Heterospin mixed-ligand heterotrinuclear Co^{II}, Gd^{III}, Co^{II} complex with nitronyl nitroxide*

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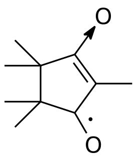
A method was developed for the synthesis of mixed-metal heterospin compounds with the direct coordination of the nitroxide fragment based on the replacement of acetonitrile molecules in the heterotrinuclear complex $[Co_2Gd(NO_3)Piv_6(CH_3CN)_2]$ with nitroxide molecules. The molecular and crystal structure of the heterospin mixed-ligand heterotrinuclear Co^{II}, Gd^{III}, Co^{II} complex $[Co_2Gd(NO_3)Piv_6(NIT\text{-}Me)_2]$, where NIT-Me is stable nitronyl nitroxide, was established. The magnetic properties of this complex were investigated in the temperature range of 2—300 K. The coordination of nitroxide groups to Co^{II} ions is responsible for strong exchange interactions between the unpaired electrons in the exchange clusters {>N—•O—Co^{II}}, resulting in the virtually complete spin coupling between each coordinated >N—•O group and one of the unpaired electrons of each Co^{II} ion at temperatures below 200 K.

Key words: cobalt(II), gadolinium(III), polynuclear compounds, nitroxides, X-ray diffraction study, magnetic measurements.

The reactions of polynuclear metal compounds with nitroxides provide an efficient approach to the synthesis of multispin compounds,[1—4] including compounds capable of cooperative magnetic ordering.[1,4]

In spite of a high synthetic potential of this approach, it often presents difficulties when the starting polynuclear complexes are virtually insoluble in organic solvents and, consequently, they cannot be involved in the reactions with nitroxides. A high catalytic activity of the polynuclear core can cause the simultaneous transformation of both the polynuclear core and the nitroxide.[5] In addition, the coordination of the nitroxide fragment, which is very favorable for highly efficient exchange interactions between the unpaired electrons of the metal ion and the nitroxide, requires the presence of easily replacable ligands in the starting polynuclear moiety, because the >N—•O group (oxidation product of the corresponding hydroxylamine) by itself is a weak donor.

We expected that the trinuclear pivalate complexes $[M^{II}{}_2M^{III}(NO_3)Piv_6(CH_3CN)_2]$, where M^{II} is the paramagnetic 3d-element ion and M^{III} is the paramagnetic 4f-element ion,[6] would meet these requirements. These complexes are soluble in low-polarity solvents and contain monodentate coordinated MeCN molecules, which are, as a rule, rather easily replacable. Actually, the study of the reaction of $[Co_2Gd(NO_3)Piv_6(CH_3CN)_2]$ with 2,4,4,5,5-pentamethyl-2-imidazoline-1-oxyl 3-oxide (NIT-Me) showed that this approach is very convenient for the preparation of heterospin heteronuclear complexes with nitroxides, in which the nitroxide fragment is involved in the direct coordination to the terminal cobalt atoms of the Co^{II}...Gd^{III}...Co^{II} triad. We chose $[Co_2Gd(NO_3)Piv_6(CH_3CN)_2]$ taking into account that ferromagnetic exchange interactions between the unpaired electrons of Co^{II} and Gd^{III} in the trinuclear fragment $\{Co_2Gd(NO_3)Piv_6\}$ have been found earlier in the structurally similar compound $[Co_2Gd(NO_3)Piv_6L_2]$, where L is quinoline.[7]



NIT-Me

Results and Discussion

Our experiments showed that the heterotrinuclear complex $[Co_2Gd(NO_3)Piv_6(MeCN)_2]$ readily reacts with NIT-Me under normal conditions in various organic solvents (Et_2O, PhMe, or CH_2Cl_2) or their mixtures. In all

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Table 1. Crystallographic characteristics for the $[Co_2Gd(NO_3)Piv_6(NIT\text{-}Me)_2]$ complex

Parameter	Characteristics	
T/K	295	240
Molecular formula	$C_{46}H_{84}Co_2GdN_5O_{19}$	
Molecular weight	1286.29	
Space group	$C2/c$	
Z	4	
a/Å	24.919(4)	24.918(5)
b/Å	11.6377(16)	11.663(2)
c/Å	21.206(3)	21.278(4)
β/deg	97.470(4)	97.623(5)
V/Å^3	6097.5(15)	6129.1(19)
d_{calc}/g cm^{-3}	1.401	1.394
μ/mm^{-1}	1.680	1.672
θ-Scan range, deg	1.93 – 28.37	1.93 – 23.32
Number of measured reflections	34129	23104
Number of independent reflections	7589	4420
R_{int}	0.0984	0.0754
Number of variables	374	374
R_1 ($I > 2\sigma_I$)	0.0416	0.0306
wR_2	0.0861	0.0862
R_1 (all data)	0.0692	0.0385
wR_2	0.0930	0.0929

cases, the $[Co_2Gd(NO_3)Piv_6(NIT\text{-}Me)_2]$ complex was obtained in the solid state regardless of the starting ratio of the reagents. This indicates that the complex was isolated in the individual state. It should also be noted that this compound is formed in a rather high yield as single crystals suitable for X-ray diffraction.

