# Synthesis, structure, and magnetic properties of heterometallic trinuclear complexes $\{M^{II}—Ln^{III}—M^{II}\}$ ($M^{II}$ = Ni, Cu; $Ln^{III}$ = La, Pr, Sm, Eu, Gd)*

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Trinuclear heterometallic complexes containing the $\{M_2Ln(Piv)_6(NO_3)\}$ ($M^{II}$ = Ni, Cu; $Ln^{III}$ = Nd, Pr, Sm, Eu, Gd; $Piv^-$ is the anion of pivalic acid) and $\{Cu_2Ln(Piv)_8)]^-$ ($Ln^{III}$ = Eu, Gd) metal cores were synthesized, their structures and magnetic properties were studied. For the most compounds, it was shown that their magnetic properties can be interpreted taking no interaction of the 3d-metal ions and a lanthanide into account. Ferromagnetic exchange interactions were found to exist between the unpaired electrons of the paramagnetic centers in the exchange clusters of the gadolinium-containing heterometallic complexes {M—Gd—M} (M = Ni or Cu).

**Key words:** heterometallic complexes, copper complexes, nickel complexes, lanthanide complexes, X-ray diffraction, magnetic properties.

In the last two decades, studies of the single-molecule magnets (SMMs) is an actively developing trend in the field of chemistry of magnetic materials.[1—5] Such compounds are distinguished by a possibility of ordering of individual molecules´ spins and, that is very important too, preserving their orientation upon the change of an external magnetic field. With different values of the so-called magnetic anisotropy barrier, single-molecule magnets exhibit hysteresis on the dependence of magnetization from magnetic field,[1,6,7] or (if this barrier is not high enough) a magnetization vector "lag" from the external field vector, or a slow relaxation of the individual molecule magnetization can be observed, that results in the occurrence of the out-of-phase signal at measurement of the sample magnetization in the alternating field.[8,9] "Magnetic molecules" are polynuclear high-spin compounds consisting of paramagnetic cores of d- and/or f-metal ions and an organic shell. The organic shell to a certain extent shields the magnetic core from possible intermolecular interactions, that enables studies of individual magnetic characteristics of the exchange cluster. In the design of molecular magnets with the high-spin metal ions, the "magnetism carriers", heteronuclear complexes can be the most interesting and promising. Such compounds contain unpaired electrons on the orbitals of different types, which can lead to various exchange interactions (ferro-, ferri-, and antiferromagnetic). In such a situation, a "differential" spin often remains even in the case of strong antiferromagnetic exchange, *i.e.* a molecule retains a potential ability in being magnetized. For a number of reasons, the molecules containing 3d- and 4f-metal ions in one molecule are of special interest. In particular, the aforementioned magnetic anisotropy barrier is governed by the product $DS^2$, where $D$ is the zero field splitting (which from the mathematical point of view is equivalent to the anisotropic component of the spin-orbit coupling), $S$ is the total spin of ground state.[6,10] Due to the high $D$ and $S$ values of 4f-metal ions themselves, their compounds can exhibit properties of molecular magnets even at low nu-

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clearity,[11—13] whereas a slow relaxation of magnetization was observed even in the case of mononuclear complexes of 4f-elements (which is unattainable for compounds of 3d-metals at temperatures apparently higher than tenth fractions of K).[14—17]

An important condition for stabilization of a ground state with the high $S$ value is the presence of ferromagnetic exchange interactions between the metal ions. A ferromagnetic type of exchange interactions among compounds containing 3d- and 4f-metal ions was for the first time found in the molecular complex $\{Cu^{II}—Gd^{III}\}$.[18] Further studies in this field showed that variations in the ratio and type of the high-spin metal ions in polynuclear complexes by the use of different types of bridging ligands (Schiff bases, anions of amino alcohols, carboxylate ligands, *etc.*) enabled obtaining molecular magnets with unique magnetic properties (slow magnetic relaxation, blocking and quantum tunneling of magnetization).[19—28]

Among heterometallic complexes containing ions of 3d- and 4f-elements, compounds of the $Gd^{III}$ ion are of particular interest due to its specific electron structure. First, the $Gd^{III}$ ion has the highest possible number of unpaired electrons ($S = 7/2$) among f-elements. Second, it is an isotropic ion, for which there is no contribution of the spin-orbit coupling, that simplifies mathematical description of magnetic properties for complexes on its basis. Nevertheless, despite the isotropic character of the individual $Gd^{III}$ ion, transition to ferromagnetically ordered state is possible in this ion complexes, which is yet another reason for the interest toward studies of magnetic properties of this element compounds.[28,29] Note that in compounds containing 3d- and 4f-metal ions, ferromagnetic exchange interactions in most cases occur between transition metal and gadolinium(III) ions.[18,28,30—42]

Earlier,[43] we have developed an approach to the formation of cobalt(II), nickel(II), and copper(II) binuclear 3d—4f-complexes with samarium(III) and gadolinium(III) ions. In the present work, we report the results of studies of a number of high-spin trinuclear heterometallic complexes of the type $\{M^{II}—Ln^{III}—M^{II}\}$ ($M^{II}$ = Ni, Cu; $Ln^{III}$ = La, Pr, Sm, Eu, Gd), which in a number of cases exhibit ferromagnetic exchange interactions between the 3d- and 4f-metal ions. The compounds synthesized were studied by X-ray diffraction, ESR spectroscopy, and magnetochemistry.

## Results and Discussion

**Synthesis of heterometallic complexes.** As it has been found earlier, the reaction of transition metal carboxylate complexes ($Co^{II}$, $Ni^{II}$, and $Cu^{II}$) containing coordinated molecules of 2,2´-bipyridyl (bpy) with 4f-metal pivalates ($Ln^{III}$ = Eu, Gd) leads to the formation of binuclear structures, in which the metal atoms are bound by three carboxylate anions.[43] In the present work, analogous nickel and copper complexes were found to react with gadolinium(III) or europium(III) nitrate ($M^{II} : Ln^{III} = 3 : 1$) and to yield trinuclear complexes $[M_2Ln(Piv)_6(NO_3)(bpy)_2] \cdot MeCN$ (M = Ni, Ln = Gd (**1**); M = Cu, Ln = Gd (**2**), Eu (**3**)). Studies on a possibility of obtaining analogous heterometallic complexes containing no N-donor ligands showed that the reaction of nickel pivalate $[Ni_9(OH)_6(Piv)_{12}(HPiv)_4]$ with 4f-element nitrates (with the ratio of metals $Ni^{II} : Ln^{III} = 3 : 1$) resulted in trinuclear complexes $[Ni_2Ln(Piv)_6(NO_3)(HPiv)_2(MeCN)_2] \cdot MeCN$ (Ln = La (**4**), Pr (**5**), Sm (**6**), Eu (**7**), Gd (**8**)). At the same time, no formation of the expected products was observed in the reaction of copper pivalate $[Cu(Piv)_2]_n$ with 4f-element nitrates (with the ratio Cu : Ln from 1 : 1 to 4 : 1).

Replacement of neutral coordinated molecules of HPiv and MeCN in compounds **6** and **8** with 2,2´-bipyridyl leads to the formation of trinuclear complexes $[Ni_2Ln(Piv)_6(NO_3)(bpy)_2] \cdot MeCN$ (a new compound in the case of $Ln^{III}$ = Sm (**9**) and already mentioned complex **1** in the case of $Ln^{III}$ = Gd).

Earlier, using cobalt heterometallic compounds as examples it was shown that when pivalate polynuclear complexes are formed from "simple salts", the structure of the reaction product is greatly affected by the ratio of reactants. Thus, a binuclear complex $[CoGd(Piv)_5(C_9H_7N)(H_2O)]$ is formed with the ratio of $Co^{II} : Gd^{III} = 1 : 1$ (the reaction mixture contains $Co(NO_3)_2 \cdot 6H_2O$ (1 mmol), $Gd(NO_3)_3 \cdot 6H_2O$ (1 mmol), HPiv (5 mmol), EtOH (60 mL), and excess of quinoline), whereas a two-fold increase in the amount of cobalt in the reaction mixture leads to trinuclear complex $[Co_2Gd(Piv)_6(C_9H_7N)_2(NO_3)]$.[44] Using $Sm^{III}$ as an example, we found that in the systems containing $Ni^{II}$ and $Ln^{III}$ under conditions for the synthesis of compounds **1** and **9** and with the ratio of metal ions 1 : 1, a heterometal ionic salt of the known composition $[Ni(MeCN)_6][Sm(NO_3)_5]$ is formed (see Ref. 45) (identity of our compounds and compounds described earlier was confirmed by X-ray powder diffraction). The ratio of metal ions $Ni^{II} : Ln^{III} = 2 : 1$ leads to the isolation of a mixture of products $[Ni(MeCN)_6][Ln(NO_3)_5]$ and $[Ni_2Ln(Piv)_6(NO_3)(HPiv)_2(MeCN)_2] \cdot MeCN$. To sum up, the ratio of the starting compounds per metals quantity $Ni^{II} : Ln^{III} = 3 : 1$ found in the present work was the optimum for the preparation of heterometallic nitratocarboxylate complexes with nickel atoms.

We also developed a procedure for the synthesis of copper(II) ionic trinuclear heterometallic complexes $(NBu_4)[Cu_2Ln(Piv)_8]$ ($Ln^{III}$ = Eu (**10**), Gd (**11**)). These compounds formed by the direct reaction of $Cu_2(Piv)_4(HPiv)_2$ and $Ln(NO_3)_3 \cdot 6H_2O$ in the presence of $NBu_4OH$.

