

The reversible inter-conversion of copper(II) dimers bearing phenolate-based ligands in their monomers: theoretical and experimental viewpoints.

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Streszczenie

Using the deprotonated forms of the tetradentate phenol amine ligands 2-(((1-methylbenzimidazol-2-yl)methyl)(pyridin-2-ylmethyl)amino)methylphenol (HL^1) and 2-(((pyridin-2-ylmethyl)(quinolin-2-ylmethyl)amino)methyl)phenol (HL^2), dinuclear copper(II) complexes were synthesized. These ligands yielded two binuclear complexes with the composition $[\text{Cu}_2(\text{L}^n)_2](\text{ClO}_4)_2$ [$n = 1$, (**1**) and $n = 2$, (**2**)] and two mononuclear complexes with the compositions $[\text{Cu}(\text{HL}^1)(\text{CH}_3\text{CN})](\text{ClO}_4)_2$ (**3**) and $[\text{Cu}(\text{HL}^2)(\text{CH}_3\text{CN})(\text{OCIO}_3)](\text{ClO}_4)$ (**4**), which have been characterized using X-ray crystallography, UV-Vis, and magnetic susceptibility measurements. The magnetic susceptibility studies of **1** and **2** indicate moderate antiferromagnetic coupling between the Cu^{II} ions through the μ -phenoxo bridges [$J = -38(2)$ and $-145(1)$ cm^{-1} , respectively], which is described by the Bleaney–Bowers dinuclear model. In contrast, **3** and **4** are devoid of any significant magnetic interactions between the mononuclear units. **3** and **4** show axial spectra typical of the d^9 ($d_{x^2-y^2}$ as the ground state) configuration. The dimer complexes **1** and **2** can be converted into the corresponding monomeric $\text{Cu}(\text{II})$ complexes **3** and **4** via adding two equivalents of an acid, such as perchloric acid (HClO_4), to a CH_3CN solution of the dimer. The dimeric core can be regenerated via adding an equivalent of a base, such as triethylamine (Et_3N). Time-dependent density functional theory (TD-DFT) calculations using the M06 functional were performed in order to rationalize the electronic structures of the complexes and to shed light on the origin of the observed electronic transitions. Additionally, DFT/B3LYP calculations helped us to unambiguously state the sign and magnitude of the magnetic coupling constants along with an approximation of the spin density distribution.

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