Table 2. Selected bond lengths for the $[Co_2Gd(NO_3)Piv_6(NIT\text{-}Me)_2]$ complex

Bond	d/Å	
	295 K	240 K
Gd—O	2.303(3) 2.303(3)	2.317(3) 2.317(3)
	2.337(3) 2.337(3)	2.349(3) 2.349(3)
	2.346(2) 2.346(2)	2.362(3) 2.362(3)
	2.480(3) 2.480(3)	2.488(3) 2.488(3)
Co—O	1.931(3) 1.934(3)	1.939(3) 1.951(3)
	1.948(3) 1.987(2)	1.959(3) 2.003(3)
N—O_{NO_3}	1.257(3)	1.276(4)
	1.209(6)	1.202(6)
	1.257(3)	1.276(4)
N—$O_{NIT\text{-}Me}$	1.310(4)	1.308(4)
	1.257(5)	1.267(5)
C—O	1.219(4) 1.256(4)	1.218(5) 1.270(5)
	1.259(4) 1.225(4)	1.239(4) 1.267(5)
	1.235(4) 1.253(4)	1.269(5) 1.240(5)

The crystallographic characteristics and selected bond lengths for $[Co_2Gd(NO_3)Piv_6(NIT\text{-}Me)_2]$ are given in Tables 1 and 2, respectively. The complex has a molecular structure. The nearest environment of the Gd atom is formed by eight O atoms (Fig. 1, *a*) of six *O,O´*-bridging pivalate anions and the bidentate-cyclic coordinated nitrate anion. The Gd—O_{NO_3} distance (2.480(3) Å) is substantially longer than the Gd—O_{Piv} distances (see Table 2). The distorted tetrahedral environment of the Co atom is formed by the O_{Piv} atoms of three pivalate anions and the O atom of the paramagnetic ligand. As a whole, the $[Co_2Gd(NO_3)Piv_6(NIT\text{-}Me)_2]$ molecule has C_2 symmetry with the symmetry axis passing through the Gd(1),

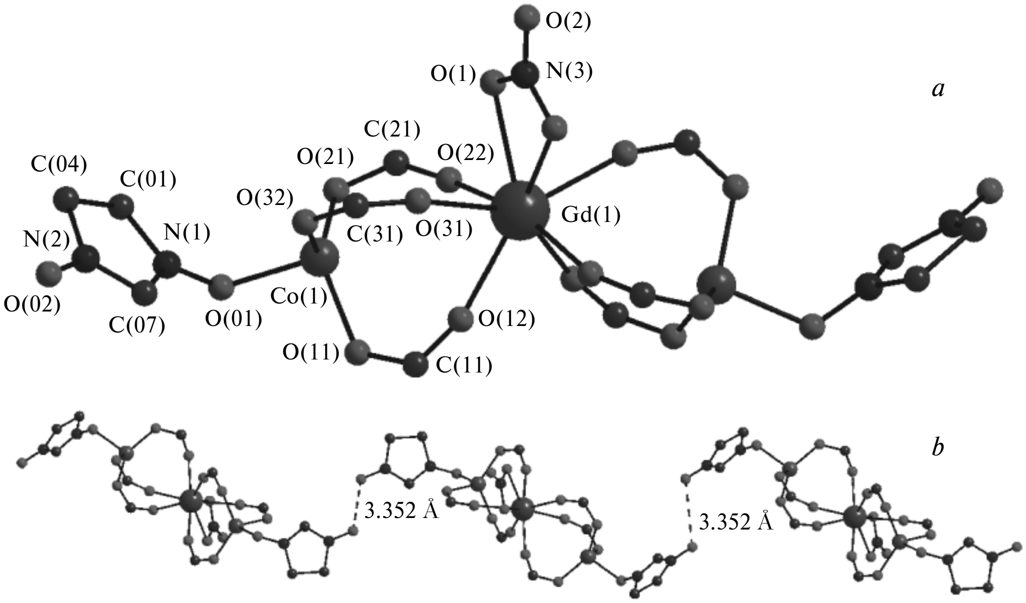

Fig. 1. Molecular structure (*a*) and the shortest distances between the paramagnetic centers of the adjacent molecules (*b*) in the crystal structure of $[Co_2Gd(NO_3)Piv_6(NIT\text{-}Me)_2]$; the Me and Bu^t groups are omitted.

