Heterospin complexes of polynuclear Ni^{II} compounds containing hexafluoroacetylacetonate and pivalate ligands with nitroxides

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The heterospin mixed-ligand complex $[Ni_{6}(OH)_{4}Piv_{4}(hfac)_{4}(NIT-Ph)_{2}]$ (1) (NIT-Ph is 4,4,5,5-tetramethyl-2-phenyl-4,5-dihydro-1*H*-imidazol-1-oxyl 3-oxide, hfac is hexafluoroacetylacetonate, and Piv is pivalate) was synthesized. The method for the synthesis of complex 1 is based on the replacement of acetone molecules in the hexanuclear complex containing the hexafluoroacetylacetonate and pivalate ligands $[Ni_6(OH)_4Piv_4(hfac)_4(Me_2CO)_4]$ by NIT-Ph molecules. Two monodentate NIT-Ph molecules replace four acetone molecules, because the coordination of the O atom of the nitroxide group results in the blocking of one of the positions in the coordination environment of Ni^{II} the access to which is hindered by the phenyl ring of NIT-Ph. As a result, these ions are in a square-pyramidal environment unusual of Ni^{II}. In the low-temperature range, the dependence of the magnetization of 1 on the magnetic field is described by the Brillouin function. The reaction of $[Ni_6Piv_4(hfac)_4(OH)_4(Me_2CO)_4]$ with the nitronyl nitroxide radicals 4,4,5,5-tetramethyl-2-(4-pyridyl)-4,5-dihydro-1H-imidazol-1-oxyl 3-oxide (NIT-p-Py) or 4,4,5,5-tetramethyl-2-(1-methyl-1H-imidazol-5-yl)-4,5-dihydro-1Himidazol-1-oxyl 3-oxide (NIT-Iz) containing the pyridine or 1-methylimidazol-5-yl substituent, respectively, in the side chain is accompanied by the decomposition of the polynuclear fragment and affords the mononuclear complexes Ni(hfac)₂(NIT-p-Py)₂ and Ni(hfac)₂(NIT-Iz)₂, respectively. The reaction of 4,4,5,5-tetramethyl-2-(1-methyl-1H-imidazol-5-yl)-4,5-dihydro-1H-imidazol-1-oxyl (Im-Iz), which is the imine analog of NIT-Iz, with $[Ni_6Piv_4(hfac)_4(OH)_4(Me_2CO)_4]$ afforded the decanuclear complex [Ni₁₀(OH)₈Piv₄(hfac)₈(Im-Iz)₂(H₂O)₆]. The molecular and crystal structures of all heterospin compounds were determined, and the magnetic properties of all compounds were investigated in the 2–300 K temperature range.

Key words: nickel(11), polynuclear compounds, nitronyl nitroxides, hexafluoroacetylacetonates, pivalates, X-ray diffraction study, magnetic measurements.

The interactions of polynuclear metal compounds with nitroxides serve as an efficient method for the synthesis of multispin compounds.¹⁻⁵ In solid phases, some of these compounds exhibit bulk magnetization.^{1,4} However, what often complicates implementation of this synthetic approach is poor solubility of the starting polynuclear complexes in organic solvents, due to which they cannot be introduced into reactions with nitroxides. In addition, the metal ions of the polynuclear fragment should possess high electron-withdrawing ability to coordinate weak donors such as the O atoms of the nitroxide groups. Finally, the starting polynuclear fragment should contain easily replaceable terminal ligands. The recently described⁶ mixed-ligand hexanuclear complex $[Ni_6(OH)_4Piv_4(hfac)_4(Me_2CO)_4]$, meets theses requirements. Thus the pivalate anions (Piv) that are present in

this complex provide the solubility in organic solvents, the hexafluoroacetylacetonate anions (hfac) enhance the electron-withdrawing properties of the Ni^{II} ions, and acetone molecules serve as easily replaceable ligands.

Results and Discussion

The experiments showed that the complex $[Ni_6(OH)_4Piv_4(hfac)_4(Me_2CO)_4]$ reacts under ordinary conditions with 4,4,5,5-tetramethyl-2-phenyl-4,5-di-hydro-1*H*-imidazol-1-oxyl 3-oxide (NIT-Ph) to form $[Ni_6(OH)_4Piv_4(hfac)_4(NIT-Ph)_2]$ (1). Complex 1 always precipitates regardless of the reactant ratio (1:1, 1:2, 1:4), which indicates that this compound is formed in the individual state.

