X-ray Crystal Structures, EPR and Magnetic Studies on Strongly Antiferromagnetically Coupled Mixed μ-Hydroxo-μ-\(N^1,N^2\)-Triazole-Bridged 1D Linear Chain Copper(II) Complexes

K. Drabent, Z. Ciunik (Wroclaw U., Poland, Chemistry) and A. Ozarowski (NHMFL)

Introduction

Four new metal-organic polymeric complexes, \{[\text{Cu(μ-OH)(μ-ClPhtrz)}][\text{H}_2\text{O})(\text{BF}_4)]\}_n (1), \{[\text{Cu(μ-OH)(μ-BrPhtrz)}][\text{H}_2\text{O})(\text{BF}_4)]\}_n (2), \{[\text{Cu(μ-OH)(μ-ClPhtrz)}][\text{H}_2\text{O})(\text{NO}_3)]\}_n (3), and \{[\text{Cu(μ-OH)(μ-BrPhtrz)}][\text{H}_2\text{O})(\text{NO}_3)]\}_n (4) (ClPhtrz – \(N\)-(4-chlorophenyl)methylidene]-4\text{H}-1,2,4-triazol-4-amine; BrPhtrz – \(N\)-(4-bromophenyl)methylidene]-4\text{H}-1,2,4-triazol-4-amine) were synthesized in a reaction of substituted 1,2,4-triazole and various copper(II) salts in water/acetonitrile solutions. The structures of 1-4 were characterized by single-crystal X-ray diffraction analysis. The Cu(II) ions are linked both by single \(N^1,N^2\)-1,2,4-triazole and hydroxo-bridges yielding a 1D linear chain polymers. The tetragonally distorted octahedral geometry of copper atoms is completed alternately by two water and two BF\(_4^-\) anion molecules in 1 and 2, but solely by two water molecules in 3 and 4.

Experimental

High-frequency EPR spectra up to 413 GHz 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.

Results and Discussion

Because well-isolated copper(II) chains are the dominant magnetic object in the compounds under investigations, the magnetic susceptibility of 1–4 may be treated in terms of eq.1 derived by Bonner and Fisher for a uniform S=1/2 infinite chain model:\(^1\):

\[
\chi = \left( \frac{N g^2 \beta^2}{kT} \right) \left( \frac{0.25 + 0.074975x + 0.075235x^2}{1.0 + 0.9931x + 0.172135x^2 + 0.757825x^3} \right)
\]

where \(x = |J|/kT\). \(J\) is the isotropic exchange integral occurring in the spin Hamiltonian \(H = -J\sum S_iS_{i+1}\).

The Cu(II) ions were found to be strongly antiferromagnetically coupled with \(J\) ranging from 390 to 608 cm\(^{-1}\). Extremely weak EPR spectra for compounds 1 and 2, that could only be observed at low temperatures, are most likely to be due to short odd-membered Cu chains. No zero-field splitting effects were observed and the spectra were characteristic for spin ½ with no resolved hyperfine structure. The \(g_x\) values were within a narrow range 2.31-2.32 and the \(g_{x,y}\) values were 2.06-2.07. The observed \(g\) values are close to the \(g\) values for monomers because the equatorial ligand planes of Cu ions are nearly parallel.

Conclusions

Novel infinite-chain copper complexes were investigated using X-ray crystallography, magnetic susceptibility measurements and high-field EPR. The nature and the magnitude of the antiferromagnetic exchange interactions were interpreted as a complementarity/countercomplementarity of the two competing bridges.\(^2\)

Acknowledgements

We thank the University of Wroclaw and the NHMFL for support. The NHMFL is funded by the NSF through the Cooperative Agreement No. DMR-0084173 and the State of Florida

References

[2] Drabent, K., \emph{et al.}, \emph{submitted to Inorg. Chem.}