N(3), and O(2) atoms. In the Piv ligands, the C—O distances involving the O atoms coordinated to the Gd atom are shorter than those with the O atoms coordinated to the Co atom (1.219(4)—1.235(4) and 1.253(4)—1.259(4) Å, respectively). In the NO_3 anion, the N—O distance with the uncoordinated O atom is substantially shorter than the other two distances (see Table 2). An analogous ratio of the N—O bond lengths is observed in the coordinated NIT-Me molecules (O(01)—N(1), 1.310(4) Å; N(2)—O(02), 1.257(5) Å). It should also be noted that the shortest distances between the paramagnetic centers of the adjacent molecules in the solid state of this compound (3.352(9) Å) are determined by the O...O contacts between the nitroxide groups (Fig. 1, *b*). This fact was taken into account in the discussion of the magnetic properties of this compound.

The temperature dependence of the effective magnetic moment of $[Co_2Gd(NO_3)Piv_6(NIT\text{-}Me)_2]$ (Fig. 2) is complex in character. The magnetic moment μ_{eff} is 9.22 μ_B at 300 K, it decreases to 9.06 μ_B as the temperature is lowered to *ca.* 200 K, and remains virtually unchanged down to *ca.* 75 K. Upon further cooling, the magnetic moment increases to 9.28 at 20 K and then sharply decreases. This character of the dependence $\mu_{eff}(T)$ can be explained by comparing it with the analogous dependence for the starting complex $[Co_2Gd(NO_3)Piv_6(CH_3CN)_2]$.

For $[Co_2Gd(NO_3)Piv_6(CH_3CN)_2]$, μ_{eff} remains virtually unchanged (10.43 μ_B) in the temperature range of 40—300 K (see Fig. 2). At temperatures below 10 K, the magnetic moment first increases to 10.92 μ_B and then sharply decreases as the liquid helium temperature is approached. The constancy of μ_{eff} in a wide temperature range indicates that the exchange clusters $\{Co^{II}...Gd^{III}...Co^{II}\}$ are substantially isolated from each other and that the exchange interactions between the unpaired electrons of the metal ions in the exchange clusters $\{Co^{II}...Gd^{III}...Co^{II}\}$ have a low energy and are manifested only at low temperatures. The ferromagnetic character of these interactions is responsible for an increase in the effective magnetic moment at low temperatures. This is completely consistent with the results of the study[7] of the structurally similar trinuclear complex $[Co_2Gd(NO_3)Piv_6L_2]$, in which quinoline serves the function of a monodentate ligand. As mentioned above, the antiferromagnetic exchange interactions between the clusters are very weak and are manifested only at very low temperatures (<3 K), resulting in a decrease in μ_{eff}. The experimental value of the magnetic moment $\mu_{eff} = 10.43\ \mu_B$ for $[Co_2Gd(NO_3)Piv_6(CH_3CN)_2]$ agrees well with the theoretical value (9.64 μ_B) calculated by summing the independent pure spin contributions of two Co^{II} ions and one Gd^{III} ion to the magnetic susceptibility with the *g* factor equal to 2. The fact that the experimental moment μ_{eff} is larger than the calculated value is attributed to the the orbital contribution to the magnetic susceptibility, which is typical of Co^{II} ions, and the *g* factor >2.

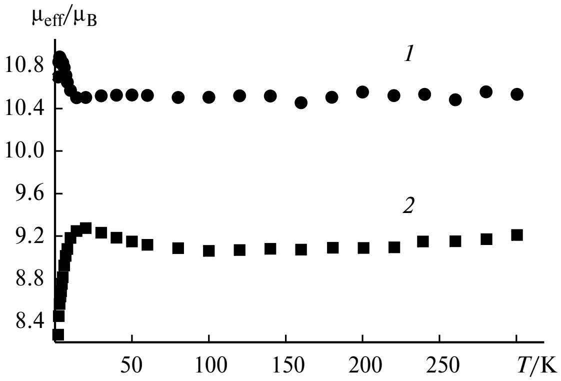

Fig. 2. Temperature dependences of the effective magnetic moment for the $[Co_2Gd(NO_3)Piv_6(CH_3CN)_2]$ (*1*) and $[Co_2Gd(NO_3)(Piv)_6(NIT\text{-}Me)_2]$ (*2*) complexes.

