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Stereo sensitivity of exchange interactions in Ni^{II} and Cu^{II} heterospin complexes with 5-formylpyrrolyl-substituted nitroxides*

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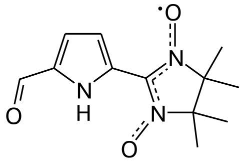
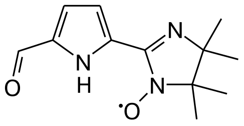
5-Formylpyrrolyl-substituted nitronyl and imino nitroxide radicals HL^1 and HL^2 were synthesized. Their solid phases are formed by packing pairs of the molecules. In the $\{HL^1...HL^1\}$ pairs, the dominant interaction is the ferromagnetic exchange with $J/k_B = 8.8$ K (Hamiltonian $H = -2J(\vec{S}_1 \cdot \vec{S}_2)$). The ferromagnetic exchange occurs also in the heterospin molecules $[Ni(L^1)_2]$, $[Cu(L^1)_2]$, and $[Ni(L^2)_2(MeOH)_2]$. In the complexes $[Ni(L^1)_2]$ and $[Cu(L^1)_2]$, a small change in the mutual orientation of the coordinated ligands has a considerable effect on the value and the sign of the energy of exchange interactions between the unpaired electrons of the metal ion and paramagnetic ligands.

Key words: copper(II) complexes, nickel(II) complexes, nitroxide radicals, pyrrole, X-ray diffraction, quantum chemical calculations.

Multispin compounds exhibiting magnetic effects under the influence of external stimuli have attracted growing interest.[1] Generally, the larger the changes induced by external stimuli in the mutual arrangement of paramagnetic centers in the phase under consideration, the stronger the influence of these stimuli on the magnetic characteristics of the solid. The magnetic effects induced by small structural changes in heterospin exchange clusters were described in the literature.[2,3] It is clear from general considerations that this situation is possible; however, it remains unclear how one can synthesize compounds, in which exchange clusters would be highly sensitive to an insignificant structural reorganization. The usefulness of such compounds is evident because they can serve as highly efficient sensors for external stimuli. For instance, the solid phase of a Cu^{II} complex with a nitronyl nitroxide radical described recently proved highly sensitive to the applied external pressure. In this case, the spin transition temperature, which abruptly changed under changes in the external pressure, served as an indicator of the applied external stimulus.[4]



HL¹



HL²

We thought that the synthesis of transition metal complexes with polydentate nitroxides, which are favorable for the meridional coordination of the paramagnetic ligand, would provide an approach to the targeted design of heterospin compounds, the exchange clusters of which are sensitive to a small structural reorganization. For this purpose, we developed a procedure for the synthesis of spin-labeled 5-formylpyrrole derivatives HL^1 and HL^2, prepared heterospin Ni^{II} and Cu^{II} complexes with these derivatives, studied their structures and magnetic properties, and performed quantum chemical calculations in order to investigate the influence of changes in the mutual orienta-

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tion of the ligands on the energy of exchange interactions between unpaired electrons of the metal ion and the coordinated nitroxide.

Results and Discussion

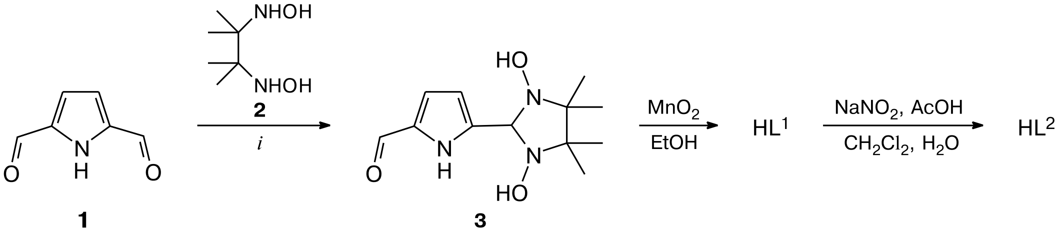
The synthesis of the paramagnetic radicals HL^1 and HL^2 is presented in Scheme 1. The condensation of 1*H*-pyrrole-2,5-dicarbaldehyde (**1**) with an equivalent amount of 2,3-bis(hydroxylamino)-2,3-dimethylbutane (**2**) was performed in toluene, in which the resulting adduct **3** is almost insoluble, which prevented the further reaction of the latter with **2**. The oxidation of **3** afforded nitronyl nitroxide HL^1, and the reduction of the latter gave imino nitroxide HL^2.

The N—O bond lengths in the compound HL^1 determined by X-ray diffraction are 1.283(1) and 1.279(1) Å, which are typical of 2-imidazoline-3-oxide-1-oxyls.[5] The angle between the planes of the pyrrole ring and the paramagnetic moiety {ONCNO} is 10.5°. The aldehyde group lies in the plane of the pyrrole ring. The compound is stabilized by the intramolecular N(3)—H(3)...O(1) hydrogen bond (N(3)—H(3), 0.88(1) Å; H(3)...O(1), 2.16(1) Å; N(3)...O(1), 2.739(2) Å; the N(3)—H(3)—O(1) angle, 122(1)°). The solid phase of HL^1 is composed of centrosymmetric pairs of the molecules. There are rather short C(9)—H(9a)...O(2´) contacts in these pairs (Fig. 1, *a*). The C(9)—H(9a) distance is 0.98(2) Å; H(9a)...O(2´), 2.39(2) Å; C(9)...O(2´), 3.154(2) Å. The distance between the O(2) atoms in each pair (4.196(2) Å) is the shortest distance between the atoms of NO groups of adjacent molecules.

The crystals of the imino nitroxide are also formed by the $\{HL^2...HL^2\}$ dimers. Each pair consists of two crystallographically independent molecules linked together by N—H...N bonds with the N...N distances of 2.939(3) Å (see Fig. 1, *b*). In both molecules, the N—O bond lengths are 1.271(3) Å.