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The molecules 1 contain the adamantane-like core (Fig. 1, *a*) in which six Ni atoms bind four μ_3 -O atoms of the hydroxy groups. The Ni...Ni distances in the core are in the range 3.0710(7)-3.5534(8) Å; the Ni-O distances are in the range 1.961(3)-2.044(3) Å. The pivalate anions



The investigation of the temperature dependence of the effective magnetic moment (μ_{eff}) showed that the hightemperature value $\mu_{eff} = 8.09 \,\mu_B$ for 1 (Fig. 2, *a*) is in good agreement with the theoretical spin value (8.07 μ_B) for eight noninteracting paramagnetic centers, including six Ni^{II} with $g \approx 2.22$ and S = 1 and two NIT-Ph with g = 2and $S = \frac{1}{2}$. An increase in μ_{eff} with decreasing temperature indicates that the ferromagnetic exchange interactions prevail in this eight-center exchange cluster. The energy of intermolecular antiferromagnetic exchange interactions is much lower and, hence, these interactions





Fig. 1. Structure of the hexanuclear adamantane-like fragment $\{Ni_6(\mu_3-O)_4\}$ (*a*) and the molecular structure of **1** (*b*). The H atoms and the Bu^t and CF₃ groups are not shown. Figure 1 is available in full color in the on-line version of the journal (http://www.springerlink.com/fulltext.pdf).

Fig. 2. Plot of the effective magnetic moment (μ_{eff}) versus temperature (*T*) (*a*) and the plot of the magnetization of the sample (σ) versus the external magnetic field (*H*) for **1** (*b*).

occur only at very low temperatures, which is responsible for a decrease in μ_{eff} at temperatures below 8 K. At low temperatures, compound **1** is characterized by the nonlinear dependence of the magnetization of the sample (σ) on the external magnetic field (Fig. 2, *b*) described by the Brillouin function with the parameters S = 5.58 and g = 2.

The reactions of $[Ni_6(OH)_4Piv_4(hfac)_4(Me_2CO)_4]$ with NIT-R containing electron-donating N atoms in the substituents R such as 4,4,5,5-tetramethyl-2-(4-pyridyl)-4,5-dihydro-1*H*-imidazol-1-oxyl 3-oxide (NIT-*p*-Py) or 4,4,5,5-tetramethyl-2-(1-methyl-1*H*-imidazol-5-yl)-4,5dihydro-1*H*-imidazol-1-oxyl 3-oxide (NIT-Iz), are accompanied by the decomposition of the polynuclear fragment and the formation of solid mononuclear hexafluoroacetylacetonate complexes Ni(hfac)₂(NIT-p-Py)₂ and Ni(hfac)₂(NIT-Iz)₂. The heterocycles containing the electron-donating N atoms are stronger donors than the O atoms of the >N-O fragments, which as a rule brings about decomposition of the polynuclear complexes to form mononuclear complexes.⁷ Figure 3 exemplifies the molecular structure of Ni(hfac)₂(NIT-p-Py)₂. The octahedral environment of the Ni atom is formed by four O atoms of the hfac anions and the N atoms of the nitroxide radicals with the Ni-N distances of 2.080(4) Å. The magnetic properties of the complexes $Ni(hfac)_2(NIT-p-Py)_2$ and Ni(hfac)₂(NIT-Iz)₂ are trivial. The magnetic moments μ_{eff} determined by the high-temperature factors (Fig. 4) agree well with the theoretical spin value (4.12 μ_B) for three noninteracting paramagnetic centers, including one Ni^{II} ion with S = 1 and two nitroxides with $S = \frac{1}{2}$. At low temperatures, weak antiferromagnetic exchange interactions between the unpaired electrons of the paramagnetic centers occur, which is manifested in a decrease in the magnetic moment μ_{eff} in the curve $\mu_{eff}(T)$.

In the reaction of the imino nitroxide 4,4,5,5tetramethyl-2-(1-methyl-1*H*-imidazol-5-yl)-4,5-dihydro-1*H*-imidazol-1-oxyl (Im-Iz) with [Ni₆(OH)₄Piv₄(hfac)₄(Me₂CO)₄], the decanuclear het-



Fig. 3. Structure of the complex $Ni(hfac)_2(NIT-p-Py)_2$. The H atoms are not shown. Figure 3 is available in full color in the on-line version of the journal (http://www.springerlink.com/fulltext.pdf).