**Structures of the complexes.** Complexes **4**—**8** are identical in their composition (see Experimental), so we es-

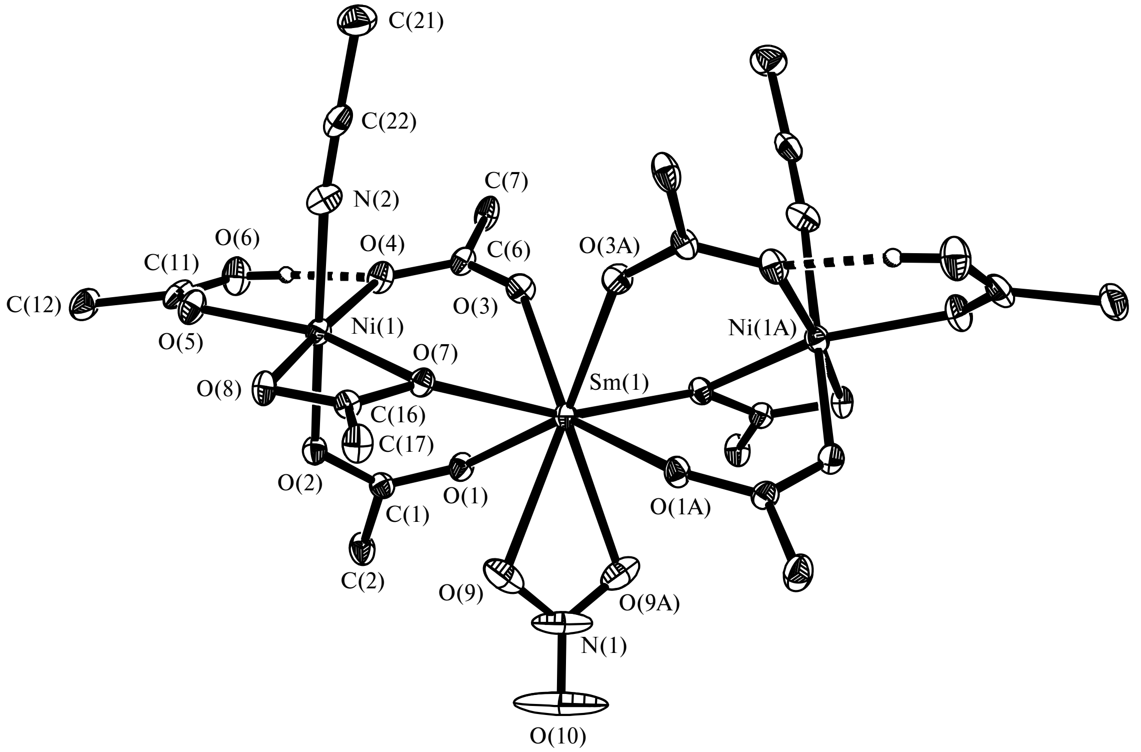

**Fig. 1.** The molecular structure of complex **6** (the solvent molecules, the methyl groups of the trimethylacetate anions, and the hydrogen atoms are not shown, thermal ellipsoids with the probability of 30%).

tablished the structure of compound **6**. Complex **6** crystallizes as a solvate with one molecule of MeCN. The complex molecule is symmetric and is located on the crystallographic axis $C_2$, which passes the Sm(1), N(1), and O(10) atoms of the nitrate group (Fig. 1). The core of the complex consists of two $Ni^{II}$ ions and one $Sm^{III}$ ion (Ni(1)...Sm(1) 3.790(1) Å, Ni(1)...Ni(1A) 7.209(2) Å, the angle Ni(1)—Sm(1)—Ni(1A) 144.04(2)°) symmetrically bound by four carboxylate bridges and two μ-O-atoms of the carboxy groups. One of the pivalate anions has a chelate coordination with the Ni atom (the principal bond distances and bond angles are given in Table 1). The nickel ion completes its environment to a distorted octahedron by coordination with one O atom of the HPiv molecule

**Table 1.** The principal bond distances (*d*) and bond angles (ω) for compounds **1**, **2**, **6**, **9**, and **10**

| Parameter (complex) | **1** | **2** | **6** | **9** | **10** |
|---|---|---|---|---|---|
| Bond distance | | | *d*/Å | | |
| M...Ln | 3.718(1) | 3.813(1) | 3.790(1) | 3.728(3) | 3.355(1), 3.360(1) |
| M...M | 7.236(1) | 7.444(2) | 7.209(2) | 7.249(7) | 6.713(2) |
| M—O(Piv) | 1.998(5)—2.317(5) | 1.921(6)—2.014(7) | 1.995(4)—2.231(3) | 2.006(5)—2.298(5) | 1.893(6)—1.927(7) |
| M—O(HPiv) | | | 2.074(4) | | |
| M—N(bpy) | 2.056(6), 2.063(6) | 2.000(7), 2.188(7) | | 2.061(5), 2.069(5) | |
| M—N(MeCN) | | | 2.069(5) | | |
| Ln—O(Piv) | 2.336(4)—2.394(5) | 2.307(6)—2.356(5) | 2.375(4)—2.391(3) | 2.362(5)—2.421(5) | 2.331(6)—2.412(6) |
| Ln—O($NO_3$) | 2.547(5) | 2.538(6) | 2.519(4) | 2.581(5) | |
| C—O(Piv) | 1.239(9)—1.271(8) | 1.216(9)—1.261(10) | 1.241(6)—1.281(6) | 1.244(7)—1.276(9) | 1.203(10)—1.250(11) |
| C—O(HPiv) | | | 1.218(6), 1.294(7) | | |
| Bond angle | | | ω/deg | | |
| M—Ln—M | 153.33(2) | 154.93(2) | 144.04(2) | 152.87(3) | 177.50(3) |
| O—C—O(Piv) | 121.5(6)—126.5(6) | 125.4(7)—126.0(7) | 119.0(4)—124.6(4) | 118.6(7)—125.3(6) | 122.1(10)—124.4(8) |

**Table 2.** Crystallographic parameters and structure refinement statistics for compounds **1**, **2**, **6**, **9**, and **10**

| Parameter | 1 | 2 | 6 | 9 | 10 |
|---|---|---|---|---|---|
| Molecular formula | $C_{52}H_{73}GdN_6Ni_2O_{15}$ | $C_{50}H_{70}Cu_2GdN_5O_{15}$ | $C_{46}H_{83}N_4Ni_2O_{19}Sm$ | $C_{52}H_{73}N_6Ni_2O_{15}Sm$ | $C_{56}H_{108}Cu_2EuNO_{16}$ |
| $M$/g mol$^{-1}$ | 1296.83 | 1265.44 | 1263.93 | 1289.93 | 1330.47 |
| $T$/K | 296(2) | 296(2) | 296(2) | 296(2) | 173(2) |
| Crystal system | Monoclinic | Monoclinic | Monoclinic | Monoclinic | Monoclinic |
| Space group | $C2/c$ | $C2/c$ | $C2/c$ | $C2/c$ | $P2_1/n$ |
| $a$/Å | 19.7904(6) | 20.075(4) | 18.913(6) | 19.772(19) | 14.2597(9) |
| $b$/Å | 15.7736(8) | 15.311(3) | 14.729(5) | 15.832(14) | 21.5048(13) |
| $c$/Å | 20.6007(4) | 20.924(4) | 22.578(7) | 20.63(2) | 23.4149(14) |
| $\beta$/deg | 101.874(9) | 104.481(3) | 92.245(10) | 101.795(18) | 99.6590(10) |
| $V$/Å$^3$ | 6293.2(4) | 6227(2) | 6285(4) | 6322(11) | 7078.4(7) |
| $Z$ | 4 | 4 | 4 | 4 | 4 |
| $d_{calc}$/g cm$^{-3}$ | 1.369 | 1.350 | 1.336 | 1.355 | 1.248 |
| $\mu$/mm$^{-3}$ | 1.694 | 1.790 | 1.580 | 1.568 | 1.526 |
| $\theta_{max}$/deg | 25.08 | 26.60 | 28.28 | 26.73 | 27.10 |
| $T_{min}/T_{max}$ | 0.5887/0.7503 | 0.7751/0.8139 | 0.5499/0.7975 | 0.7440/0.7440 | 0.6328/0.8263 |
| Number of measured reflections | 5743 | 18532 | 27549 | 19056 | 48742 |
| Number of reflections with $I > 2\sigma(I)$ | 3577 | 4314 | 6022 | 5113 | 8696 |
| $R_{int}$ | 0.0486 | 0.0845 | 0.0459 | 0.0460 | 0.0505 |
| GOOF | 1.090 | 1.069 | 1.149 | 1.107 | 1.048 |
| $R_1$ ($I > 2\sigma(I)$) | 0.0466 | 0.0639 | 0.0652 | 0.0561 | 0.0655 |
| $wR_2$ ($I > 2\sigma(I)$) | 0.1338 | 0.1773 | 0.1820 | 0.1716 | 0.1857 |

and one N atom of the MeCN molecule. The $Sm^{III}$ ion is in the environment of six O atoms of the monodentate coordinated $Piv^-$ anions and two O atoms of the chelate nitrate group. The coordination polyhedron of the samarium ion can be described best as a single-capped pentagonal bipyramid. A hydrogen bond is formed between the H atom of the coordinated pivalic acid and the O atom of the bridging carboxylate group, which has the following parameters: O(6)—H 0.84 Å, H...O(4) 1.77 Å, O(6)...O(4) 2.591 Å, the angle O(6)—H—O(4) 167.2° (see Fig. 1).

The compounds $[Ni_2Ln(Piv)_6(NO_3)(bpy)_2] \cdot MeCN$ ($Ln^{III}$ = Gd (**1**), Sm (**9**)) are isostructural (Table 2) and crystallize as solvates with one molecule of MeCN. In general the structure of the metal-nitrato-carboxylate core is similar to that in the case of compound **6**: the axis $C_2$ passes the central $Ln^{III}$ ion and the N and O atoms of the nitrate group. The metal atoms are symmetrically bound to four bridging and two chelato-bridging pivalate anions (Fig. 2, see Table 1). The nickel ions complete their environment to a distorted octahedron by the chelate coordination of the bpy molecule. It should be also noted that a replacement of the monodentate ligand with bpy leads to the increase in the angle Ni—Ln—Ni and decrease in the distance Ni...Ln (153.33(2)° and 3.718(1) Å for **1**, 152.87(3)° and 3.728(3) Å for **9**, respectively).

The complex $[Cu_2Gd(Piv)_6(NO_3)(bpy)_2] \cdot MeCN$ (**2**) (the structure was solved taking no the MeCN solvent molecule into account, which was not localized; the composition was determined by elemental analysis, see Experimental) is crystallographically isostructural to compounds **1** and **9**, but analysis of its structure showed that the carboxylate groups perform only the $\mu_2$-bridging function in the binding the $Cu^{II}$ and $Gd^{III}$ ions (Fig. 3, see Table. 1). Thus, the $Cu^{II}$ ions environment with allowance for the chelate coordination of the bpy molecule is a distorted square pyramid, $\tau$ = 0.23.[46] The Cu—Gd—Cu angle (154.93(2)°) and the Cu...Gd distance (3.813(1) Å) are close to the corresponding values found for the nickel analogs **1** and **9**.