The compounds HL^1 and HL^2 have different magnetic properties. In HL^1, the dominant interaction is the ferromagnetic exchange, whereas the antiferromagnetic exchange occurs in HL^2 (Fig. 2). An analysis of the experimental temperature dependences of the effective magnetic moment (μ_{eff}) using the exchange-coupled dimer model (Hamiltonian $H = -2J(\vec{S}_1 \cdot \vec{S}_2)$) gave the following optimal values of the *g*-factor and the exchange interaction parameter: 1.98 (±0.01) and 8.8 (±0.4) K for HL^1; 2.02 (±0.01) and −7.2 (±0.2) K for HL^2. The quantum chemical calculations confirmed the ferromagnetic exchange with J/k_B = 2.7 K in the $\{HL^1...HL^1\}$ dimers and revealed the much weaker antiferromagnetic exchange between the

Scheme 1



i. Toluene.

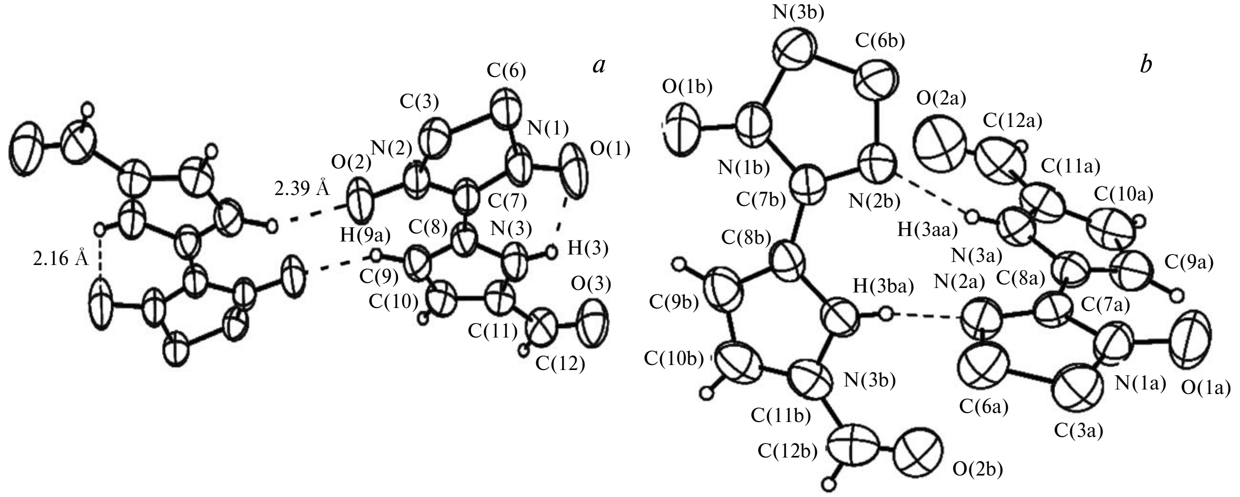


Fig. 1. Structures of the $\{HL^1...HL^1\}$ (*a*) and $\{HL^2...HL^2\}$ (*b*) dimers; hereinafter, the *gem*-methyl groups are not shown.

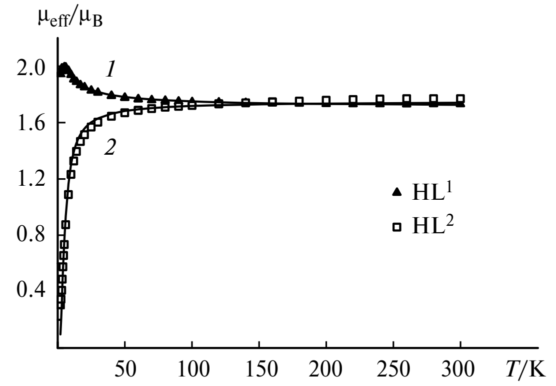


Fig. 2. Temperature dependences of the effective magnetic moment for the nitroxide radicals HL^1 (*1*) and HL^2 (*2*). The points correspond to the experimental data; the calculated curves are shown as solid lines.

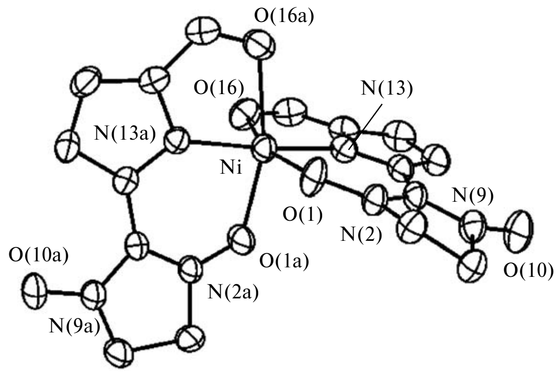


Fig. 3. Structure of complex **4**.

dimers (–0.15 cm^{-1}). The latter is consistent with the X-ray diffraction data, according to which the distances between the paramagnetic fragments of adjacent dimers are rather large (>5.3 Å).

The complexes $[Ni(L^1)_2]$ (**4**), $[Cu(L^1)_2]$ (**5**), and $[Ni(L^2)_2(MeOH)_2]$ (**6**) were synthesized by the reaction of methanol solutions of metal acetates with the nitroxide radicals HL^1 and HL^2. In molecule **4**, both L^1 ligands are coordinated in a tridentate fashion (Fig. 3). The environment of the Ni atom is formed by the N atoms of the pyrrole ring and the O atoms of the aldehyde group ($O_{C=O}$) and the NO group (O_{NO}) and has the C_2 pseudosymmetry. The Ni—N distances are substantially shorter (1.944(2), 1.946(2) Å) than the Ni—O_{NO} distances (2.111(2), 2.121(2) Å) and the Ni—$O_{C=O}$ distances (2.218(2), 2.238(2) Å). The angles between the planes of the pyrrole ring and the {NCN} fragment of the imidazoline ring in the ligands are 6.7 and 9.8° (Table 1). The angle between the planes passing through the Ni atom and the electron-donating atoms of the ligand (*i.e.*, Ni—O(1)—N(13)—O(16) and Ni—O(1a)—N(13a)—O(16a)) is 87.3°. The distances for the coordinated >NO groups (1.310(3) and 1.312(2) Å) are substantially longer than the corresponding distances for both terminal groups (1.270(3) Å). The shortest O(10)...O(10´) distances between the O_{NO} atoms of two adjacent molecules **4** are larger than 3.9 Å. The shortest intermolecular contacts are the C...O distances between the aldehyde groups (3.292(3) Å) in pairs of adjacent molecules (Fig. 4). Therefore, the data on the structure of the solid phase of this compound suggest that the highest-energy exchange interactions between the paramagnetic