Fig. 4. Plot of the effective magnetic moment (μ_{eff}) versus the temperature (*T*) for Ni(hfac)₂(NIT-Iz)₂ (*I*) and Ni(hfac)₂(NIT-*p*-Py)₂ (*2*).

erospin complex containing two imino nitroxide molecules $[Ni_{10}(OH)_8Piv_4(hfac)_8(Im-Iz)_2(H_2O)_6] \cdot 0.5C_7H_{16}$ (2) was isolated in the solid phase. Previously, it has been noted that the nuclearity of the pivalate-containing Ni^{II} template can be changed in the reaction with spin-labeled methylimidazole.⁴ The formation of 2 is another example of such transformations.

The metal core of molecule 2 having the symmetry C_2 contains the heterocubane moiety formed by four nickel atoms (Ni(1), Ni(4), Ni(4'), and Ni(1')) and the O atoms of four µ₃-OH groups (Ni–O, 2.036(2)–2.074(2) Å). The Ni(1) atom is linked to the Ni(3) atom through the O atoms of the μ_3 -OH groups and the μ_2 -H₂O molecules and to the Ni(2) and Ni(5) atoms through the O atoms of the μ_3 -OH groups (Ni-O, 1.999(2)-2.177(2) Å). The Piv anions serve as bidentate-bridging ligands linking the Ni(2) and Ni(5) atoms (Ni-0, 2.011(2)-2.029(3) A) and as tridentate-bridging ligands linking the Ni(2), Ni(3), and Ni(5) atoms (Ni–O, 1.996(3)–2.105(2) Å). The octahedral coordination environment of the Ni(2), Ni(3), Ni(4), and Ni(5) atoms involves also the O atoms of the hfac ligands. The coordination environment of the Ni(5) and Ni(3) atoms involves the O atoms of the H_2O molecules. The Ni(7) and Ni(4') atoms are coordinated by the N atoms of the imidazole ring of Im-Iz (Ni-N, 2.071(3) Å) (Fig. 5).

It should be noted that complex 2 crystallizes from an acetone—heptane mixture containing the reactants $[Ni_6(OH)_4Piv_4(hfac)_4(Me_2CO)_4]$ and Im-Iz in the ratio 1 : 1. When the fraction of the imino nitroxide was increased to $[Ni_6(OH)_4Piv_4(hfac)_4(Me_2CO)_4]/Im-Iz = 1 : 2$, the centrosymmetric mononuclear complex Ni(hfac)_2(Im-Iz)_2 was isolated in the solid phase along with complex 2. The magnetic moment μ_{eff} of 2 remains virtually constant (10.57 μ_B) in the 60–300 K temperature range (Fig. 6, *a*).



Fig. 5. Structure of the metal core in molecule **2** (*a*) and the molecular structure of **2** (*b*). The H atoms and the Bu^t and CF₃ groups are not shown. Figure 5 is available in full color in the online version of the journal (http://www.springerlink.com/full-text.pdf).

This value is higher than the theoretically calculated magnetic moment (10.20 μ_B ; with $g \approx 2.2$ for Ni^{II}) estimated by the summation of independent spin contributions of 10 Ni^{II} ions with $g \approx 2.22$ and S = 1 and two Im-Iz radicals with g = 2 and $S = \frac{1}{2}$ to the magnetic susceptibility. This indicates that the spin compensation is absent in multicenter exchange clusters **2**. At temperatures below 60 K, the magnetic moment μ_{eff} first increases to 10.78 μ_B and then sharply decreases as the temperature approaches the liquid helium temperature, at which weak intercluster antiferromagnetic exchange interactions occur. This is evidence that intramolecular ferromagnetic exchange interactions prevail in the 12-center exchange clusters **2**, like in eight-center exchange clusters **1**.

The magnetic moment μ_{eff} =4.19 μ_B for Ni(hfac)₂(Im-Iz)₂ at room temperature agrees well with the theoretical value for a system consisting of three paramagnetic centers: one Ni^{II} ion and two nitroxides (4.12 μ_B ; the *g* factors for the Ni^{II} ion and the nitroxide are ~2.2 and ~2, respectively) (Fig. 6, *b*). At temperatures below 4 K, there are weak intermolecular antiferromagnetic exchange interactions between the nitroxide groups of adjacent molecules.

Thus, we prepared first heterospin polynuclear Ni^{II} complexes with nitroxide-containing Piv and hfac ligands along with stable nitroxides in the ligand shell of the poly-



Fig. 6. Plots of the effective magnetic moment (μ_{eff}) versus the temperature (*T*) for complexes **2** (*a*) and Ni(hfac)₂(Im-Iz)₂ (*b*).

nuclear fragment. It was found that ferromagnetic exchange interactions prevail in multicenter heterospin exchange clusters 1 and 2.