The trinuclear complex $(NBu_4)[Cu_2Eu(Piv)_8]$ (**10**) is built of the $[Cu_2Eu(Piv)_8]^-$ anions, whose charge is compensated by the $NBu_4^+$ cations. In the $[Cu_2Eu(Piv)_8]^-$ anion, each $Cu^{II}$ ion is bound to the central $Eu^{III}$ ion with four bridging carboxylate groups. The complex anion is almost linear, the Cu—Eu—Cu angle is 177.50(3)° (Fig. 4, see Table 1). The $Cu^{II}$ ions in the $[Cu_2Eu(Piv)_8]^-$ anion are not equivalent and are located in the distorted square-planar environment of four O atoms (the Cu(1) and Cu(2) ions come out of the $O_4$ plane by 0.113(3) and 0.114(4) Å, respectively). The $Eu^{III}$ ion environment is a distorted quadrangular antiprism. Due to binding of the metal ions (pair-to-pair) to four carboxylate groups (like transition metal binuclear complexes $LM(\mu_2\text{-}O_2CR)_4ML$ (R = Me, $Bu^t$, Ph, *etc.*)), the Cu...Eu distances are considerably shortened, to 3.355(1) and 3.360(1) Å (*cf.* with complex **2**). The packing of ions in the crystal **10** is realized in such a way that the N atom of the tetrabutylammonium cation is located almost on the line drawn be-

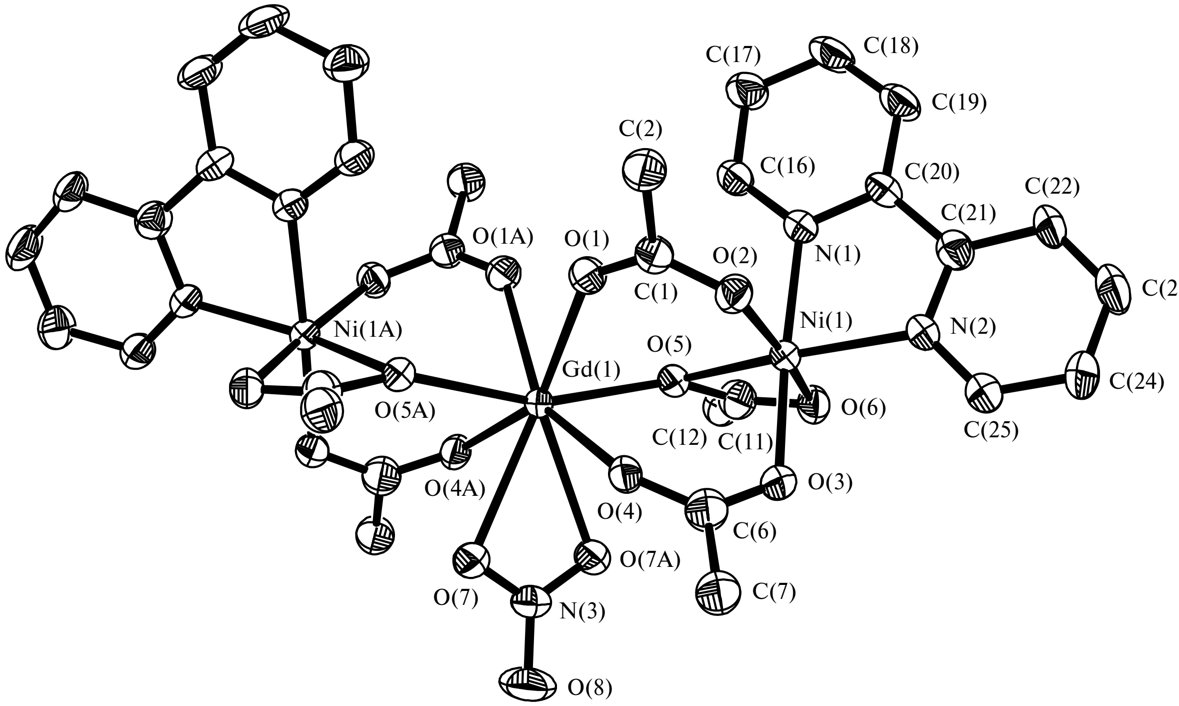

**Fig. 2.** The molecular structure of complex **1** (the solvent molecules, the methyl groups of the trimethylacetate anions, and the hydrogen atoms are not shown, thermal ellipsoids with the probability of 30%).

tween the proximate Cu ions (Cu...Cu 8.062(2) Å) of two neighboring $[Cu_2Eu(Piv)_8]^-$ fragments (Fig. 5).

**Magnetic properties of complexes.** Magnetic properties of complexes **4**, **5**, **7**, and **8** were characterized by the measurement of the temperature dependence of their magnetic susceptibility ($\chi_M$) in the range of 2—300 K (Fig. 6), of compounds **1**, **5**, and **12** in the range of 5—300 K, and of **2** and **11** in the range of 6—300 K.

The $\chi_M T$ value for complex **4** ($Ni_2Ln$ metal core, diamagnetic $Ln^{III}$ ion) remains almost unchanged in the

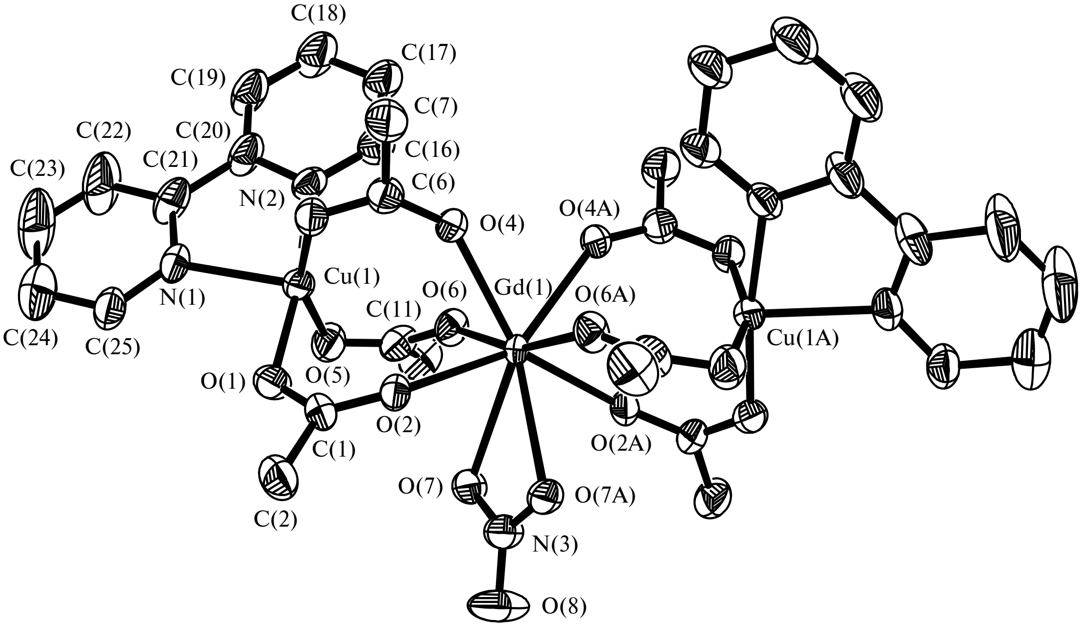

**Fig. 3.** The molecular structure of complex **2** (the solvent molecules, the methyl groups of the trimethylacetate anions, and the hydrogen atoms are not shown, thermal ellipsoids with the probability of 30%).

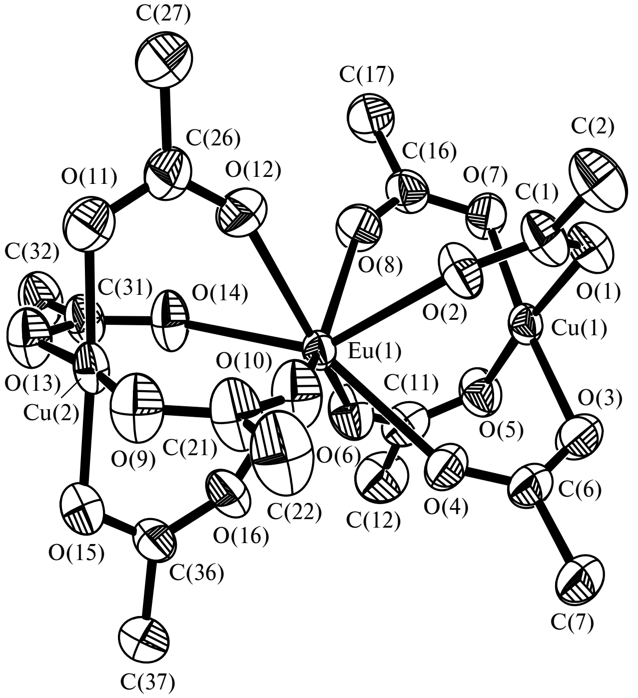

**Fig. 4.** The structure of the anionic fragment of complex **10** (the methyl groups of the trimethylacetate anions and the hydrogen atoms are not shown, thermal ellipsoids with the probability of 30%).

region of temperatures 300—20 K (2.61—2.49 cm$^3$ K mol$^{-1}$, $\mu_{\text{eff}}$ = 4.57—4.46 $\mu_B$) and is somewhat higher than the expected spin-only value for the complex containing two isolated Ni$^{\text{II}}$ ions with $S = 1$ (2 cm$^3$ K mol$^{-1}$, $\mu_{\text{eff}} = 4\ \mu_B$). In the range of 20—2 K, the $\chi_M T$ value for complex **4** decreases to 0.93 cm$^3$ K mol$^{-1}$ ($\mu_{\text{eff}} = 2.73\ \mu_B$, $T = 2$ K), which can indicate the domination of the antiferromagnetic-type exchange interactions in this compound, or can be a result of the zero-field splitting (ZFS) of spin levels of Ni$^{\text{II}}$ ion.