Table 1. Selected bond lengths and dihedral angles between the heterocycles in the nitroxide radicals HL^1 and HL^2 and complexes **4—6**

Parameter	HL^1	HL^2	**4**	**5**	**6**
Bond			d/Å		
M—O_{NO}	— —	— —	2.111(2), 2.121(2)	2.158(2), 2.195(2)	— —
M—$O_{C=O}$	— —	— —	2.218(2), 2.238(2)	2.350(2), 2.345(2)	— —
Ni—O_{MeOH}	—	—	—	—	2.080(1), 2.091(1)
M—N	—	—	1.944(2), 1.946(2)	1.899(2), 1.902(2)	2.098(2), 2.101(1), 2.102(1), 2.106(2)
N—O	1.283(1), 1.279(1)	1.271(3), 1.271(3)	1.310(3), 1.270(3), 1.312(3), 1.270(3)	1.310(2), 1.267(2), 1.311(2), 1.265(2)	1.274(2), 1.277(2)
O_{NO}...O_{NO}	4.196(2)	>5 Å	4.646(3)	4.062(3)	3.895(3)
Angle			ω/deg		
Pyr—{N_2C}	10.5	17.6, 9.2	6.7, 9.8	9.3, 9.8	1.0, 7.0

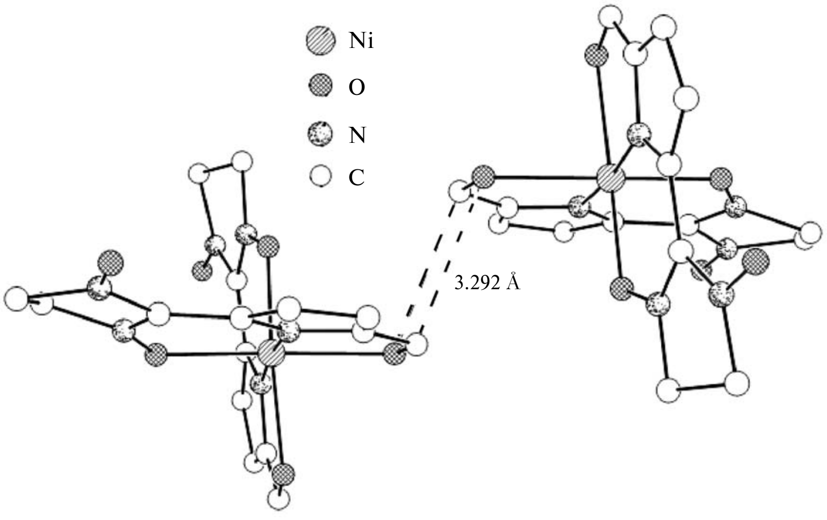


Fig. 4. Shortest intermolecular contacts in structure **4**.

centers (these interactions are analyzed below) occur within molecules **4**.

Molecule **5** has a similar structure with the difference that the distances to the $O_{C=O}$ atoms (2.345(2) and 2.350(2) Å; see Table 1) are substantially longer than those in **4**. An elongation of these bonds is attributed to the Jahn—Teller effect typical of the Cu^{II} ion. The highest-energy exchange interaction between the paramagnetic centers in the solid phase of **5** occurs also within the bis-chelate molecules.

In molecule **6**, the nitroxide group is not coordinated to the Ni^{II} ion; the L^2 ligand is coordinated in a bidentate fashion through the N atoms of the 2-imidazoline and pyrrole rings (Fig. 5). The central atom is also coordinated by the O atoms of two MeOH molecules. The Ni—O and Ni—N bond lengths are in the range of 2.080(1)—2.106(2) Å. The hydroxy groups of MeOH form strong intramolecular hydrogen bonds with the $O_{C=O}$ atoms (O(1s)—H(1s), 0.86(3) Å; H(1s)...O(16a), 1.71(3) Å; O(1s)...O(16a), 2.570(2) Å; the O(1s)—H(1s)—O(16a) angle, 176(3)°; O(2s)—H(2s), 0.80(2) Å; H(2s)...O(16b), 1.78(2) Å; O(2s)...O(16b), 2.573(3) Å; the O(2s)—H(2s)—O(16b) angle, 175(3)°). The N—O bonds have almost equal lengths (1.274(2) and 1.277(2) Å). The shortest intermolecular $O_{NO}...O_{NO}$ distances are 3.895(3) Å (see Table 1).

The experimental dependences $\mu_{eff}(T)$ for complexes **4—6** are shown in Fig. 6. The values of μ_{eff}, which are 4.07, 3.12, and 4.68 μ_B at 300 K, gradually increase to 4.17 (60 K), 3.38 (20 K), and 5.07 μ_B (60 K) and then decrease to 2.55, 2.14, and 3.41 μ_B at 2 K for **4**, **5**, and **6**, respectively. This character of the dependence $\mu_{eff}(T)$ is indicative of a rather strong intramolecular ferromagnetic exchange in the complexes, resulting in an increase in μ_{eff} with a decrease in the temperature. A decrease in μ_{eff} at temperatures below 20 K is attributed to weaker intermolecular antiferromagnetic exchange interactions and/or the zero-field splitting.

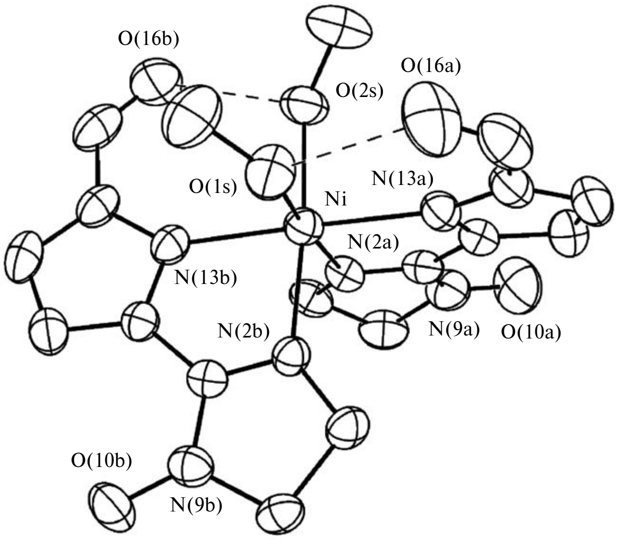


Fig. 5. Molecular structure of **6**. Dashed lines represent intramolecular hydrogen bonds.

