Paramagnetic resonance and magnetism of copper(II) complexes with *N, N',N'',N'''*-tetrakis(2-pyridylmethyl)-1,4,8,11-tetraazacyclotetradecane.

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Streszczenie

EPR (X- and Q-band) and magnetic susceptibility over the temperature range 4.2–300 K are reported for a number of dinuclear Cu(II) complexes derived from N,N',N'',N'''-tetrakis(2-pyridylmethyl)-1,4,8,11-tetraazacyclotetradecane (tpmc). $[Cu_2X(tpmc)](ClO_4)_3 \cdot n$ (X=N_3, F (n=$2CH_3CN$), Cl (n=H_2O), Br, I (n=H_2O), NO_2), where the X anions bridge two copper ions and the tpmc ligand has the boat coordination mode, $[Cu_2tpmc](ClO_4)_4$ and $[Cu_2X_2tpmc](ClO_4)_2$ (X=N_3, NCS), where the X anions occupy apical positions and the tpmc ligand has the chair coordination mode. It is established that the properties of the complexes are determined by intramolecular exchange interactions occurring through both the bridging anion X and the tpmc ligand as well as by magnetic dipole–dipole interactions. In the majority of the compounds the exchange is weak, e.g. it corresponds to J equals 2.0 cm^{-1} for $[Cu_2N_3(tpmc)](ClO_4)_3$ and 3.4 cm^{-1} for $[Cu_2(N_3)_2(tpmc)](ClO_4)_2$. $[Cu_2OH(tpmc)](ClO_4)_3 \cdot 2H_2O$ is an exception in which antiferromagnetic (AF) exchange of about several tens of wave numbers is operating. The EPR spectrum of this complex is described by the following spin Hamiltonian parameters: $g_z=2.25$, $g_y=2.05$, $g_x=2.04$, $D=0.06$ cm^{-1}, $E=0.005$ cm^{-1}. Moreover, an extremely strong influence of lattice perturbations on the exchange interactions is recognized for this compound: a partial loss of the H_2O molecules (coordinated at a greater distance) by a small amount of dinuclear fragments results in a transformation of an AF exchange into a ferromagnetic or a weak AF one with different values of the anisotropic spin–spin interaction parameters (for example, $D=0.172$ cm^{-1}, $E=0.015$ cm^{-1}). The EPR spectra of frozen solutions of all the complexes in NMF are typical for the triplet state, with a distinctly resolved hyperfine structure for the $\Delta M_S=1$ and $\Delta M_S=2$ signals, and show very similar values of g factors, hyperfine and fine structure parameters ($g_z=2.255$, $A_z=0.0087$ cm^{-1}, $g_{x,y}=2.052$, $D=0.025$ cm^{-1}), implying the same molecular structure for dinuclear complexes formed in solution as a result of the loss of one bridging X by dimers with the boat configuration or two X anions by dimers with the chair configuration.

Słowa kluczowe

Magnetism, Copper complexes, Azamacrocyclic complexes

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