Since compound **4** contains two paramagnetic centers (the Ni$^{\text{II}}$ ions) bound through the diamagnetic Ln$^{\text{III}}$ ion, its magnetic properties can be described by the model of a dimer for paramagnetic ions with the spins $S = 1$. The $\chi_M T$ *vs.* $T$ dependence for compound **4** can be satisfactorily interpreted in terms of two models, corresponding to the exchange Hamiltonian $H_{\text{ex}}$ given below (Eq. (1)) and the Hamiltonian $H_{\text{ZFS}}$, which takes ZFS into account (Eq. (2)):

$$H_{\text{ex}} = -2J_{\text{ex}}S_1S_2, \tag{1}$$

$$H_{\text{ZFS}} = D[S_z^2 - (1/3)S(S+1)], \tag{2}$$

where $J_{\text{ex}}$ is the parameter characterizing energy of the exchange interaction between Ni$^{\text{II}}$ ions (in contrast to the quantum number of total angular momentum $J$, which is defined as a sum of the spin and orbital moment quantum numbers $S + L$ and will be used below), $D$ is the value of ZFS for the Ni$^{\text{II}}$ ion. In the first model, the experimental data were optimized using an analytical expression obtained by the insertion of eigenvalues of the Hamiltonian (1) into the Van Vleck equation,[47] whereas in the second model, the data were simulated by the full-matrix diagonalization of the Hamiltonian (2) using the Mjollnir software.[48] In both cases, a member, which takes into account for the temperature-independent paramagnetism (tip), was also introduced. Possible intermolecular interactions were considered in terms of the molecular field model:[49,50]

$$\chi_{\text{MF}} = \chi_M/[1 - zJ'\chi_M/(N_A g^2 \mu_B{}^2)]. \tag{3}$$

To avoid over-parametrization, the model, which includes the exchange interactions and ZFS at the same time, was not used since determination of both these pa-

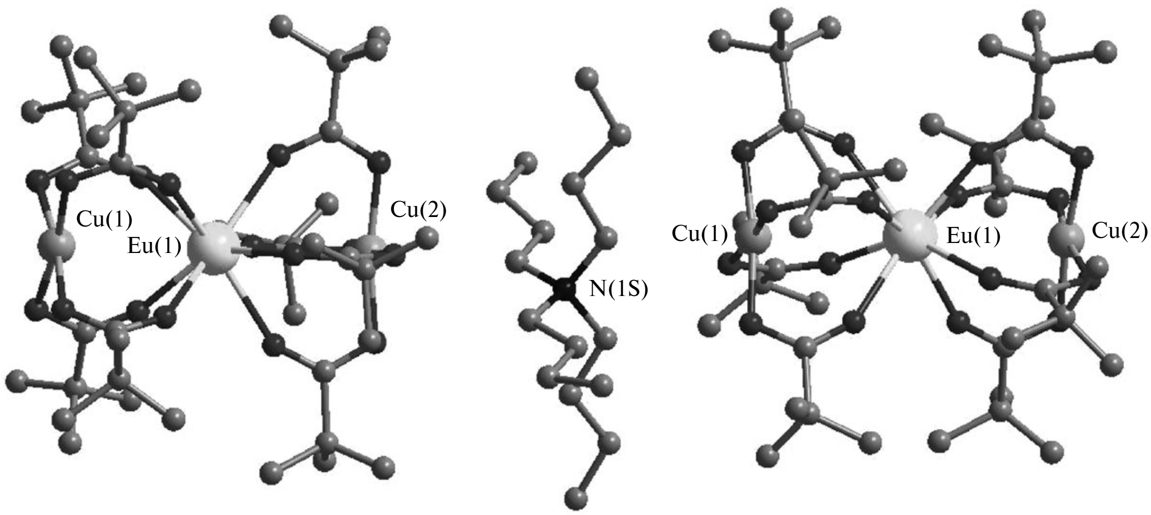

**Fig. 5.** The packing pattern of the ionic complex **10** in the crystal (the hydrogen atoms are not shown).

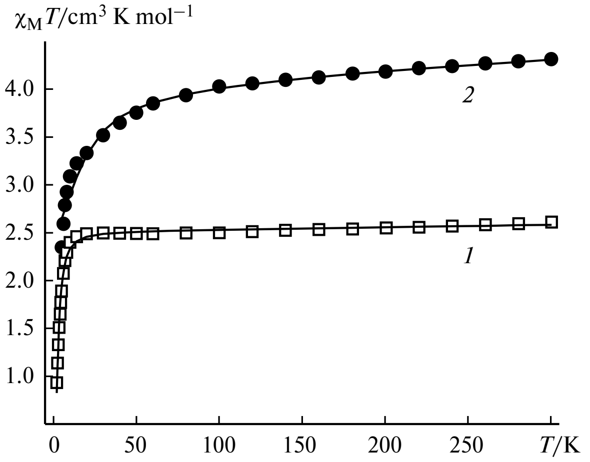

**Fig. 6.** The $\chi_M T$ *vs.* $T$ dependences for complexes **4** (*1*) and **5** (*2*); the dots are the experiment, the curves are the calculation.

rameters when their values are comparable solely on the basis of the $\chi_M T$ *vs.* $T$ dependence is not correct.

Analysis of the experimental data gave the following optimum parameters: $J_{ex} = -1.0(3)$ cm$^{-1}$, $g = 2.24(1)$ and $zJ' = +0.9(1)$ cm$^{-1}$, tip = $2.4(9) \cdot 10^{-4}$ ($R^2 = 2.6 \cdot 10^{-4}$, where $R^2 = \Sigma[(\chi_M T)_{exp} - (\chi_M T)_{theor}]^2/[\Sigma(\chi_M T)_{exp}{}^2]$) in terms of the first model (see Fig. 6) or $D = 6.0(5)$ cm$^{-1}$, $g = 2.227(1)$, $zJ' = +0.05(1)$ cm$^{-1}$, tip = $3.6(5) \cdot 10^{-4}$ ($R^2 = 2.5 \cdot 10^{-3}$) in terms of the second model. The best agreement between the experimental data and the calculated curve was achieved in terms of the model for an exchange dimer. It should be noted that the very possibility of simulation of the $\chi_M T$ *vs.* $T$ dependence curve with allowance only for the ZFS (without allowance for the intramolecular exchange interactions) indicate that the $J_{ex}$ value was close to zero. In both cases, the intermolecular interactions were found to have ferromagnetic character. A low (in modulus) value of $J_{ex}$ is in good agreement with the large distance between the Ni$^{II}$ ions in complex **4** (about 7.2 Å, as far as it can be suggested by analogy with complex **6**, whose structure was determined by X-ray diffraction). Previously,[51] it has been shown that the exchange interactions of the Ni$^{II}$ ions were very poorly transmitted already at the distance of 6.0 Å even through the system of conjugated bonds.

In the case of complex **5** (Ni$_2$Pr metal core), a decrease in temperature from 300 to 5 K causes a monotonous decrease in the $\chi_M T$ value from 4.32 to 2.35 cm$^3$ K mol$^{-1}$ ($\mu_{eff}$ lie within 5.88—5.08 $\mu_B$, respectively) (see Fig. 6).

At present, there are no models which adequately describe exchange interactions of 3d- and 4f-metals, which is attributed to the principal differences in the structure of these element electron shells described by the models of LS- and JJ-coupling, respectively (except Gd$^{III}$, which is frequently considered as a "spin-only" ion without an orbital contribution). The Pr$^{III}$ ion electron structure is described by a spin number of the total angular momentum $J$ ($J = L + S$), the ground state is represented by the term $^3H_4$, which is split to a number of sub-levels (differing in the $m_J$ values).

In the first approximation, magnetic properties of complex **5** can be represented as a superposition of the contributions of two independent Ni$^{II}$ ions with the spin $S = 1$ and the Pr$^{III}$ ion with $J = 4$:

$$\chi_M T(\mathrm{Ni_2Pr}) = 2\chi_M T(\mathrm{Ni}) + \chi_M T(\mathrm{Pr}) = \\ = g(\mathrm{Ni})^2 S_{\mathrm{Ni}}(S_{\mathrm{Ni}} + 1)/4 + \chi_M T(\mathrm{Pr}). \qquad (4)$$

The splitting of the Pr$^{III}$ levels is described in terms of the model based on the Hamiltonian

$$H = \Delta J_z{}^2, \qquad (5)$$

where $\Delta$ is the parameter of splitting by the crystal field of axial symmetry. Similar model was suggested in the work.[52] The formula for $\chi_{\|}$ obtained by the authors of this work was used several times for the description of magnetic properties of Pr$^{III}$ compounds in terms of the Hamiltonian (5) and in the assumption that $\chi = \chi_{\|}$, *i.e.*, without accounting for the contribution of $\chi_{\perp}$.[53—55]

In the present work, the Pr$^{III}$ ion energy levels were determined using a full-matrix diagonalization of the Hamiltonian (5). The insertion of the values obtained into the Van Vleck equation enabled to calculate of the $\chi_M T$(Pr) value (see Eq. (4)). The calculation was performed using the Mjollnir software.[48] The $\chi_M T$ *vs.* $T$ dependence for compound **5** can be satisfactorily described by a set of parameters $g$(Pr) = 0.81, $g$(Ni) = 2.21, $\Delta = 50.0$ cm$^{-1}$, tip = 0.0009 ($R^2 = 5.6 \cdot 10^{-4}$). Consideration the Ni$^{II}$ ions exchange interactions in terms of the Hamiltonian (1) or the intermolecular interactions in terms of the molecular field model (see Eq. (3)) did not lead to a decrease in $R^2$. Note that the $g$-factor of the Pr$^{III}$ ion in complex **5** obtained by simulation is close to the value for the free ion ($g_J$(Pr) = 0.8),[56] that confirms a weak effect of the ligand coordinations on the electron structure of the lanthanide ions. A possibility of satisfactory description of magnetic properties of complex **5** without allowance for the exchange interactions can indicate the low $J_{ex}$ values, that agrees with the results obtained for complex **4**.

For compound **7** (Ni$_2$Eu), a monotonous decrease in the $\chi_M T$ value from 3.70 to 2.40 cm$^3$ K mol$^{-1}$ (the $\mu_{eff}$ values lie within 5.44—4.38 $\mu_B$) was observed when temperature decreased from 300 to 10 K, whereas further decrease in temperature to 2 K caused a sharp drop in the $\chi_M T$ value to 0.90 cm$^3$ K mol$^{-1}$ ($\mu_{eff}$ = 2.69 $\mu_B$, Fig. 7). Magnetic properties of compounds containing the Eu$^{III}$ ion are usually described taking into account the population of the ground (7F$_0$) and low-lying exited states ($^7$F$_J$, where $J$ = 1, 2, 3, *etc.*).[57—59]

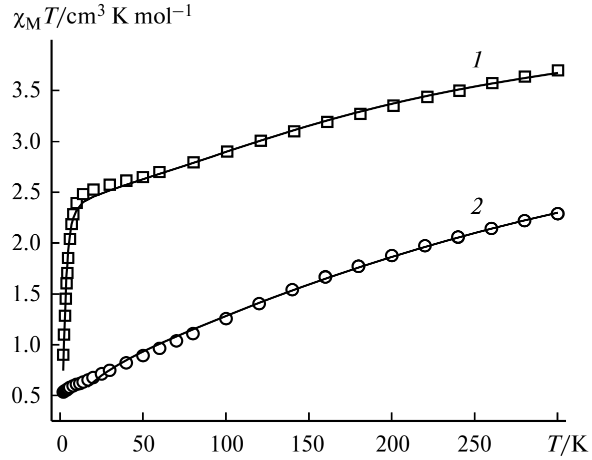

**Fig. 7.** The $\chi_M T$ *vs.* $T$ dependences for the europium-containing complexes **7** (*1*) and **3** (*2*); the dots are the experiment, the curves are the calculation.

