Copper(II) complexes with bulky N-substituted diethanolamines: high-field electron paramagnetic resonance, magnetic, and catalytic studies in oxidative cyclohexane amidation.

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Streszczenie

The novel coordination compounds $[Cu_2(H^tBuDea)_2(OAc)_2]$ (**1**) and $[Cu_2(H^nBuDea)_2Cl_2]\cdot nH_2O$ (**2**) have been prepared through the reaction of the respective copper(II) salts with *N-tert*-butyldiethanolamine ($H_2{}^tBuDea$, for **1**) or *N*-butyldiethanolamine ($H_2{}^nBuDea$, for **2**) in methanol solution. Crystallographic analysis reveals that, in spite of the common binuclear $\{Cu_2(\mu\text{-}O)_2\}$ core, the supramolecular structures of the complexes are drastically different. In **1** binuclear molecules are linked together by H-bonds into 1D chains, while in **2** the neighboring pairs of binuclear molecules are H-bonded, forming tetranuclear aggregates. Variable-temperature (1.8–300 K) magnetic susceptibility measurements of **1** and **2** show a dominant antiferromagnetic behavior. Both complexes are also studied by HF-EPR spectroscopy. While the interaction between Cu(II) centers in **1** can be described by a single coupling constant J = 130.1(3) cm^{-1} (using $H = JS_1S_2$), the crystallographically different $\{Cu_2(\mu\text{-}O)_2\}$ pairs in **2** are expected exchange from ferro- to antiferromagnetic behavior (with J ranging from −32 to 110 cm^{-1}, according to DFT calculations). Complexes **1** and **2** act as catalysts in the amidation of cyclohexane with benzamide, employing $^tBuOO^tBu$ as oxidant. The maximum achieved conversion of benzamide (20%, after 24 h reaction time) was observed in the **1**/$^tBuOO^tBu$ system. In the cases of $^tBuOO(O)CPh$ or ^tBuOOH oxidants, no significant amidation product was observed, while for $^tBuOO(O)CPh$, the oxidative dehydrogenation of cyclohexane occurred, giving cyclohexene, to afford the allylic ester (cyclohex-2-en-1-yl benzoate) as the main reaction product.