SELF-ASSEMBLY OF THE UNIQUE HETEROTRIMETALLIC Cu/Co/M COMPLEXES POSSESSING TRIANGULAR ANTIFERROMAGNETIC \{Cu_2CoPb\}_2 AND LINEAR FERROMAGNETIC \{Cu_2CoCd_2\} CORES

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Introduction

Two novel heterotrimetallic complexes possessing discrete heterotrimetallic units have been prepared. The Cu\textsuperscript{II}Co\textsuperscript{II} core in the octanuclear complex \([Cu_2CoPbCl_4(L)_4]\) \((1)\) is triangular, while a linear arrangement was found in the pentanuclear molecule of \([Cu_2CoCd_2Cl_6(L)_4(HOME)_2]\) \((2)\). HL is 2-(dimethylamino)ethanol.

Experimental

High-frequency EPR spectra were recorded on the transmission spectrometer at the EMR facility of the 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 Bruker SMART CCD area-detector diffractometer (ω rotation scans with narrow frames) equipped with graphite monochromated Mo-K\(\alpha\) radiation (\(\lambda = 0.71073\) Å).

Results and Discussion

The exchange interactions Co-Cu and Cu-Cu as well as zero-field splitting on high-spin cobalt(II) ions had to be taken into account in fitting the magnetic susceptibility data. The Hamiltonian was used in a form

\[
H = J_{CoCu}(S_{Co}S_{Cu}+S_{Co}S_{Cu}^{+}) + J_{CuCu}(S_{Cu}S_{Cu}^{+}) + D_{Co}S_{zCo}^{2} + D_{CoCu}(S_{zCo}S_{zCu}^{+}S_{zCo}^{+}S_{zCu}) + \mu_{B}B(g_{Co}S_{Co}^{+}g_{Cu}S_{Cu}^{+}g_{Co}S_{Co}g_{Cu}S_{Cu})
\]

The \(g\) components of Cu\textsuperscript{II} ion, \(g_{xy} = 2.051\) and \(g_{z} = 2.237\) were found from the high-field EPR spectra. Other parameters, shown in Fig. 1 caption resulted from the fitting of the magnetic susceptibility data. The difference in \(D_{Co}\) magnitudes in 1 and 2 can be rationalized. It is known that high-spin Co\textsuperscript{II} shows in tetrahedral geometry moderately large zero-field splitting of several wavenumbers, while extremely large splitting of sometimes hundreds of wavenumbers was observed in octahedral geometry\(^1\). Also, the pattern of exchange interactions appears to be in agreement with the structures – in 1 the angles Cu(3)–O(4)–Cu(2), Cu(2)–O(2)–Co(4) and Cu(3)–O(3)–Co(4) are 113.5(2)°, 107.6(2)° and 108.0(2)°, respectively, thus favoring antiferromagnetic exchange interactions. In 2, the angles [93.5(3)° for Cu(2)–O(1)–Co(3) and 97.0(4)° for Cu(2)–O(2)–Co(3)] that are close to the borderline separating antiferromagnetic interactions from ferromagnetic interactions (97°), result in \(J_{CuCo}\) close to zero.

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References