The $\chi_M T$ *vs.* $T$ dependence for complex **7** can be described in terms of the following model:

$$\chi_M T(\mathrm{Ni_2Eu}) = \chi_M T(\mathrm{Ni_2}) + \chi_M T(\mathrm{Eu}), \qquad (6)$$

where the $\chi_M T(\mathrm{Ni_2})$ member takes into account the exchange interactions of the Ni$^{II}$ ions (Hamiltonian (1); by analogy with compound **4**), whereas $\chi_M T$(Eu) is calculated using analytical expressions obtained earlier.[57—59] The rest of possible exchange interactions were considered in terms of the molecular field model (see Eq. (3)), a contribution of the temperature-independent paramagnetism (which can be caused by the presence of Ni$^{II}$ ions in the complex) was also taken into account. The best agreement of the experimental data and the calculated curve was achieved with the parameter values $\lambda$ = 400(35) cm$^{-1}$, $J_{\mathrm{ex(Ni—Ni)}} = -1.10(5)$ cm$^{-1}$, $zJ' = 1.3(5)$ cm$^{-1}$, $g$(mol. field) = = 2.1(5), tip = 0.0003(1) ($R^2 = 3.5 \cdot 10^{-4}$). The $g$(Ni) value was fixed on the level of 2.15. Since the $g$-factor of the main term of the Eu$^{III}$ ion is equal to zero and for all the exited states it is equal to 3/2,[60] the $g$(mol. field) falls into the "reasonable" range of expected values (between $g$(Eu) and $g$(Ni)). The $\lambda$ value for the Eu$^{III}$ ion is close to typical values.[57,60] Note that approximation of the experimental $\chi_M T$ *vs.* $T$ dependence for complex **7** without consideration of the exchange interactions between the nickel ions (by the equation analogous to formula (4)) gives about the same value of $\lambda$ for Eu$^{III}$ as found previously, but the curve kink at 10 K cannot be reproduced.

For complex **3** (Cu$_2$Eu), a monotonous decrease in $\chi_M T$ from 2.29 to 0.54 cm$^3$ K mol$^{-1}$ is observed upon the decrease of temperature from 300 to 2 K ($\mu_{\mathrm{eff}}$ decreases from 4.28 to 2.09 $\mu_B$, see Fig. 7).

The $\chi_M T$ *vs.* $T$ dependence for complex **3** can be described in terms of the model similar to equation (4) (with the difference that $\chi_M T$(Eu), calculated using the known formula,[57—59] was inserted instead of $\chi_M T$(Pr), and instead of $\chi_M T$(Ni) was used $\chi_M T$(Cu) with $g$(Cu) and $S_{\mathrm{Cu}}$, respectively). Possible exchange interactions were considered in terms of the molecular field model (see Eq. (3)). This approach resulted in a satisfactory agreement of the curve at temperatures 16 K and higher, whereas the minimum $R^2$ corresponds to the parameters $\lambda$ = 437(24) cm$^{-1}$, $zJ' = -7.0(4)$ cm$^{-1}$, tip = 0.0014(1) ($R^2 = 2.2 \cdot 10^{-4}$). To avoid over-parametrization, the $g$(Cu)-factor was fixed on the level of 2.13 (that corresponds to the ESR data, see below), whereas the $g$-factor of molecular field was fixed on the level of 1.5. Like in the case of complex **7**, the $\lambda$ value of the Eu$^{III}$ ion is close to the values reported earlier.[57—59] The data obtained do not allow us to unambiguously conclude on the absence of the exchange interactions between Cu$^{II}$ ions or between Cu$^{II}$ ion and Eu$^{III}$ ion, but the very possibility of simulation of experimental data in terms of the model suggested indicates that the energy of such interactions, if they do exist, is low.

The ESR spectrum of compound **3** at room temperature has the pattern typical of the copper(II) mononuclear complexes. Two signals are observed in the spectrum, which can be interpreted as $g_\perp$ = 2.061 and $g_\parallel$ = 2.272 ($g_{\mathrm{av}}$ = 2.131), $A$ = 193 G (Fig. 8). The absence of signs of the exchange interactions of the Cu$^{II}$ ions in the ESR spectrum can be explained by a large distance between these ions in the complex. In addition, it indicates low efficiency of the Eu$^{III}$ ion bound by pivalates as a bridge for the transmission of the exchange interactions. This conclusion agrees with the results of interpretation of the $\chi_M T$ *vs.* $T$ dependence for complex **3**. The $zJ'$ value found for complex **3** is apparently overestimated since the registration of the resolved structure of HFC on the Cu$^{II}$ ions indicate that both the intramolecular and intermolecular exchange interactionss are weak (<1 cm$^{-1}$). Though reasons for the overestimation of $zJ'$ are not yet clear, the data of magnetochemical and ESR studies unambiguous-

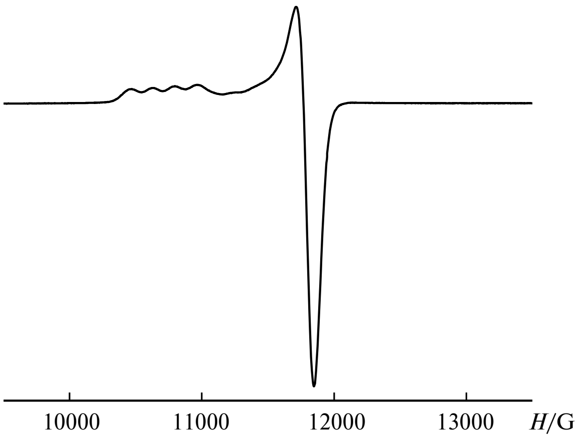

**Fig. 8.** The ESR spectrum (the Q-region, 34 GHz, ~20 °C, solid compound) of complex **3**.

ly indicate that the exchange interactions between $Eu^{III}$ and $Cu^{II}$ ions are weak.

In the case of compound **1** ($Ni_2Gd$ metal core), a monotonous increase in $\chi_M T$ from 9.94 to 10.2 $cm^3$ K $mol^{-1}$ is observed on the decrease of temperature from 300 to 10 K ($\mu_{eff}$ is within 8.92—9.01 $\mu_B$), after which the $\chi_M T$ value sharply drops to 9.91 $cm^3$ K $mol^{-1}$ at 5 K ($\mu_{eff}$ = 8.91 $\mu_B$) (Fig. 9). The $\chi_M T$ value for complex **1** at 300 K is somewhat higher than the expected spin-only values of $\chi_M T$ for the complex containing two separate $Ni^{II}$ ions with $S = 1$ and the $Gd^{III}$ ion with $S = 7/2$ (9.875 $cm^3$ K $mol^{-1}$, $\mu_{eff}$ = 8.89 $\mu_B$), which is probably attributed to the fact that the *g*-factor for $Ni^{II}$ differs from the spin-only value.

Magnetic properties of compound **1** can be simulated using the model based on the following Hamiltonian:

$$H = -2J_{ex(Ni-Gd)}(S_{Ni(1)}S_{Gd} + S_{Ni(2)}S_{Gd}) - - 2J_{ex(Ni-Ni)}(S_{Ni(1)}S_{Ni(2)}), \quad (7)$$

where $J_{ex(Ni-Gd)}$ and $J_{ex(Ni-Ni)}$ are the exchange integrals responsible for the interactions of the $Ni^{II}$—$Gd^{III}$ and $Ni^{II}$—$Ni^{II}$ ions, respectively. The calculation was performed by the full-matrix diagonalization using the Mjollnir software.[48] The simulation of the $\chi_M T$ *vs.* $T$ dependence for complex **1** gave the parameters $J_{ex(Ni-Gd)} = 0.105(5)$ $cm^{-1}$, $J_{ex(Ni-Ni)} = -0.70(5)$ $cm^{-1}$, $g(Ni) = 2.015(1)$, $g(Gd) = 2.00$ (fixed value), tip = 0.0001 ($R^2 = 1.28 \cdot 10^{-5}$).

In the case of complex **8** ($Ni_2Gd$), the $\chi_M T$ value monotonously increases from 9.47 to 10.01 $cm^3$ K $mol^{-1}$ upon the decrease in temperature in the range of 300—10 K ($\mu_{eff}$ within 8.70—8.95 $\mu_B$), after which a sharp decrease in $\chi_M T$ to 8.13 $cm^3$ K $mol^{-1}$ is observed at 2 K ($\mu_{eff}$ = = 8.07 $\mu_B$) (see Fig. 9). The $\chi_M T$ value for complex **8** at 300 K is somewhat lower than the expected for the spin-only value of $\chi_M T$ (9.875 $cm^3$ K $mol^{-1}$) for the $Ni_2Gd$ system (see above) and can be explained by the presence of diamagnetic or paramagnetic (with the spin smaller than the spin of **8**) impurity.

The $\chi_M T$ *vs.* $T$ dependence was simulated using the Hamiltonian (7), and the best agreement between the experimental data and the calculated curve was achieved with the parameters $J_{ex(Ni-Gd)} = 0.44(2)$ $cm^{-1}$, $J_{ex(Ni-Ni)} = -2.25(5)$ $cm^{-1}$, $g(Ni) = g(Gd) = 2.00$ (fixed value), the molar content (ρ) of the impurity with $S = 1$ was equal to 5.5% ($R^2 = 1.5 \cdot 10^{-4}$). Ferromagnetic interaction exists between the $Ni^{II}$ and $Gd^{III}$ ions, whereas the exchange between two $Ni^{II}$ ions is antiferromagnetic, like in the complex **1** described above.

Compound **1** can be considered as a result of substitution of the neutral HPiv and MeCN molecules in complex **8** by bpy. As it follows from the comparison of properties of complexes **1** and **8**, the replacement of HPiv and MeCN with bpy led to a significant weakening the exchange interactions both in the pairs of ions $Ni^{II}$—$Gd^{III}$ and between the "terminal" $Ni^{II}$ ions, that can be caused by the electronic influence of bipyridyl or the changes in geometric characteristics of the bridging groups.