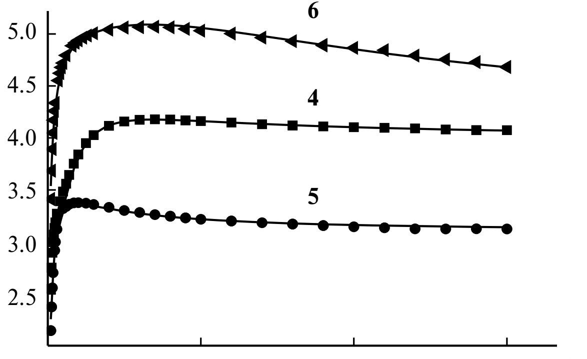


Fig. 6. Temperature dependences $m_{eff}(T)$ for complexes **4**, **5**, and **6**. The points correspond to the experimental data, the calculated curves are shown as solid lines.

It should be noted that, despite the fact that all the heterospin compounds under study contain the deprotonated pyrrole ring, the paramagnetic ligand in molecule **6** is coordinated in a fashion different from that observed in $[M(L^1)_2]$ (**4** and **5**). This fact was not evident and cannot be predicted in advance until compounds **4**—**6** were synthesized and structurally characterized, especially since chelate complexes of transition metals with nitronyl nitroxides or imino nitroxides containing the pyrrole substituent have not been known earlier. The structural investigation of complexes **4**—**6** suggests that the synthesis of chelate complexes with other spin-labeled pyrrole derivatives would be expected to result in a change in the set of electron-donating atoms in going from nitronyl nitroxide to its imino nitroxide analog, as it was observed in going from L^1 to L^2.

The strong ferromagnetic exchange is typical of complexes with imino nitroxides, in which (like in complex **6**) the N atom of the paramagnetic moiety is involved in the coordination,[6—8] whereas this type of exchange is rarely observed in complexes with nitronyl nitroxides,[9] and this fact needs to be explained. The results of the quantum chemical calculations confirmed the possibility of ferromagnetic exchange in complexes **4** and **5** and also demonstrated high sensitivity of the exchange even to small changes in the geometry of the coordination unit.

Figure 7 shows a set of magnetic orbitals for complex **4**, which was obtained using the unrestricted self-consistent field method for the state with the maximum value of the total spin. Two orbitals, both localized on the nitronyl nitroxide fragments, are symmetric and antisymmetric combinations of the singly occupied orbitals of the ligands; the other orbitals are metal-based ($d_{x^2-y^2}$ and d_{z^2}).

For the pair of paramagnetic centers *2*—*3*, the magnetic orbitals of the Ni^{II} ion and the nitronyl nitroxide fragment are nearly orthogonal to each other; however, in the pair *1*—*2*, the orthogonal arrangement is substantially disturbed (see Fig. 7), which is reflected in the calculated values of J_{1-2} and J_{2-3} (Table 2). For the calculated parameters, the ground state is triplet; however, the quintet level is only 0.7 cm^{-1} higher in energy. It should also be noted that, according to the results of quantum chemical calculations, the energy of intramolecular exchange interaction between the unpaired electrons of nitroxides (J_{1-3}) in all complexes is not higher than 0.3 cm^{-1}.

In accordance with the results of quantum chemical calculations, the experimental dependences $\mu_{eff}(T)$ were analyzed using the Hamiltonian $H = -2J_{1-2}(\vec{S}_{NO}\cdot\vec{S}_{M}) - 2J_{2-3}(\vec{S}_{M}\cdot\vec{S}_{NO})$ taking into account intermolecular exchange interactions in the molecular field approximation (zJ'). For complex **4**, we obtained the following optimal

