



Dinuclear metallacycles with single M—X—M bridges (X = Cl[−], Br[−]; M = Fe(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II)) : strong antiferromagnetic superexchange interactions.

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Streszczenie

A series of monochloride-bridged, dinuclear metallacycles of the general formula $[M_2(\mu\text{-Cl})(\mu\text{-L})_2](\text{ClO}_4)_3$ have been prepared using the third-generation, ditopic bis-(pyrazolyl)methane ligands $L = m\text{-bis}[\text{bis}(1\text{-pyrazolyl})\text{methyl}]\text{-benzene}$ (L_m), $M = \text{Cu(II)}$, Zn(II) , and $L = m\text{-bis}[\text{bis}(3,5\text{-dimethyl-1-pyrazolyl})\text{methyl}]\text{benzene}$ (L_m^*), $M = \text{Fe(II)}$, Co(II) , Ni(II) , Cu(II) , Zn(II) , Cd(II) . These complexes were synthesized from the direct reactions of $M(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$, MCl_2 , and the ligand, L_m or L_m^* , in the appropriate stoichiometric amounts. Three analogous complexes of the formula $[M_2(\mu\text{-Cl})(\mu\text{-L})_2](\text{BF}_4)_3$, $L = L_m$, $M = \text{Cu(II)}$, and $L = L_m^*$, $M = \text{Co(II)}$, Cu(II) , were prepared from the reaction of $[M_2(\mu\text{-F})(\mu\text{-L})_2](\text{BF}_4)_3$ and $(\text{CH}_3)_3\text{SiCl}$. The bromide-bridged complex $[\text{Cu}_2(\mu\text{-Br})(\mu\text{-L}_m^*)_2](\text{ClO}_4)_3$ was prepared by the first method. Three acyclic complexes, $[\text{Co}_2(\mu\text{-L}_m)\mu\text{-Cl}_4]$, $[\text{Co}_2(\mu\text{-L}_m^*)\text{Cl}_4]$, and $[\text{Co}_2(\mu\text{-L}_m^*)\text{Br}_4]$, were also prepared. The structures of all $[M_2(\mu\text{-X})(\mu\text{-L})_2]^{3+}$ ($X = \text{Cl}^-$, Br^-) complexes have two ditopic bis(pyrazolyl)methane ligands bridging two metals in a metallacyclic arrangement. The fifth coordination site of the distorted trigonal bipyramidal metal centers is filled by a bridging halide ligand that has an unusual linear or nearly linear $M\text{-X-M}$ angle. The NMR spectra of $[\text{Zn}_2(\mu\text{-Cl})(\mu\text{-L}_m^*)_2](\text{ClO}_4)_3$ and especially $[\text{Cd}_2(\mu\text{-Cl})(\mu\text{-L}_m^*)_2](\text{ClO}_4)_3$ demonstrate that the metallacycle structure is maintained in solution. Solid state magnetic susceptibility data for the copper(II) compounds show very strong antiferromagnetic exchange interactions, with $-J$ values of 536 cm^{-1} for $[\text{Cu}_2(\mu\text{-Cl})(\mu\text{-L}_m)_2](\text{ClO}_4)_3 \cdot x\text{CH}_3\text{CN}$, 720 cm^{-1} for $[\text{Cu}_2(\mu\text{-Cl})(\mu\text{-L}_m^*)_2](\text{ClO}_4)_3$, and 945 cm^{-1} for $[\text{Cu}_2(\mu\text{-Br})(\mu\text{-L}_m^*)_2](\text{ClO}_4)_3 \cdot 2\text{CH}_3\text{CN}$. Smaller but still substantial

antiferromagnetic interactions are observed with other first row transition metals, with $-J$ values of 98 cm^{-1} for $[\text{Ni}_2(\mu\text{-Cl})(\mu\text{-Lm}^*)_2](\text{ClO}_4)_3$, 55 cm^{-1} for $[\text{Co}_2(\mu\text{-Cl})(\mu\text{-Lm}^*)_2](\text{ClO}_4)_3$, and 34 cm^{-1} for $[\text{Fe}_2(\mu\text{-Cl})(\mu\text{-Lm}^*)_2](\text{ClO}_4)_3$. EPR spectra of $[\text{Cu}_2(\mu\text{-Cl})(\mu\text{-Lm}^*)_2](\text{BF}_4)_3$ confirm the d_{z^2} ground state of copper(II). In addition, the sign of the zero-field splitting parameter

D was determined to be positive for $[\text{Cu}_2(\mu\text{-F})(\mu\text{-Lm}^*)_2](\text{BF}_4)_3$. Electronic spectra of the copper(II) complexes as well as Mössbauer spectra of the iron(II) complexes were also studied in relation with the EPR spectra and magnetic properties, respectively. Density functional theory calculations were performed using ORCA, and exchange integral values were obtained that parallel but are slightly higher than the experimental values by about 30%.

Adres publiczny

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