For comparison, we studied magnetic properties of the binuclear heterometallic complex $[(\eta^2\text{-bpy})NiGd(Piv)_5(H_2O)] \cdot 2HPiv$ (**12**) obtained earlier[43] (Fig. 10). A monotonous growth of $\chi_M T$ from 9.06 to 11.16 $cm^3$ K $mol^{-1}$ with the temperature decrease from 300 to 5 K ($\mu_{eff}$ within 8.52—9.45 $\mu_B$) can be the sign of domination of ferromagnetic exchange interactions in this compound. The $\chi_M T$ value at 300 K is slightly higher than the spin-only value expected for the isolated $Ni^{II}$ and $Gd^{III}$ ions (8.875 $cm^3$ K $mol^{-1}$).

The $\chi_M T$ *vs.* $T$ dependence for complex **12** was simulated by the full-matrix diagonalization using the Hamiltonian for a binuclear complex:

$$H = -2J_{ex(Ni-Gd)}S_{Ni(1)}S_{Gd}. \quad (8)$$

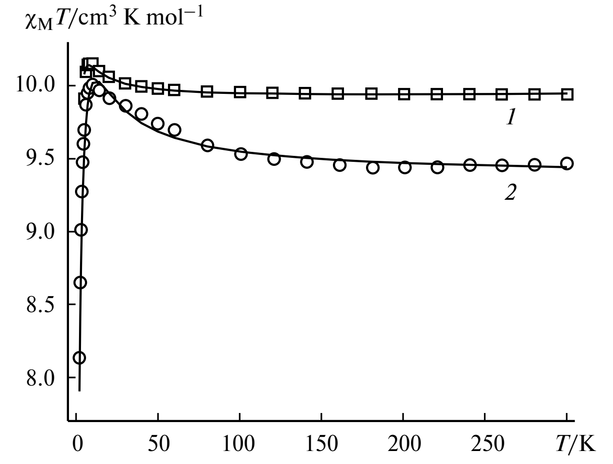

**Fig. 9.** The $\chi_M T$ *vs.* $T$ dependences for complexes **1** (*1*) and **8** (*2*) with the $Ni_2Gd$ metal core; the dots are the experiment, the curves are the calculation.

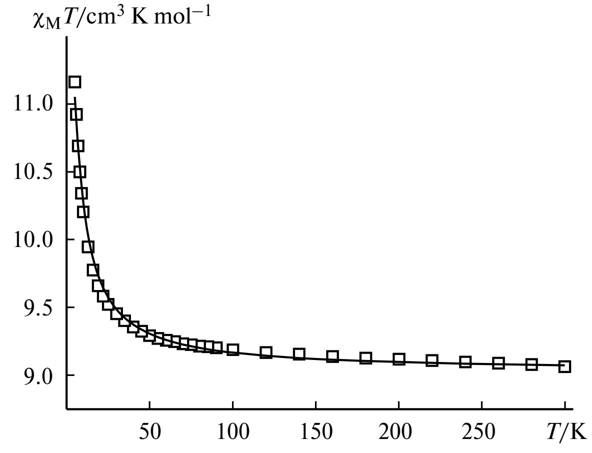

**Fig. 10.** The $\chi_M T$ *vs.* $T$ dependence for complex **12** with the NiGd metal core; the dots are the experiment, the curves are the calculation.

The best agreement of the experimental data and the calculated curve was achieved with $J_{ex(Ni-Gd)}$ = = 0.44(5) cm$^{-1}$, $g$(Ni) = 2.14(1) (with $g$(Gd) = 2.00; $R^2 = 1.92 \cdot 10^{-5}$) (see Fig. 10).

In the case of compound **2** ($Cu_2Gd$ metal core), a decrease in the $\chi_M T$ value from 9.68 to 9.31 cm$^3$ K mol$^{-1}$ is observed upon the decrease of temperature from 300 to 40 K ($\mu_{eff}$ decreases from 8.80 to 8.63 $\mu_B$) (Fig. 11), that is somewhat higher than the spin-only value of $\chi_M T$ expected for two isolated Cu$^{II}$ ions and one Gd$^{III}$ ion (8.625 cm$^3$ K mol$^{-1}$). Below 40 K, the $\chi_M T$ value grows and reaches 10.02 cm$^3$ K mol$^{-1}$ at 6 K ($\mu_{eff}$ = 8.95 $\mu_B$).

Magnetic properties of complex **2** were simulated in terms of the model based on the Hamiltonian similar to Eq. (7) with the only difference that the $S_{Cu}$ operators were taken instead of $S_{Ni}$, and the corresponding exchange integrals $J_{ex}$ related the exchange interactions between Cu$^{II}$ and Gd$^{III}$ ions. The calculation was performed by the full-matrix diagonalization using the Mjollnir software.[48] The best agreement of the experimental and the calculated curves was achieved with $J_{ex(Cu-Gd)}$ = 0.32 cm$^{-1}$, $J_{ex(Cu-Cu)}$ = 0 cm$^{-1}$, $g$(Cu) = 2.20, $g$(Gd) = 2.02, and tip = $2.5 \cdot 10^{-3}$ ($R^2 = 3.8 \cdot 10^{-5}$) (see Fig. 11).

For complex **11** ($Cu_2Gd$ metal core), the $\chi_M T$ value almost does not change and varies from 9.24 to 9.13 cm$^3$ K mol$^{-1}$ ($\mu_{eff}$ = 8.61—8.56 $\mu_B$) upon the decrease in temperature from 300 to 50 K (see Fig. 11). Below 50 K, the $\chi_M T$ value rises, reaching 9.86 cm$^3$ K mol$^{-1}$ ($\mu_{eff}$ = 8.67 $\mu_B$) at 6 K. The experimental data were processed as described above for compound **2**. The best agreement of the experimental data and the calculated curve was obtained with $J_{ex(Cu-Gd)}$ = 0.23 cm$^{-1}$, $J_{ex(Cu-Cu)}$ = = 0 cm$^{-1}$, $g$(Cu) = 2.18, $g$(Gd) = 2.03, tip = $8 \cdot 10^{-4}$ ($R^2 = 8.4 \cdot 10^{-6}$) (see Fig. 11).

In this case, the weak exchange interactions of the neighboring copper(II) and gadolinium(III) ions are observed, which are comparable to the values obtained for complex **2**. Shortening the Cu...Cu distance (from 7.443(2) for **2** to 6.7136(11) for Å **10** (the isostructural analog with Eu)) does not lead to the occurence of the exchange interactions between the copper(II) ions in terms of the suggested model, that is yet another confirmation of a conclusion made earlier regarding the low efficiency of the Gd$^{III}$ and Eu$^{III}$ ions as "bridges" in the transmission of exchange interactions.

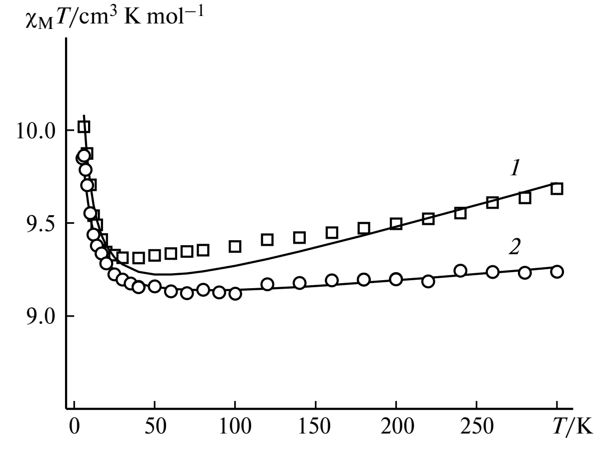

**Fig. 11.** The $\chi_M T$ *vs.* $T$ dependences for complexes **2** (*1*) and **11** (*2*) with the $Cu_2Gd$ metal core; the dots are the experiment, the curves are the calculation.

In the present work, we developed approaches to the preparation of a number of trinuclear heterometallic complexes containing the {M$^{II}$—Ln$^{III}$—M$^{II}$} metal core, where M$^{II}$ = Ni, Cu; Ln$^{III}$ = La, Pr, Sm, Eu, Gd. In these compounds, the metal ions are bound to the bridging pivalate anions, and the lanthanide ion is placed between the 3d-metal ions. The $\chi_M T$ *vs.* $T$ dependence for compounds containing Pr$^{III}$, Sm$^{III}$, and Eu$^{III}$ ions can be interpreted in the assumption that the exchange interactions between 3d- and 4f-metal ions are absent, however, the weak antiferromagnetic interactions between the 3d-metal ions "through the lanthanide" do exist. Properties of complex **4** with the Ni—La—Ni metal core, in which the nickel(II) ions are bound *via* a diamagnetic bridge, evidence in favor of the presence of such exchange interactions between the 3d-metal ions. At the same time, magnetic properties of the gadolinium-containing complexes can be interpreted with allowance for the weak ferromagnetic interactions Ni—Gd or Cu—Gd. Analysis of the data obtained allows us to draw a conclusion that the Ni—Pr, Ni—Eu, and Cu—Eu interactions are not of ferromagnetic character, they are weak and the contribution of such interactions to the decrease in $\chi_M T$ upon the temperature decrease cannot be distinguished from the influence of the spin-orbit coupling and interactions between the 3d-metal ions.

An approach to the synthesis of heterometallic complexes developed in the present work can be apparently used for the synthesis of a wide range of coordination compounds with different lanthanide ions. The gadolinium-containing complexes are found the most promising among the compounds under study for the preparation of molecules with a high-spin ground state.