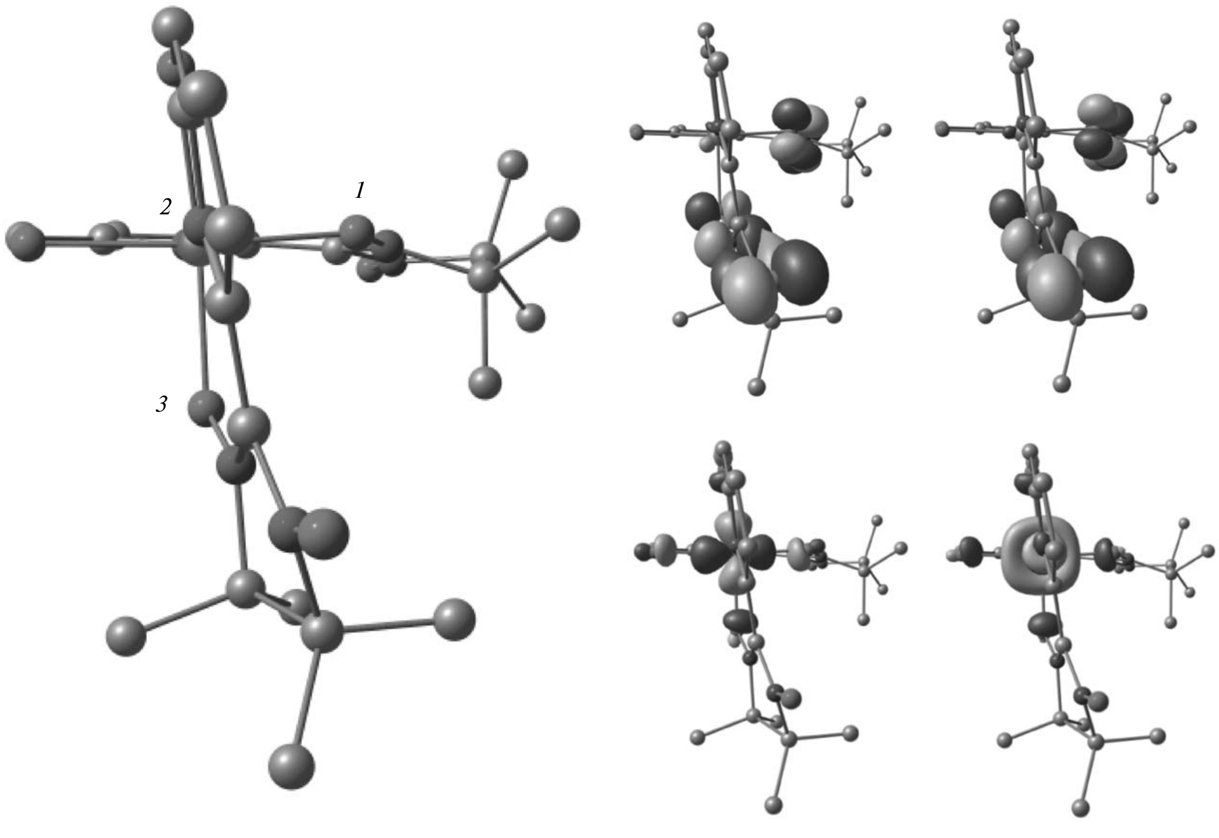


Fig. 7. The spatial configuration, the numbering of the paramagnetic centers (*1*—*3*), and the magnetic orbitals of complex **4**.

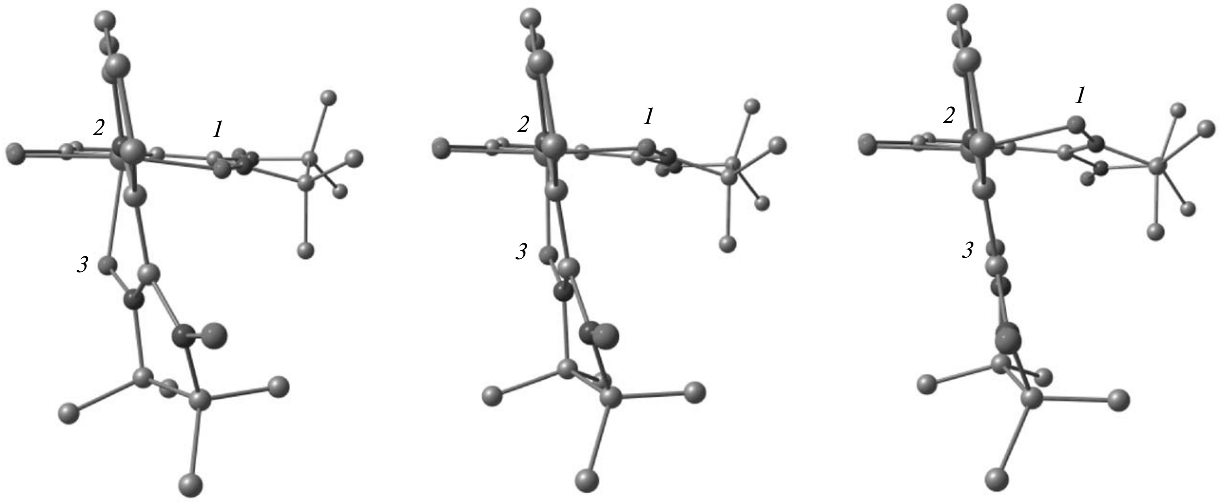


Fig. 8. Initial ($\Delta\omega = 0°$) and final ($\Delta\varphi = -10°$ and $10°$) structures used for the construction of the magneto-structural correlation.

values of the *g*-factor, J_{1-2}, J_{2-3}, and zJ': 2.09 (±0.01), 0 (fixed), 37 (±3), and −1.4 (±0.1) cm^{-1}, respectively. These values are in rather good agreement with the calculated data (Table 2). A substantial difference in the calculated values of J_{1-2} and J_{2-3} attests to high sensitivity of the exchange in the Ni^{II}—ON< fragment of complex **4** to small geometric distortions.

In order to confirm the latter fact, we performed quantum chemical calculations for modified complex **4***. In this complex, the mutual arrangement of the atoms of L^1 in the fragment *1—2* is the same as in the fragment *2—3*, due to which the mutual orientation of the *d* and *p* orbitals involved in the exchange in the pair *1—2* approximates that in the pair *2—3*. The calculated J_{1-2} for complex **4*** increased to 54 cm^{-1} (see Table 2) and it is even higher than J_{2-3}. In this case, the quintet is the ground state, which lies 100.4 cm^{-1} lower than the first excited triplet state.

Since both imino nitroxides in complex **6** are coordinated in a similar fashion, it can be assumed that $J_{1-2} = J_{2-3} = J$. The optimal values of the parameters g_R, g_{Ni}, J, and zJ', which provide the best description of the experimental dependence $\mu_{eff}(T)$, are 2.0 (fixed), 2.25 (±0.01), 85 (±4), and −0.36 (±0.1) cm^{-1}, respectively.

Table 2. The M—O distances and calculated values of the exchange parameters for the molecules [M(L^1)$_2$] and the modified molecules [M(L^1)$_2$]* (M = Ni, Cu)

Complex	*d*/Å		*J*/cm^{-1}		
	d_{1-2}	d_{2-3}	J_{1-2}	J_{2-3}	J_{1-3}
4	2.111	2.121	−0.1	45.5	−0.3
4*	2.111	2.121	53.6	45.8	1.1
5	2.158	2.195	24.8	49.1	0.2
5*	2.158	2.195	69	49	1

Like in complex **4**, the fragments *1—2* and *2—3* in complex **5** are structurally and magnetically nonequivalent (see Table 2). Actually, the best description of the experimental dependence $\mu_{eff}(T)$ was obtained by independently varying the exchange parameters J_{1-2} and J_{2-3}. For complex **5**, the optimal values of the *g*-factor, J_{1-2}, J_{2-3}, and the energy of intermolecular exchange interaction zJ' are 2.04 (±0.01), 5.4 (±0.4), 25.8 (±0.8), and −0.8 (±0.1) cm^{-1}, respectively. Therefore, the exchange interactions in complex **5**, like those in complex **4**, are very sensitive to small geometric changes that affect the orthogonal arrangement of the magnetic orbitals. We confirmed this fact by the appropriate calculations for modi-

Table 3. The M—O distances and calculated values of the exchange parameters for the modified molecular structures of complexes **4** and **5**, which were used for the construction of the magneto-structural correlation

Complex	$\Delta\varphi$ /deg*	*d*/Å		*J*/cm^{-1}		
		d_{1-2}	d_{2-3}	J_{1-2}	J_{2-3}	J_{1-3}
4	−10	2.095	2.245	63	−42	1
	−5	2.091	2.171	52	1	0
	0	2.112	2.119	0	46	0
	5	2.159	2.092	−68	66	1
	10	2.229	2.090	−122	45	1
5	−10	2.138	2.331	83	−2	1
	−5	2.136	2.253	63	22	0
	0	2.158	2.195	25	49	0
	5	2.204	2.159	−19	68	1
	10	2.272	2.149	−56	67	2

* At each point, the angle φ for each nitronyl nitroxide fragment was changed by 5°. The planes of the nitronyl nitroxide fragments were rotated in one direction: either counterclockwise ($\Delta\varphi = -5°, -10°$) or clockwise ($\Delta\varphi = 5°, 10°$).

