Magnetic and HF EPR Studies of Monobridged Cyanide and Azide Dinuclear Copper(II) Complexes

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Introduction

Dinuclear copper(II) complexes bridged by a single anion can serve as model compounds for the treatment of superexchange interactions in more complicated systems. We have previously reported the linearly bridged complexes of the type $[Cu_2(\mu\text{-}X)(\mu\text{-}\mathbf{L}_m^*)_2](ClO_4)_3$ where X = F^-, Cl^-, OH^-, Br^- and $\mathbf{L}_m^*$ = *m*-bis[bis(3,5-dimethyl-1-pyrazolyl)methyl]benzene, showing that this system supports extremely strong antiferromagnetic superexchange interactions, with J = 340, 720, 808 and 945 cm^{-1}, respectively ($\hat{\mathbf{H}} = J\,\hat{\mathbf{S}}_1\hat{\mathbf{S}}_2$) [1, 2]. We report here the structure, magnetic and EPR properties of complexes containing more complex bridges, end-on (μ-1,1) N_3^- and end to end CN^-.

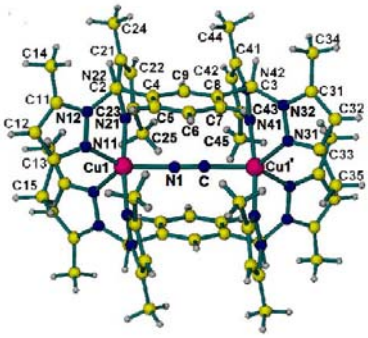

Fig.1. Structure of the cyanido-bridged complex **3**.

Experimental

Complexes$[Cu_2(\mu\text{-}CN)(\mu\text{-}L_m)_2](ClO_4)_3$,(**1**), $[Cu_2(\mu\text{-}N_3)(\mu\text{-}L_m)_2](BF_4)_3$, (**2**) and $[Cu_2(\mu\text{-}CN)(\mu\text{-}L_m^*)_2](ClO_4)_3$, (**3,** Fig. 1**)**) were prepared as described in [3]. High-field EPR spectra were recorded on the transmission instrument of the EMR facility and the 15/17 T SC magnet. Magnetic measurements were performed at the Wroclaw University.

Results and Discussion

Magnetic studies revealed strong antiferromagnetic exchange interactions, although not as strong as in the single-atom bridged systems [1, 2]. Well resolved HF EPR spectra were interpreted in terms of the spin Hamiltonian [1]:

$$\hat{H} = \mu_B \boldsymbol{B}\cdot\{\boldsymbol{g}\}\cdot\hat{\boldsymbol{S}} + D\{\hat{\boldsymbol{S}}_z^2 - S(S+1)/3\} + E(\hat{\boldsymbol{S}}_x^2 - \hat{\boldsymbol{S}}_y^2) \quad [1]$$

In the single-crystal spectra, two identical, symmetry-related molecules "a" and "b" are seen separately (Fig. 2: left: "perpendicular" orientation; right: "parallel"). The intensity pattern allowed determination of the positive sign of the D parameter.

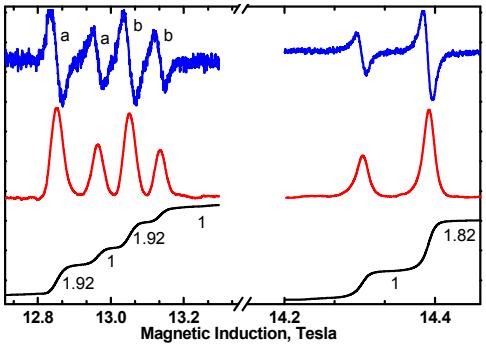

Fig.2. Single-crystal HF EPR spectra of **3** at 406.4 GHz, 30 K (blue). The red traces are integrated spectra and black traces are doubly-integrated, representing the intensity.

Conclusions

The very close to 2 g_z values in **1** and **3** indicate that the ground state of the Cu^{2+} ions is d_{z^2}, rather than the more commonly encountered $d_{x^2-y^2}$. Determination of the positive signs of the zero-field splitting parameters (zfs) D and E of equation [1], made possible evaluation of the dipole-dipole and anisotropic exchange-related contributions to zfs. The zfs is clearly dominated by the latter interactions. Calculations using the Density Functional Theory (DFT) confirmed the d_{z^2} ground state in **1** and **3** while predicting $d_{x^2-y^2}$ in **2**, for which no EPR spectra could be obtained.

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References

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