Throughout the measurement range for the $[Co_2Gd(NO_3)Piv_6(NIT\text{-}Me)_2]$ complex with the stable nitroxide, μ_{eff} is substantially smaller than that of $[Co_2Gd(NO_3)Piv_6(CH_3CN)_2]$ (see Fig. 2). This is conclusive evidence for the presnece of strong antiferromagnetic exchange interactions between the unpaired electrons of the coordinated NIT-Me molecules and the Co^{II} atoms. These interactions are manifested in the decrease in μ_{eff} from 9.22 to 9.06 μ_B as the temperature decreases from 300 to 200 K and lead to the virtually complete spin coupling between each coordinated >N—•O group and one of the unpaired electrons of each Co^{II} ion at temperatures lower than 200 K. The experimental value of the magnetic moment μ_{eff} (9.06 μ_B) in the temperature range of 75—200 K is in good agreement with the value of 8.89 μ_B calculated by summing the independent pure spin contributions of two paramagnetic centers with $S = 1$ and one paramagnetic center with $S = 7/2$ (for each center, the *g* factor was taken to be equal to 2) to the magnetic susceptibility. As mentioned above, the increase in μ_{eff} in the temperature range of 20—74 K reflects antiferromagnetic exchange interactions between the unpaired electrons of the metal ions in the exchange clusters $\{Co^{II}...Gd^{III}...Co^{II}\}$. A comparison of the two experimental curves $\mu_{eff}(T)$ presented in Fig. 2 in the low temperature range shows that the magnetic moment μ_{eff} of $[Co_2Gd(NO_3)Piv_6(NIT\text{-}Me)_2]$ begins to decrease at a higher temperature (20 K) compared to that of the $[Co_2Gd(NO_3)Piv_6(CH_3CN)_2]$ compound (<3 K). This is a consequence of substantially more efficient intermolecular antiferromagnetic exchange interactions in the solid state of $[Co_2Gd(NO_3)Piv_6(NIT\text{-}Me)_2]$, in which the O atoms of the >N—O groups of the adjacent molecules are rather closely spaced (3.352(9) Å; see Fig. 1, *b*).

Therefore, the present study showed that the reaction of the $[M^{II}{}_2M^{III}(NO_3)Piv_6(CH_3CN)_2]$ complex with stable nitronyl nitroxides containing no donor groups other than >N—•O can be used as a procedure for the synthesis of mixed-metal heterospin compounds with the direct coordination of the nitroxide fragment, which is formed as a result of the easy replacement of acetonitrile molecules in the heterotrinuclear complex with nitroxide molecules.

Experimental

Synthesis of (*O*,*O*´)-hexakis(μ_2-2,2-dimethylpropionate-*O*,*O*´)-bis(2,4,4,5,5-pentamethyl-2-imidazoline-1-oxyl 3-oxide)gadolinium(III)dicobalt(II) nitrate. A solution of nitroxide (0.017 g, 0.1 mmol) in Et_2O (3—4 mL) was gradually added through a filter to a filtered solution of $Co_2Gd(NO_3)(C_5H_9O_2)_6(CH_3CN)_2$ (0.1 g, 0.1 mmol) in Et_2O (4 mL) at room temperature. Upon storage of the reaction mixture for 1—2 days, its volume decreased by *ca.* 1/3 and dark-violet crystals suitable for X-ray diffraction grew. The crystals were filtered off and dried in air. The yield was 0.04 g (65% based on consumed nitroxide). Found (%): C, 43.7; H, 6.6; N, 5.0. $Co_2Gd(NO_3)(C_5H_9O_2)_6(C_8H_{15}N_2O_2)_2$. Calculated (%): C, 43.0; H, 6.6; N, 5.4. The microanalysis was carried out on a Carlo Erba 1106 analyzer at the Vorozhtsov Novosibirsk Institute of Organic Chemistry of the Siberian Branch of the Russian Academy of Sciences. This complex was obtained also with the use of a CH_2Cl_2—toluene mixture as the solvent.

X-ray diffraction study. The single-crystal X-ray diffraction data sets were collected on a SMART APEX CC diffractometer (Bruker AXS) (Mo-Kα, λ = 0.71073 Å, absorption correction 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 located in difference electron density maps and refined isotropically together with the nonhydrogen atoms. All calculations associated with the structure solution and refinement were carried out with the use of the Bruker Shelxtl program package (Version 6.14). The crystallographic characteristics and the X-ray diffraction data collection and refinement statistics are given in Table 1. Selected bond lengths are listed in Table 2.

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

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

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

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