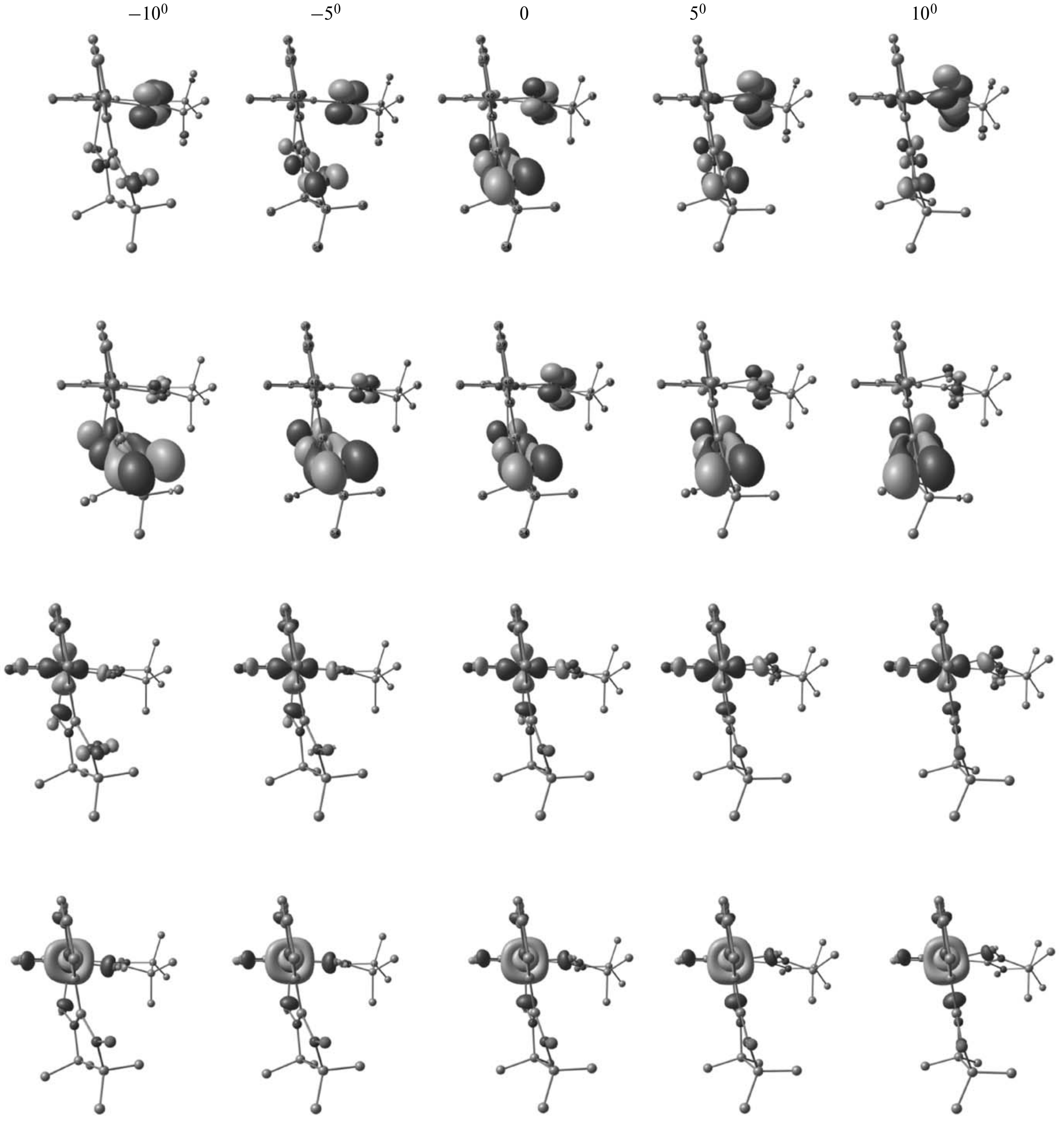


Fig. 9. Magnetic orbitals for the structures used for the construction of the magneto-structural correlation (for complex **4**).

fied complex **5***, in which the mutual arrangement of the atoms of L^1 in the fragment *1—2* is the same as in the fragment *2—3* (see Table 2).

Larger variations in the mutual orientation of the magnetic orbitals in complexes **4** and **5** resulted in changes not only in the exchange energy but also in its sign. The results presented in Table 3 and the magnetic orbitals for the modified molecular structures of complexes **4** and **5** shown in Figs 8 and 9 demonstrate that the changes in the dihedral angle φ (N(9)—C—C—N(13) or N(9a)—C—C—N(13a); see Fig. 3), *i.e.*, the rotation of the plane of the nitronyl nitroxide fragment, lead to the weakening of ferromagnetic exchange and the strengthening of antiferromagnetic exchange.

To summarize, we synthesized the heterospin complexes $[Ni(L^1)_2]$ and $[Cu(L^1)_2]$ with 5-formylpyrrolyl-substituted nitronyl nitroxides characterized by the meridional coordination of paramagnetic ligands and intramolecular ferromagnetic exchange. It was found that this exchange is sensitive to even small changes in the coordination environment of the metal ion. The rotation of the plane of the nitronyl nitroxide fragment by a few degrees may change by an order of magnitude the energy of the exchange interaction between the unpaired electrons of the M^{II} ion and the L^1 ligand, as well as its sign. As mentioned in the Introduction, this heterospin complexes may be potentially more efficient sensors for external stimuli.

