

Syntheses, structures, and magnetic properties of acetato- and diphenolato-bridged 3d-4f binuclear complexes $[M(3\text{-MeOsaltn})(\text{MeOH})_x(\text{ac})\text{Ln}(\text{hfac})_2]$ ($M=\text{Zn}^{\text{II}}, \text{Cu}^{\text{II}}, \text{Ni}^{\text{II}}, \text{Co}^{\text{II}}$; $\text{Ln}=\text{La}^{\text{III}}, \text{Gd}^{\text{III}}, \text{Tb}^{\text{III}}, \text{Dy}^{\text{III}}$; $3\text{-MeOsaltn}=\text{N},\text{N}'\text{-bis}(3\text{-methoxy-2-oxybenzylidene})\text{-1,3-propanediaminato}$; $\text{ac}=\text{acetato}$; $\text{hfac}=\text{hexafluoroacetylacetonato}$; $x=0$ or 1).

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Streszczenie

A series of 3d-4f binuclear complexes, $[M(3\text{-MeOsaltn})(\text{MeOH})_x(\text{ac})\text{Ln}(\text{hfac})_2]$ ($x = 0$ for $M = \text{Cu}(\text{II}), \text{Zn}(\text{II})$; $x = 1$ for $M = \text{Co}(\text{II}), \text{Ni}(\text{II})$; $\text{Ln} = \text{Gd}(\text{III}), \text{Tb}(\text{III}), \text{Dy}(\text{III}), \text{La}(\text{III})$), have been synthesized and characterized, where 3-MeOsaltn, ac, and hfac denote N,N'-bis(3-methoxy-2-oxybenzylidene)-1,3-propanediaminato, acetato, and hexafluoroacetylacetonato, respectively. The X-ray analyses demonstrated that all the complexes have an acetato- and diphenolato-bridged $M(\text{II})\text{-Ln}(\text{III})$ binuclear structure. The $\text{Cu}(\text{II})\text{-Ln}(\text{III})$ and $\text{Zn}(\text{II})\text{-Ln}(\text{III})$ complexes are crystallized in an isomorphous triclinic space group $P1$, where the $\text{Cu}(\text{II})$ or $\text{Zn}(\text{II})$ ion has square pyramidal coordination geometry with N_2O_2 donor atoms of 3-MeOsaltn at the equatorial coordination sites and one oxygen atom of the bridging acetato ion at the axial site. The $\text{Co}(\text{II})\text{-Ln}(\text{III})$ and $\text{Ni}(\text{II})\text{-Ln}(\text{III})$ complexes are crystallized in an isomorphous monoclinic space group $P2(1)/c$, where the $\text{Co}(\text{II})$ or $\text{Ni}(\text{II})$ ion at the high-spin state has an octahedral coordination environment with N_2O_2 donor atoms of 3-MeOsaltn at the equatorial sites, and one oxygen atom of the bridged acetato and a methanol oxygen atom at the two axial sites. Each $\text{Ln}(\text{III})$ ion for all the complexes is coordinated by four oxygen atoms of two phenolato and two methoxy oxygen atoms of "ligand-complex" $M(3\text{-MeOsaltn})$, four oxygen atoms of two hfac(-), and one oxygen atom of the bridging acetato ion; thus, the coordination number is nine. The temperature dependent magnetic susceptibilities from 1.9 to 300 K and the field-dependent magnetization up to 5 T at 1.9 K were measured. Due to the important orbital contributions of the $\text{Ln}(\text{III})$ ($\text{Tb}(\text{III}), \text{Dy}(\text{III})$) and to a lesser extent the $M(\text{II})$ ($\text{Ni}(\text{II}), \text{Co}(\text{II})$) components, the magnetic interaction between $M(\text{II})$ and $\text{Ln}(\text{III})$ ions were investigated by an empirical approach based on a comparison

of the magnetic properties of the M(II)-Ln(III), Zn(II)-Ln(III), and M(II)-La(III) complexes. The differences of $\chi(M)T$ and $M(H)$ values for the M(II)-Ln(III), Zn(II)-Ln(III) and those for the M(II)-La(III) complexes, that is, $\Delta(T) = (\chi(M)T)(MLn) - (\chi(M)T)(ZnLn) - (\chi(M)T)(MLa) = J(MLn)(T)$ and $\Delta(H) = M(MLn)(H) - M(ZnLn)(H) - M(MLa)(H) = J(MLn)(H)$, give the information of 3d-4f magnetic interaction. The magnetic interactions are ferromagnetic if M(II) = (Cu(II), Ni(II), and Co(II)) and Ln = (Gd(III), Tb(III), and Dy(III)). The magnitudes of the ferromagnetic interaction, $J(MLn)(T)$ and $J(MLn)(H)$, are in the order Cu(II)-Gd(III) > Cu(II)-Dy(III) > Cu(II)-Tb(III), while those are in the order of M(II)-Gd(III) $\approx$ M(II)-Tb(III) > M(II)-Dy(III) for M(II) = Ni(II) and Co(II). Alternating current (ac) susceptibility measurements demonstrated that the Ni(II)-Tb(III) and Co(II)-Tb(III) complexes showed out-of-phase signal with frequency-dependence and the Ni(II)-Dy(III) and Co(II)-Dy(III) complexes showed small frequency-dependence. The energy barrier for the spin flipping was estimated from the Arrhenius plot to be 14.9(6) and 17.0(4) K for the Ni(II)-Tb(III) and Co(II)-Tb(III) complexes, respectively, under a dc bias field of 1000 Oe.

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