AN UNPRECEDENTED HETEROTRIMETALLIC Fe/Cu/Co CORE FOR MILD AND HIGHLY EFFICIENT CATALYTIC OXIDATION OF CYCLOALKANES BY HYDROGEN PEROXIDE

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Introduction

Self-assembly synthesis of heteropolynuclear complexes is an expanding field in modern chemistry, stimulated by the aesthetic beauty and originality of such compounds, and also by the simplicity of this synthetic procedure and the significance of heterometallic materials e.g. in sorption, optics, conductivity, molecular magnetism and catalysis.[1] Although many heterometallic heterogeneous catalysts are known and applied in various industrial-scale processes, multimetallic homogeneous catalysts, particularly heteronuclear ones, are rather scant and mainly based on polyoxometalates. This contrasts with the developed field of bio-inspired homometallic complexes with a $M_2(\mu\text{-}O)_2$ (M = Fe, Cu, Co) core, which mimic the functions of various enzymes. In this work, we report a new hexanuclear self-assembled complex $[FeCuCo(L)_3(NCS)_2(MeOH)]_2\cdot 3.2H_2O$ (**1**, H_2L = diethanolamine) which, to our knowledge, represents the first example of an inorganic heterotrimetallic Fe/Cu/Co system containing two $Cu(\mu\text{-}O)_2Co(\mu\text{-}O)_2Fe$ cores, that acts as a remarkable catalyst for the peroxidative oxidation of cycloalkanes under mild conditions[1].

Experimental

High-frequency EPR spectra were recorded on the transmission spectrometer at the EMR facility of NHMFL. Magnetic susceptibility data of a powdered sample were measured with a SQUID magnetometer (Quantum Design MPMSXL-5) over the temperature range 1.8–300 K at the magnetic induction of 0.5 T. X-Ray structure was determined on a Xcalibur-3 diffractometer. The results of this work have been published in [1].

Results and Discussion

The EPR spectra at 5 K are characteristic of a monomeric Cu^{II} center, with g_x=2.042, g_y=2.058, g_z=2.303, while at higher temperatures a broad unresolved signal due to a Fe^{III} binuclear system appears. The molecular structure suggests that two Fe^{III} high spin ions are involved in strong exchange interactions, while Cu(II) ions should be less strongly coupled to the iron ions. The spin Hamiltonian operator for the system was used in the form

$$H = J_{FeFe}\mathbf{S}_{Fe1}\mathbf{S}_{Fe2} + J_{CuFe}(\mathbf{S}_{Fe1}\mathbf{S}_{Cu1}+\mathbf{S}_{Fe2}\mathbf{S}_{Cu2}) + J'_{CuFe}(\mathbf{S}_{Fe1}\mathbf{S}_{Cu2}+\mathbf{S}_{Fe2}\mathbf{S}_{Cu1}) + D_{Fe}[\mathbf{S}_{zFe}^2-(1/3)S_{Fe}(S_{Fe}+1)] + \mu_B B g_{Fe}(\mathbf{S}_{Fe1} + \mathbf{S}_{Fe2}) + \mu_B B g_{Cu}(\mathbf{S}_{Cu1} + \mathbf{S}_{Cu2})$$

The least-squares fitting of the magnetic susceptibilities gave g_{Cu} = 2.134, g_{Fe} = 2.00, D_{Fe} = -8.5 cm^{-1}, J_{FeCu} = -7.9 cm^{-1}, J'_{FeCu} = -7.0 cm^{-1}, J_{FeFe} = 27.3 cm^{-1}.

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References

[1] Nesterov, D.S. *et al*., Chemical Communications (Cambridge), **44,** 4605-4607, (2006)