## Experimental

The following solvents and reactants were used in the synthesis without additional purification: MeCN, *o*-xylene, pivalic acid (99%, Alfa Aesar), 2,2´-bipyridyl (99%, Alfa Aesar), $Bu_4NOH$ (40% aqueous solution, Alfa Aesar), $Ln(NO_3)_3 \cdot 6H_2O$ (Ln = La, Pr, Sm, Eu, Gd; >99%, Lankhit). The starting compounds $Ni_9(OH)_6(Piv)_{12}(HPiv)_4$, $(bpy)_2M_2(Piv)_4(H_2O)$ (M = Co, Ni), and $Cu_2(Piv)_4(HPiv)_2$ were obtained according to the known procedures.[61—64] A complex $[(\eta^2\text{-bpy})NiGd(Piv)_5(H_2O)] \cdot 2HPiv$ (**12**) was synthesized according to the procedure described earlier.[43] IR spectra for complexes **1—9** were recorded on a Specord M-80 IR spectrophotometer in KBr pellets, for **10** and **11**, on a Perkin—Elmer Spectrum 65LS Fourier-transform IR spectrophotometer in KBr pellets. Microanalysis for compounds was performed on a Carlo Erba analyzer. Static magnetic susceptibility was measured on Quantum—Design MPMS*XL* (compounds **1**—**5**, **8**, **11**) and Quantum Desing PPMS (compound **12**) magnetometers in the temperature range of 2—300 K and magnetic field 5 kE. The paramagnetic components of magnetic susceptibility $\chi$ were determined with allowance for the diamagnetic contribution estimateded on the basis of Pascal constants. Effective magnetic moments were calculated using the formula $\mu_{\mathrm{eff}}(T) = \{[3k/(N_{\mathrm{A}}\mu_{\mathrm{B}}{}^2)]\chi T\}^{1/2}\ \ (8\chi_{\mathrm{M}}T)^{1/2}$. ESR spectra in the Q-band for the sample **3** in the solid state were measured on a Bruker Elexsys E-580 spectrometer at ~20 °C.

**Bis($\eta^2$-2,2´-bipyridyl-*N,N´*)($\eta^2$-nitro-*O,O´*)tetrakis($\mu_2$-trimethylacetato-*O,O´*)bis($\mu_2$,$\eta^2$-trimethylacetato-*O,O,O´*)dinickel(II)-gadolinium(III) acetonitrile solvate, $[Ni_2Gd(Piv)_6(NO_3)(2,2´\text{-}bpy)_2]\cdot MeCN$ (1).** *A*. Weighed amounts of $(bpy)_2Ni_2(Piv)_4(H_2O)$ (0.51 g, 0.60 mmol) and $Gd(NO_3)_3\cdot 6H_2O$ (0.18 g, 0.40 mmol) in MeCN (40 mL) were stirred on heating (80 °C) until the reactants were completely dissolved (30 min). A green solution that formed was concentrated to the volume of 10 mL and kept at ~20 °C for 24 h. The green crystals that formed, suitable for X-ray diffraction, were separated from the solution by decantation, washed with cold MeCN, and dried in air. The yield of compound **1** was 0.53 g (67%, calculated for nickel). Found (%): C, 48.1; H, 5.5; N, 6.5. $C_{52}H_{73}GdN_6Ni_2O_{15}$. Calculated (%): C, 48.16; H, 5.67; N, 6.48. IR, $\nu$/cm$^{-1}$: 2968 m, 2932 m, 2864 m, 1716 w, 1684 w, 1664 w, 1636 m, 1608 s, 1584 s, 1568 s, 1536 m, 1520 m, 1484 m, 1444 m, 1436 m, 1416 m, 1376 m, 1360 m, 1316 m, 1224 m, 1172 w, 1156 w, 1104 w, 1028 m, 936 w, 908 w, 808 m, 792 m, 768 m, 740 m, 652 m, 636 m, 604 m, 564 w, 476 w, 420 m.

*B*. A mixture of the complex **8** (0.15 g, 0.12 mmol) and 2,2´-bpy (0.037 g, 0.24 mmol) in MeCN (30 mL) was stirred at 80 °C for 30 min. A green solution that formed was cooled to ~20 °C. The green crystals formed within 12 h and suitable for X-ray diffraction were separated from the solution by decantation, washed with cold MeCN, and dried in air. The yield of compound **1** was 0.13 g (82%, calculated for nickel). Found (%): C, 48.1; H, 5.7; N, 6.4. $C_{52}H_{73}GdN_6Ni_2O_{15}$. Calculated (%): C, 48.16; H, 5.67; N, 6.48. IR, $\nu$/cm$^{-1}$: 2968 m, 2932 m, 2864 m, 1716 w, 1684 w, 1664 w, 1636 m, 1608 s, 1584 s, 1568 s, 1536 m, 1520 m, 1484 m, 1444 m, 1436 m, 1416 m, 1376 m, 1360 m, 1316 m, 1224 m, 1172 w, 1156 w, 1104 w, 1028 m, 936 w, 908 w, 808 m, 792 m, 768 m, 740 m, 652 m, 636 m, 604 m, 564 w, 476 w, 420 m.

**Bis($\eta^2$-2,2´-bipyridyl-*N,N´*)($\eta^2$-nitro-*O,O´*)hexakis($\mu_2$-trimethylacetato-*O,O´*)dicopper(II)gadolinium(III) acetonitrile solvate, $[Cu_2Gd(Piv)_6(NO_3)(2,2´\text{-}bpy)_2]\cdot MeCN$ (2).** Weighed amounts of $Cu_2(Piv)_4(HPiv)_2$ (0.2 g, 0.3 mmol) and 2,2´-bpy (0.09 g, 0.6 mmol) in MeCN (40 mL) were stirred at 80 °C for 30 min to result in the formation of a greenish blue solution, that was followed by addition of $Gd(NO_3)_3\cdot 6H_2O$ (0.09 g, 0.2 mmol) and stirring at 80 °C for 1 h. A green solution obtained was filtered and kept at ~20 °C for 24 h. The green crystals formed were suitable for X-ray diffraction, they were separated from the solution by decantation, washed with MeCN, and dried in air. The yield of compound **2** was 0.25 g (65%, calculated for copper). Found (%): C, 47.9; H, 5.5; N, 6.4. $C_{52}H_{73}Cu_2GdN_6O_{15}$. Calculated (%): C, 47.80; H, 5.63; N, 6.43. IR, $\nu$/cm$^{-1}$: 2968 m, 2932 m, 2864 m, 1716 w, 1684 w, 1664 w, 1636 m, 1608 s, 1584 s, 1568 s, 1536 m, 1520 m, 1484 m, 1444 m, 1436 m, 1416 m, 1376 m, 1360 m, 1316 m, 1224 m, 1172 w, 1156 w, 1104 w, 1028 m, 936 w, 908 w, 808 m, 792 m, 768 m, 740 m, 652 m, 636 m, 604 m, 564 w, 476 w, 420 m.

**Bis($\eta^2$-2,2´-bipyridyl-*N,N´*)($\eta^2$-nitro-*O,O´*)hexakis($\mu_2$-trimethylacetato-*O,O´*)dicopper(II)europium(III) acetonitrile solvate, $[Cu_2Eu(Piv)_6(NO_3)(2,2´\text{-}bpy)_2]\cdot MeCN$ (3).** Complex **3** was obtained according to the procedure similar to the synthesis of complex **2** using $Eu(NO_3)_3\cdot 6H_2O$. The yield of compound **3** was 60%. Found (%): C, 48.1; H, 5.6; N, 6.4. $C_{52}H_{73}Cu_2EuN_6O_{15}$. Calculated (%): C, 48.00; H, 5.65; N, 6.46. IR, $\nu$/cm$^{-1}$: 2964 m, 2932 m, 2864 m, 1716 w, 1680 w, 1664 w, 1640 m, 1608 s, 1584 s, 1568 s, 1536 m, 1520 m, 1484 m, 1444 m, 1436 m, 1416 m, 1376 m, 1356 m, 1320 m, 1224 m, 1172 w, 1156 w, 1104 w, 1028 m, 936 w, 908 w, 808 m, 792 m, 768 m, 740 m, 652 m, 636 m, 604 m, 564 w, 480 w, 420 m.

**Bis($\eta^1$-acetonitrile-*N*)bis($\eta^1$-trimethylacetic acid-*O*)($\eta^2$-nitro-*O,O´*)tetrakis($\mu_2$-trimethylacetato-*O,O´*)bis($\mu_2$,$\eta^2$-trimethylacetato-*O,O,O´*)dinickel(II)lanthanum(III) acetonitrile solvate, $[Ni_2La(Piv)_6(NO_3)(HPiv)_2(MeCN)_2]\cdot MeCN$ (4).** A mixture of $Ni_9(OH)_6(Piv)_{12}(HPiv)_4$ (0.35 g, 0.156 mmol), $La(NO_3)_3\cdot 6H_2O$ (0.20 g, 0.467 mmol), and HPiv (0.95 g, 0.936 mmol) in MeCN (30 mL) was stirred at 80 °C for 30 min. A green solution that formed was filtered, concentrated to the volume of 15 mL, and cooled to ~20 °C. The green crystals formed within 24 h were suitable for X-ray diffraction, they were separated from the solution by decantation, washed with cold MeCN, and dried in air. The yield of compound **4** was 0.47 g (54%, calculated for nickel). Found (%): C, 44.1; H, 6.3; N, 4.6. $C_{46}H_{81}LaN_4Ni_2O_{19}$. Calculated (%): C, 44.18; H, 6.53; N, 4.48. IR, $\nu$/cm$^{-1}$: 2968 s, 2932 m, 2872 m, 1700 w, 1684 m, 1664 m, 1588 s, 1564 m, 1552 w, 1532 w, 1484 s, 1456 m, 1420 s, 1420 s, 1384 s, 1360 s, 1316 m, 1224 s, 1208 s, 1100 w, 1036 m, 944 w, 904 m, 872 m, 804 s, 792 s, 768 w, 736 w, 608 m, 568 w, 540 w, 420 m.

**Bis($\eta^1$-acetonitrile-*N*)bis($\eta^1$-trimethylacetic acid-*O*)($\eta^2$-nitro-*O,O´*)tetrakis($\mu_2$-trimethylacetato-*O,O´*)bis($\mu_2$,$\eta^2$-trimethylacetato-*O,O,O´*)dinickel(II)praseodymium(III) acetonitrile solvate, $[Ni_2Pr(Piv)_6(NO_3)(HPiv)_2(MeCN)_2]\cdot MeCN$ (5).** Complex **5** was obtained according to the procedure similar to the synthesis of **4**, using $Pr(NO_3)_3\cdot 6H_2O$. The yield of compound **5** was 58%. Found (%): C, 44.2; H, 6.4; N, 4.4. $C_{46}H_{81}N_4Ni_2O_{19}Pr$. Calculated (%): C, 44.11; H, 6.52; N, 4.47. IR, $\nu$/cm$^{-1}$: 2968 s, 2932 m, 2872 m, 1700 w, 1680 m, 1664 m, 1592 s, 1564 m, 1552 w, 1536 w, 1484 s, 1460 m, 1420 s, 1376 s, 1360 s, 1316 m, 1224 s, 1208 s, 1032 m, 940 w, 904 m, 876 m, 812 s, 792 s, 768 w, 736 w, 612 m, 568 w, 540 w, 420 m.

