.06(1)
c/Å	15.679(2)	15.666(3)	15.237(1)	15.057(2)	23.626(5)	23.72(2)
α/deg	90	90	90	115.11(1)	90	90
β/deg	93.584(3)	93.72(2)	92.006(1)	98.46(1)	101.58(3)	101.34(2)
γ/deg	90	90	90	109.49(1)	90	90
V/Å^3	3488.4(7)	3510(2)	3499.1(4)	2053.5(5)	4244(2)	4286(5)
Z	4	4	4	2	4	4
d_{calc}/g cm^{-3}	1.503	1.494	1.453	1.330	1.443	1.435
μ/mm^{-1}	0.639	0.572	0.571	0.527	0.731	0.673
θ Scan range/deg	1.98—28.35	1.98—25.02	2.01—28.34	1.89—24.99	1.45—23.32	1.45—23.43
N^a/N^{*b}	21033/8154	10173/6186	21202/8156	6426/6094	18023/6111	14431/5982
R_{int}	0.1618	0.0035	0.0683	0.0416	0.1939	0.2495
N^{**c}/n^d	2581/535	5266/607	4332/562	3844/701	2679/550	2238/546
GOOF	0.812	1.005	0.878	0.969	0.920	0.927
R_1 (for N^{**})	0.0816	0.0596	0.0641	0.0571	0.0933	0.2062
wR_2	0.1330	0.1577	0.1390	0.1152	0.2091	0.1140
R_1 (for N^*)	0.2474	0.0688	0.1195	0.1119	0.1900	0.2585
wR_2	0.1856	0.1670	0.1630	0.1386	0.2584	0.2603

[a] N is the number of measured reflections.

[b] N^* is the number of independent reflections.

[c] N^{**} is the number of reflections with $I > 2\sigma(I)$.

[d] n is the number of parameters in the refinement.

Table 5. Crystallographic characteristics of Cu^{II} complexes **8—11**

Parameter	CuL^{Ph}$_2$ (**8**)	CuL^{CF_3}$_2$·MeCN (**9**)	CuL^{CF_3}(hfac) (**10**)	[CuL^{Ph}(hfac)]$_4$ (**11**)
Molecular weight	630.19	655.07	545.83	553.92
Diffractometer	«SMART Apex»	«Bruker AXS P4»	«Bruker AXS P4»	«SMART Apex»
T/K	293	293	293	293
Crystal system	Orthorhombic	Orthorhombic	Triclinic	Tetragonal
Space group	$Fdd2$	$Pca2_1$	$P\bar{1}$	$I4_1/a$
a/Å	26.820(6)	14.045(2)	12.010(3)	19.0770(8)
b/Å	36.780(9)	12.342(2)	14.654(2)	19.0770(8)
c/Å	6.237(2)	17.259(3)	19.456(2)	26.888(2)
α/deg	90	90	77.18(1)	90
β/deg	90	90	80.09(2)	90
γ/deg	90	90	81.48(2)	90
V/Å^3	6153(3)	2991.7(8)	3267.4(10)	9785.4(8)
Z	8	4	2	16
d_{calc}/g cm^{-3}	1.361	1.454	1.664	1.504
μ/mm^{-1}	0.756	0.809	1.106	0.970
θ Scan range/deg	1.88—23.30	2.36—24.99	1.91—24.00	1.31—23.31
$N^a/N^{*\,b}$	6556/1882	2723/2723	99 9291/8697	20936/3518
R_{int}	0.0729	0.0000	0.0916	0.0701
$N^{**\,c}/n^d$	1549/228	2138/406	3110/941	2742/404
GOOF	1.086	1.024.	1.048	1.006
R_1 (for N^{**})	0.0706	0.0576	0.0983	0.0585
wR_2	0.1418	0.1427	0.1926	0.1788
R_1 (for N^*)	0.0872	0.0753	0.2592	0.0719
wR_2	0.1549	0.1575	0.2654	0.1936

[a] N is the number of measured reflections.

[b] N^* is the number of independent reflections.

[c] N^{**} is the number of reflections with $I > 2\sigma(I)$.

[d] n is the number of parameters in the refinement.

The main crystallographic characteristics, details of X-ray diffraction study, selected bond lengths, and bond angles are given in Tables 1, 2, 4, and 5. Poor quality of the crystals of the compounds (particularly, of **6** and **7**; in spite of numerous crystallization experiments) did not allow us to achieve lower values of R_{int} and, correspondingly, of the final R_1 and wR_2 factors.

Magnetic measurements. The magnetic properties of polycrystalline samples were studied on a SQUID Quantum Design magnetometer in the temperature range of 2—300 K using the strength of the external magnetic field up to 5 kOe. The molar magnetic susceptibilities (χ) were calculated taking into account diamagnetism of atoms according to the Pascal additive scheme. In the paramagnetic region, the effective magnetic moments were calculated by the equation

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

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

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