Experimental

The solvents were purified before use by known procedures.**[10]** 2,5-Diformylpyrrole**[11]** and 2,3-bis(hydroxylamino)-2,3-dimethylbutane**[12]** were synthesized by methods described in the literature. The commercial reagents and solvents were used as is. The TLC analysis was performed using Silica Gel 60 F_{254} coated aluminum-backed TLC sheets. The column chromatography was carried out using 0.063—0.200 mm silica gel (Merck). The elemental analysis was performed on a Euro EA 3000 microanalyzer. The IR spectra were recorded as KBr pellets on a Bruker Vector-22 spectrophotometer. Magnetochemical measurements were carried out on a Quantum Design MPMSXL SQUID magnetometer in the temperature range of 2—300 K under a magnetic field of 5 kOe. The paramagnetic components of the magnetic susceptibility were determined taking into account the diamagnetic contribution estimated from Pascal constants. The effective magnetic moment was calculated by the equation $\mu_{\text{eff}} = [3k\chi T/(N_A\mu_B{}^2)]^{1/2}$, where N_A is Avogadro's number, μ_B is the Bohr magneton, and k is the Boltzmann constant.

2-(5-Formyl-1*H*-pyrrol-2-yl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazole-3-oxide-1-oxyl (HL^1). A suspension of 1*H*-pyrrole-2,5-dicarbaldehyde (**1**) (0.150 g, 1.218 mmol) and 2,3-bishydroxylamino-2,3-dimethylbutane (**2**) (0.180 g, 1.218 mmol) in toluene (12 mL) was stirred under an inert atmosphere at room temperature for 7 days. The yellow-orange product (0.234 g) was filtered, and then EtOH (10 mL) and MnO_2 (1.00 g, 0.0115 mol) were added to the product. The mixture was stirred at room temperature for 1 h, the precipitate was filtered off, and the mother liquor was concentrated *in vacuo* and passed through a layer of silica gel (2×12 cm, EtOAc). The crystallization of the residue from a mixture of CH_2Cl_2 and heptane ($v/v = 1 : 2$) afforded dark-turquoise-colored crystals suitable for X-ray diffraction. The yield was 0.155 g (51%), m.p. 104—106 °C, R_f (SiO_2, EtOAc) 0.61. IR, ν/cm^{-1}: 3348, 3160, 3002, 2985, 2854, 1668, 1583, 1522, 1452, 1399, 1379, 1348, 1290, 1203, 1173, 1126, 1035, 895, 868, 805, 766, 742, 684, 657, 594, 541, 460. Found (%): C, 58.0; H, 6.3; N, 17.0. $C_{12}H_{16}N_3O_3$. Calculated (%): C, 57.6; H, 6.4; N, 16.8.

2-(5-Formyl-1*H*-pyrrol-2-yl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazole-1-oxyl (HL^2). Water (0.5 mL), $NaNO_2$ (0.099 g, 1.44 mmol), and AcOH (0.086 g, 1.44 mmol) were added with stirring to a solution of 2-(5-formyl-1*H*-pyrrol-2-yl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazole-3-oxide-1-oxyl (HL^1) (0.240 g, 0.959 mmol) in $CHCl_3$ (5 mL). After 1 min, the reaction mixture turned crimson. The mixture continued to be stirred for 5 min and then neutralized with $NaHCO_3$ (0.130 g). The layers were separated using a separatory funnel. The organic layer was dried with Na_2SO_4, concentrated *in vacuo*, and filtered through a layer of silica gel (2×8 cm, CH_2Cl_2 as the eluent). The residue was crystallized from a heptane—diethyl ether mixture at 5 °C for 20 h. Crimson-colored crystals. The yield was 0.145 g (64%). R_f (SiO_2, EtOAc) 0.61. IR, ν/cm^{-1}: 3082, 2982, 2935, 2853, 2809, 2715, 1762, 1666, 1599, 1531, 1484, 1449, 1434, 1413, 1391, 1378, 1369, 1323, 1282, 1264, 1239, 1213, 1137, 1039, 1008, 945, 886, 819, 805, 783, 763, 762, 703, 636, 622, 598, 562, 528, 464. Found (%): C, 61.6; H, 6.6; N, 17.8. $C_{12}H_{16}N_3O_2$. Calculated (%): C, 61.5; H, 6.9; N, 17.9. Single crystals of HL^2 suitable for X-ray diffraction were grown from a CH_2Cl_2—heptane mixture.

Bis[2-(5-formyl-1*H*-pyrrol-2-yl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazole-3-oxide-1-oxyl]nickel, $[Ni(L^1)_2]$ (4). A solution of HL^1 (0.0570 g, 0.23 mmol) in MeOH (2 mL) and one drop of Et_3N (0.2 mL, 1.4 mmol) were added to a solution of $Ni(OAc)_2(H_2O)_4$ (0.0283 g, 0.11 mmol) in MeOH (3 mL) at 25 °C. After 12 h, the dark-green crystals that formed were filtered, washed with cold methanol, and dried in air. The yield was 83%. Complex **4** is soluble in CH_2Cl_2. Found (%): C, 51.9; H, 5.3; N, 15.1. $C_{24}H_{30}N_6NiO_6$. Calculated (%): C, 51.7; H, 5.4; N, 15.1.

Bis[2-(5-formyl-1*H*-pyrrol-2-yl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazole-3-oxide-1-oxyl]copper, $[Cu(L^1)_2]$ (5) was synthesized as described above. Dark-green crystals. The yield was 76%. Complex **5** is also soluble in CH_2Cl_2. Found (%): C, 51.1; H, 5.3; N, 14.9. $C_{24}H_{30}N_6O_6Cu$. Calculated (%): C, 51.3; H, 5.4; N, 15.0.

Bis(methanol)-bis[2-(5-formyl-1*H*-pyrrol-2-yl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazole-1-oxyl]nickel, $[Ni(L^2)_2(MeOH)_2]$ (6). A mixture of $Ni(OAc)_2(H_2O)_4$ (0.0266 g, 0.11 mmol) and HL^2 (0.0500 g, 0.21 mmol) was dissolved in MeOH (5 mL) with heating (~50 °C). The blue-violet solution was slowly (for 3—4 h) cooled to room temperature. The dark-blue needle-like crystals that formed were filtered, washed with cold MeOH, and dried in air. The yield was 68%. Complex is soluble in CH_2Cl_2. Found (%): C, 52.6; H, 6.3; N, 14.1. $C_{26}H_{38}N_6NiO_6$. Calculated (%): C, 53.0; H, 6.5; N, 14.3.