Experimental

The complexes $[Ni_6Piv_4(hfac)_4(OH)_4(Me_2CO)_4]$ and nitronyl nitroxide radicals required for the synthesis of heterospin complexes were synthesized according to known procedures.^{6,8,9,10}

Tetrakis(hexafluoroacetylacetonato)tetra(μ_3 -hydroxo)tetrakis[μ_3 -(2,2-dimethylpropionato-O, O, O')]bis(4,4,5,5-tetramethyl-2-phenyl-4,5-dihydro-1*H*-imidazol-1-oxyl 3-oxide)hexanickel(n), [Ni₆(OH)₄Piv₄(hfac)₄(NIT-Ph)₂] (1). A solution of NIT-Ph (0.022 g, 0.093 mmol) in acetone (1 mL) was added at room temperature to a solution of [Ni₆Piv₄(hfac)₄(OH)₄(Me₂CO)₄] (0.088 g, 0.047 mmol) in acetone (2 mL) and then heptane (3 mL) was added. After 4 days, aggregates of dark-violet crystals of 1 that formed were filtered off, washed with cold heptane, and dried under an air stream. The yield was 0.033 g (33%). Found (%): C 37.7; H, 3.6; N, 2.3. Ni₆C₆₆H₇₈N₄O₂₄F₂₄. Calculated (%): C, 37.4; H, 3.7; N, 2.6.

Bis(hexafluoroacetylacetonato)bis[4,4,5,5-tetramethyl-2-(4pyridyl)-4,5-dihydro-1*H*-imidazol-1-oxyl 3-oxide]nickel(II), Ni(hfac)₂(NIT-*p*-Py)₂. A mixture of $[Ni_6Piv_4(hfac)_4-(OH)_4(Me_2CO)_4]$ (0.1 g, 0.053 mmol) and NIT-*p*-Py (0.012 g, 0.053 mmol) was dissolved with stirring in a mixture of CH_2Cl_2 (2–3 mL) and hexane (5 mL) at room temperature. After 1–2 days, dark-green crystal aggregates that formed were filtered off, washed with cold hexane, and dried under an air stream. The yield was 0.02 g (20 %). Found (%): C 43.3; H, 3.7; N, 8.8. NiC₃₄H₃₄N₆O₈F₁₂. Calculated (%): C, 43.4; H, 3.6; N, 8.9.

Bis(hexafluoroacetylacetonato)bis[4,4,5,5-tetramethyl-2-(1methyl-1*H*-imidazol-5-yl)-4,5-dihydro-1*H*-imidazol-1-oxyl 3-oxide]nickel(11), Ni(hfac)₂(NIT-Iz)₂. A mixture of NIT-Iz (0.025 g, 0.11 mmol) and $[Ni_6Piv_4(hfac)_4(OH)_4(Me_2CO)_4]$ (0.1 g, 0.053 mmol) was dissolved in a mixture of acetone (1 mL) and heptane (5 mL) at room temperature. After 2–3 days, darkblue crystals suitable for X-ray diffraction study were obtained. The crystals were filtered off, washed with cold heptane, and dried under an air stream. The yield was 0.03 g (30 %). Found (%): C, 40.7; H, 4.1; N, 11.8. NiC₃₂H₃₆N₈O₈F₁₂. Calculated (%): C, 40.6; H, 3.8; N, 11.8.

 $Octakis(hexafluoroacetylacetonato)octa(\mu_3-hydroxo)bis[\mu_3-hydroxo]bis[\mu_3-hydroxo)bis[\mu_3-hydroxo)bis[\mu_3-hydroxo]bis[\mu_3-h$ (2,2-dimethyl propionato-0,0,0)]bis[μ_2 -(2,2-dimethyl propionato-0,0)]bis[4,4,5,5-tetramethyl-2-(1-methyl-1H-imidazol-5-yl)-4,5-dihydro-1*H*-imidazol-1-oxyl]hexaaquadecanickel(II) heptane solvate, $[Ni_{10}(OH)_8Piv_4(hfac)_8(Im-Iz)_2(H_2O)_6] \cdot 0.5C_7H_{16}$ (2). A solution of nitroxide Im-Iz (0.013 g, 0.058 mmol) in acetone (2 mL) was added at room temperature to a solution of [Ni₆Piv₄(hfac)₄(OH)₄(Me₂CO)₄] (0.11 g, 0.058 mmol) in acetone (3 mL) followed by heptane (3 mL). After 3 days, the orange prismatic crystals of 2 that formed were filtered off, washed with MeCN, and dried under an air stream. The yield was 0.03 g (30 %). Found (%): C, 32.8; H, 3.6; N, 3.7. Ni₁₀C₈₉H₁₁₄O₄₀N₈F₄₈. Calculated (%): C, 31.1; H, 3.3; N, 3.3. When the starting [Ni₆Piv₄(hfac)₄(OH)₄(Me₂CO)₄]/Im-Iz ratio was increased to 1/2, prismatic crystals of the complex Ni(hfac)₂(Im-Iz)₂ were also obtained. Found (%): C, 43.1; H, 3.9; N, 10.4. NiC₃₄H₃₈N₈O₆F₁₂. Calculated (%): C, 43.4; H, 4.1; N 11.9.