**Bis($\eta^1$-acetonitrile-*N*)bis($\eta^1$-trimethylacetic acid-*O*)($\eta^2$-nitro-*O,O´*)tetrakis($\mu_2$-trimethylacetato-*O,O´*)bis($\mu_2$,$\eta^2$-trimethylacetato-*O,O,O´*)dinickel(II)samarium(III) acetonitrile solvate, $[Ni_2Sm(Piv)_6(NO_3)(HPiv)_2(MeCN)_2]\cdot MeCN$ (6).** Complex **6** was obtained according to the procedure similar to the synthesis of **4**, using $Sm(NO_3)_3\cdot 6H_2O$. The yield of compound **6** was 54%. Found (%): C, 43.7; H, 6.5; N, 4.2. $C_{46}H_{81}N_4Ni_2O_{19}Sm$. Calculated (%): C, 43.78; H, 6.47; N, 4.44. IR, $\nu$/cm$^{-1}$: 2976 s, 2932 m, 2868 m, 1700 w, 1684 m, 1588 s, 1564 m, 1548 w, 1536 w, 1484 s, 1456 m, 1420 s, 1376 s, 1360 s, 1316 m, 1228 s, 1208 s, 1100 w, 1032 m, 944 w, 912 m, 876 m, 812 s, 792 s, 772 w, 740 w, 612 m, 568 w, 540 w, 420 m.

**Bis($\eta^1$-acetonitrile-*N*)bis($\eta^1$-trimethylacetic acid-*O*)($\eta^2$-nitro-*O,O´*)tetrakis($\mu_2$-trimethylacetato-*O,O´*)bis($\mu_2$,$\eta^2$-trimethylacetato-*O,O,O´*)dinickel(II)europium(III) acetonitrile solvate, $[Ni_2Eu(Piv)_6(NO_3)(HPiv)_2(MeCN)_2]\cdot MeCN$ (7).** Complex **7** was obtained according to the procedure similar to the synthesis of **4**, using $Eu(NO_3)_3 \cdot 6H_2O$. The yield of compound **7** was 50%. Found (%): C, 43.7; H, 6.3; N, 4.3. $C_{46}EuH_{81}N_4Ni_2O_{19}$. Calculated (%): C, 43.73; H, 6.46; N, 4.43. IR, ν/cm$^{-1}$: 2976 s, 2928 m, 2864 m, 1700 w, 1684 m, 1672 m, 1588 s, 1572 m, 1548 w, 1536 w, 1484 s, 1460 m, 1424 s, 1376 s, 1360 s, 1316 m, 1228 s, 1208 s, 1100 w, 1032 m, 940 w, 912 m, 876 m, 804 s, 792 s, 772 w, 736 w, 612 m, 568 w, 540 w, 420 m.

**Bis(η$^1$-acetonitrile-*N*)bis(η$^1$-trimethylacetic acid-*O*)(η$^2$-nitro-*O,O´*)tetrakis(μ$_2$-trimethylacetato-*O,O´*)bis(μ$_2$,η$^2$-trimethylacetato-*O,O,O´*)dinickel(II)gadolinium(III) acetonitrile solvate, $[Ni_2Gd(Piv)_6(NO_3)(HPiv)_2(MeCN)_2] \cdot MeCN$ (8).** Complex **8** was obtained according to the procedure similar to the synthesis of **4**, using $Gd(NO_3)_3 \cdot 6H_2O$. The yield of compound **8** was 58%. Found (%): C, 43.4; H, 6.3; N, 4.5. $C_{46}H_{81}GdN_4Ni_2O_{19}$. Calculated (%): C, 43.55; H, 6.43; N, 4.42. IR, ν/cm$^{-1}$: 2976 s, 2928 m, 2864 m, 1700 w, 1688 m, 1672 m, 1588 s, 1568 m, 1552 w, 1536 w, 1484 s, 1456 m, 1420 s, 1376 s, 1360 s, 1312 m, 1228 s, 1208 s, 1100 w, 1032 m, 936 w, 912 m, 872 m, 812 s, 792 s, 768 w, 744 w, 612 m, 568 w, 540 w, 420 m.

**Bis(η$^2$-2,2´-bipyridyl-*N,N´*)(η$^2$-nitro-*O,O´*)tetrakis(μ$_2$-trimethylacetato-*O,O´*)bis(μ$_2$,η$^2$-trimethylacetato-*O,O,O´*)dinickel(II)samarium(III) acetonitrile solvate, $[Ni_2Sm(Piv)_6(NO_3)(2,2´\text{-bpy})_2] \cdot MeCN$ (9).** Complex **9** was obtained according to the procedure similar to the synthesis of **1** (method *B*), using complex **6**. The yield of compound **9** was 80%. Found (%): C, 48.3; H, 6.5; N, 5.8. $C_{52}H_{73}N_6Ni_2O_{15}Sm$. Calculated (%): C, 48.42; H, 6.52; N, 5.70. IR, ν/cm$^{-1}$: 2970 m, 2936 m, 2864 m, 1712 w, 1684 w, 1664 w, 1632 m, 1608 s, 1584 s, 1568 s, 1536 m, 1520 m, 1484 m, 1440 m, 1436 m, 1420 m, 1376 m, 1364 m, 1312 m, 1224 m, 1172 w, 1152 w, 1104 w, 1028 m, 936 w, 908 w, 808 m, 92 m, 768 m, 740 m, 652 m, 636 m, 604 m, 564 w, 476 w, 424 m.

**Octakis(μ$_2$-trimethylacetato-*O,O´*)dicopper(II)europium(III)-tetrabutylammonium, $(Bu_4N)[Cu_2Eu(Piv)_8]$ (10).** The compound $Cu_2(Piv)_4(HPiv)_2$ (0.33 g, 0.45 mmol) was added to a weighed amount of $Eu(NO_3)_3 \cdot 6H_2O$ (0.198 g, 0.44 mmol) in MeCN (15 mL). The solution obtained was treated with 40% solution of $Bu^n{}_4NOH$ (0.40 mL, 1.78 mmol) and stirred for 30 min, then filtered, concentrated to the volume of 5—7 mL, and diluted with *o*-xylene (5 mL). The rhombic violet crystals formed within 48 h, suitable for X-ray diffraction, were separated from the solution by decantation, washed with cold MeCN, and dried in air. The yield of compound **10** was 0.09 g (15%, calculated for copper). Found (%): C, 50.4; H, 8.1; N, 0.9. $C_{56}H_{108}Cu_2EuNO_{16}$. Calculated (%): C, 50.55; H, 8.18; N, 1.05. IR, ν/cm$^{-1}$: 3650—3290 br.w, 2961 s, 2927 m, 2877 m, 1605 v.s, 1484 s, 1457 w, 1416 v.s, 1376 s, 1360 s, 1228 s, 1152 w, 1106 w, 1030 w, 938 w, 896 m, 798 w, 788 m, 738 w, 624 m, 568 w, 442 m.

**Octakis(μ$_2$-trimethylacetato-*O,O´*)dicopper(II)gadolinium(III)-tetrabutylammonium, $(Bu_4N)[Cu_2Gd(Piv)_8]$ (11).** Complex **11** was obtained according to the procedure similar to the synthesis of **10**, using $Gd(NO_3)_3 \cdot 6H_2O$. The yield of compound **11** was 15%. Found (%): C, 50.1; H, 8.1; N, 1.1. $C_{56}H_{108}Cu_2GdNO_{16}$. Calculated (%): C, 50.36; H, 8.15; N, 1.05. IR, ν/cm$^{-1}$: 3672—3232 br.w, 2962 s, 2923 m, 2877 m, 1606 v.s, 1484 s, 1457 w, 1416 v.s, 1376 s, 1360 s, 1228 s, 1153 w, 1030 w, 938 w, 896 m, 799 w, 788 m, 740 w, 625 m, 558 w, 444 m.

**Hexa(η$^1$-acetonitrile-*N*)nickel dication penta(η$^2$-nitro-*O,O´*)-samarium dianion, $[Ni(MeCN)_6][Sm(NO_3)_5]$.** A mixture of $Ni_9(OH)_6(Piv)_{12}(HPiv)_4$ (0.50 g, 0.222 mmol) and $Sm(NO_3)_3 \cdot 6H_2O$ (0.89 g, 1.997 mmol) in MeCN (45 mL) was stirred at 80 °C for 30 min. A green solution that formed was concentrated to the volume of 20 mL and cooled to ~20 °C. The light green crystals formed within 20 h were separated from the solution by decantation, washed with cold MeCN, and dried in air. The yield of $[Ni(MeCN)_6][Sm(NO_3)_5]$ was 0.60 g (~40%, calculated for nickel). Found (%): C, 18.8; H, 2.3; N, 20.2. $C_{12}H_{18}N_{11}NiO_{15}Sm$. Calculated (%): C, 18.83; H, 2.37; N, 20.13.

**X-ray diffraction studies** for complex **1** were performed on an Enraf Nonius Cad-4 diffractometer (Mo-Kα irradiation, λ = 0.71073 Å, graphite monochromator),[65] for complexes **2**, **6**, **9**, and **10** — on a Bruker Apex II diffractometer equipped with a CCD-detector (Mo-Kα irradiation, λ = 0.71073 Å, graphite monochromator).[66] A semiempirical correction for absorption was applied for all the compounds.[67] The structures of all the complexes were solved by direct methods. In the structures of compounds **1** and **6**, all the atoms, except those of the MeCN solvent molecules, were refined in the full-matrix anisotropic approximation for all the nonhydrogen atoms. For compounds **2**, **9**, and **10**, the refinements were performed in the full-matrix anisotropic approximation for all the nonhydrogen atoms. The solvent molecules of MeCN in the complex **2**, which is isostructural to compound **1**, were not considered in the structure solution because their disordering (the number of the solvent molecules was determined by elemental analysis). The hydrogen atoms on the carbon and oxygen atoms of organic ligands were generated geometrically and refined using the riding model. The calculations were performed using the SHELXS-97 and SHELXL-97 program packages.[68] Crystallographic parameters and structure refinement statistics are given in Table 2.

X-ray diffraction studies for $[Ni(MeCN)_6][Sm(NO_3)_5]$ were performed in the Guinier chamber G670(HUBER), Cu-Kα$_1$ irradiation. The X-ray diffraction pattern is identical to that calculated for $[Ni(MeCN)_6][Gd(NO_3)_5]$.[45]

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