X-ray diffraction study. Single-crystal X-ray diffraction data sets were collected on Bruker AXS and SMART APEX II diffractometers (T = 296 K; absorption corrections were applied using the 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 nonhydrogen atoms. The hydrogen atoms were positioned geometrically and refined using a riding model. All calculations associated with the structure solution and refinement were carried out with the Bruker SHELXTL software, Version 6.14. The complete structural data were deposited at the Cambridge Crystallographic Data Centre (CCDC 1008886—1008890; deposit@ccdc.cam.ac.uk; http://www.ccdc.cam.ac.uk/data_request/cif).

Nitroxide radical HL^1. $C_{12}H_{16}N_3O_3$, M = 250.28 g mol^{-1}, a = 11.5148(16) Å, b = 8.4587(12) Å, c = 13.398(2) Å, β = = 95.498(7)°; V = 1299.0(3) Å^3; $P2_1/c$, Z = 4, d_{calc} = 1.280 g cm^{-3}, μ(Mo-Kα) = 0.094 mm^{-1}, 2.85 < θ < 27.99°, 11914 I_{hkl} were measured, of which 3113 I_{hkl} are unique, 1779 reflections with $I_{hkl} > 2\sigma(I)$ (R_{int} = 0.0439), 180 refined parameters; GOOF = = 0.887; R_1 = 0.0398, wR_2 = 0.1017 for $I > 2\sigma(I)$; R_1 = 0.0729, wR_2 = 0.1128 based on all I_{hkl}; residual electron density, max/min 0.171/–0.132 e Å^{-3}.

Nitroxide radical HL^2. $C_{12}H_{16}N_3O_2$, M = 234.28 g mol^{-1}, a = 10.7652(17) Å, b = 9.3815(16) Å, c = 25.511(5) Å, β = = 100.141(13)°; V = 2536.2(7) Å^3; $P2_1/n$, Z = 8, d_{calc} = 1.227 g cm^{-3}, μ(Cu-Kα) = 0.699 mm^{-1}, 3.52 < θ < 65.15°, 13381 I_{hkl} were measured, of which 4178 reflections are unique, 2416 reflections with $I > 2\sigma(I)$ ($R_{\text{int}} = 0.0709$), 307 refined parameters; GOOF = = 1.014; $R_1 = 0.0595$, $wR_2 = 0.1589$ for $I > 2\sigma(I)$; $R_1 = 0.0959$, $wR_2 = 0.1780$ based on all I_{hkl}; residual electron density, max/min 0.251/–0.250 e Å^{-3}.

Complex Ni(L^1)$_2$ (4). $C_{24}H_{30}N_6NiO_6$, $M = 557.25$ g mol^{-1}, $a = 8.7000(3)$ Å, $b = 12.2750(4)$ Å, $c = 12.9494(5)$ Å, α = = 79.108(2)°, β = 86.025(2)°, γ = 71.251(2)°; V = 1285.87(8) Å^3; $P\bar{1}$, $Z = 2$, $d_{\text{calc}} = 1.439$ g cm^{-3}, μ(Cu-Kα) = 1.524 mm^{-1}, $3.48 < \theta < 59.97°$, 12117 I_{hkl} were measured, of which 3728 reflections are unique, 3245 reflections with $I > 2\sigma(I)$ ($R_{\text{int}} = 0.0360$), 334 refined parameters; GOOF = 1.011; $R_1 = 0.0401$, wR_2 = = 0.1109 for $I > 2\sigma(I)$; $R_1 = 0.0467$, $wR_2 = 0.1194$ based on all I_{hkl}; residual electron density, max/min 0.320/–0.408 e Å^{-3}.

Complex Cu(L^1)$_2$ (5). $C_{24}H_{30}CuN_6O_6$, $M = 562.08$ g mol^{-1}, $a = 8.7912(2)$ Å, $b = 12.3410(3)$ Å, $c = 12.9217(3)$ Å, α = = 78.313(1)°, β = 86.865(1)°, γ = 71.086(2)°; V = 1298.63(5) Å^3; $P\bar{1}$, $Z = 2$, $d_{\text{calc}} = 1.437$ g cm^{-3}, μ(Mo-Kα) = 0.896 mm^{-1}, $2.15 < \theta < 28.32°$, 22378 I_{hkl} were measured, of which 6420 reflections are unique, 4051 reflections with $I > 2\sigma(I)$ (R_{int} = = 0.0550), 334 refined parameters; GOOF = 0.954; $R_1 = 0.0433$, $wR_2 = 0.0923$ for $I > 2\sigma(I)$; $R_1 = 0.0808$, $wR_2 = 0.1014$ based on all I_{hkl}; residual electron density, max/min 0.301/–0.343 e Å^{-3}.

Complex Ni(L^2)$_2$(MeOH)$_2$ (6). $C_{26}H_{38}N_6NiO_6$, M = = 589.33 g mol^{-1}, $a = 9.6199(3)$ Å, $b = 16.1679(5)$ Å, c = = 19.2587(6) Å, β = 97.433(2)°; V = 2970.20(16) Å^3; $P2_1/n$, Z = 4, $d_{\text{calc}} = 1.318$ g cm^{-3}, μ(Mo-Kα) = 0.701 mm^{-1}, $2.74 < \theta < 28.15°$, 28021 I_{hkl} were measured, of which 7251 reflections are unique, 4553 reflections with $I > 2\sigma(I)$ ($R_{\text{int}} = 0.0444$), 360 refined parameters; GOOF = 0.929; $R_1 = 0.0393$, $wR_2 = 0.0939$ for $I > 2\sigma(I)$; $R_1 = 0.0728$, $wR_2 = 0.1031$ based on all I_{hkl}; residual electron density, max/min 0.296/–0.333 e Å^{-3}.

Quantum chemical calculations. The isotropic exchange parameters were computed by the broken-symmetry approach[13] with the GAUSSIAN09 program package[14] using the X-ray diffraction data, the B3LYP functional,[15,16] and the TZVP basis set.[17]

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