X-ray diffraction study. The single-crystal X-ray diffraction data sets were collected on a SMART APEX CCD diffractometer (Bruker AXS) (Mo-K α radiation, $\lambda = 0.71073$ Å, 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 nonhydrogen atoms. The positions of H atoms were partially located in difference electron density maps (other hydrogen atoms were positioned geometrically) and refined isotropically together with nonhydrogen atoms using a rigid-group model. All calculations associated with the structure solution and refinement were carried out with the use of the Bruker Shelxtl software (Version 6.14).

 $\begin{array}{l|l} \hline \mbox{Complex} & [Ni_6(OH)_4 Piv_4(hfac)_4(NIT-Ph)_2] & (1): \\ C_{66}H_{78}F_{24}N_4Ni_6O_{24}, {\it M} = 2119.58, {\it T} = 295~K, \mbox{monoclinic crystals}, \mbox{space group} {\it C2/c}, {\it a} = 20.5572(19)~\AA, {\it b} = 19.5942(19)~\AA, {\it c} = 22.490(2)~\AA, {\it \beta} = 92.333(2)^\circ, {\it V} = 9051.4(15)~\AA^3, {\it Z} = 4, {\it d}_{calc} = 1.555~g~cm^{-3}, {\it \mu} = 1.340~mm^{-1}, 29775~measured~reflections~(1.44 < 0 < 26.43^\circ), of which 4990~independent~reflections were with {\it I} > 2\sigma({\it I}), {\it R}_1 = 0.0543, {\it w}{\it R}_2 = 0.1071. \end{array}$

Complex [Ni₁₀(OH)₈Piv₄(hfac)₈(Im-Iz)₂(H₂O)₆] · C₇H₁₆ (2): C₈₉H₁₁₄F₄₈N₈Ni₁₀O₂₀, M = 3434.98, T = 295 K, monoclinic crystals, space group C2/c; a = 23.034(5) Å, b = 26.704(5) Å, c = 24.020(5) Å, $\beta = 108.70(3)^{\circ}$, V = 13995(5) Å³, Z = 4, $d_{calc} =$ = 1.630 g cm⁻³, $\mu = 1.450$ mm⁻¹, 51486 measured reflections (1.77 < θ < 26.68°), of which 7397 independent reflections were with $I > 2\sigma(I)$, $R_1 = 0.0483$, $wR_2 = 0.0821$. **Complex Ni(hfac)₂(NIT-***p***-Py)₂**: $C_{34}H_{34}F_{12}N_6NiO_8$, M = 941.38, T = 295 K, monoclinic crystals, space group C2/c, a = 27.685(4) Å, b = 11.4073(19) Å, c = 27.303(4) Å, $\beta = 112.711(9)^\circ$, V = 7954(2) Å³, Z = 8, $d_{calc} = 1.572$ g cm⁻³, $\mu = 0.601$ mm⁻¹, 24750 measured reflections (1.59 < $\theta < 28.32^\circ$), of which 2031 independent reflections were with $I > 2\sigma(I)$, $R_1 = 0.0533$, $wR_2 = 0.1107$.

Magnetic properties of the complexes were measured on a SQUID magnetometer (MPMSXL, Quantum Design) in the temperature range 2–300 K in a magnetic field of 5 kOe. The paramagnetic terms of the magnetic susceptibility χ were evaluated taking into account the diamagnetic contribution, which was estimated from the Pascal constants. The effective magnetic moment was calculated by the equation

$$\mu_{\rm eff} = \left(\frac{3k}{N_{\rm A}\beta^2} \,\chi \,T\right)^{1/2} \approx (8\chi T)^{1/2},$$

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

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