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LETTER

Letter: Comments on a cyclic tetranuclear copper(II) complex

Albert Escuer and Joan Ribas

Departament de Química Inorgànica, Universitat de Barcelona, c/ Martí Franquès 1-11, Barcelona-08028, Spain

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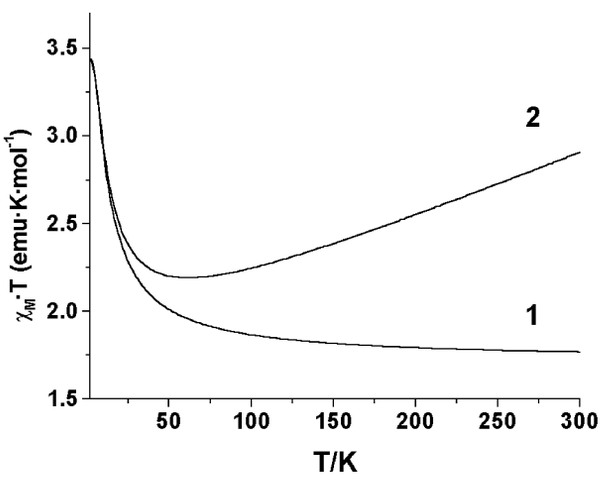
In a recent paper[1] unusual ferrimagnetic properties were reported for the complex $[Cu(phen)(glyOH)]_4(NO_3)_4$. The study describes a cyclic Cu_4 compound in which the metallic ions are linked by *syn–anti* carboxylate bridges from glycolato bridging ligands. Structural data show that the four bridges are equivalent and the tetranuclear units are well isolated by the large 1,10-phenanthroline ligands. The published magnetic properties of this compound can be summarised in a decay of the $\chi_M T$ *vs.* T plot between room temperature and approximately 50 K and a further increase below this temperature up to a value close to 3.5 emu K mol^{-1}. The position of the minimum of $\chi_M T$, susceptibility temperature values in the whole range of temperature and the values of the coupling constants are described as field dependent.

At low temperature the $\chi_M T$ value agrees with that expected for a ferromagnetically-coupled tetranuclear copper system (maintaining the value of $g = 2.12$), but the most evident problem of the $\chi_M T$ *vs.* T plot is the high-temperature value close to 2.75 emu K mol^{-1}. For a weakly coupled system the $\chi_M T$ value should be close to that expected for the isolated paramagnetic centres, *i.e.*, 1.685 emu K mol^{-1} in this case, for four isolated Cu^{II} ions and assuming the 2.12 g value. Substantial deviations from this situation are possible only if the coupling constants were of the order of hundreds of cm^{-1}.

The reasons for the anomalous magnetic response may be found in factors other than those reported by the authors. It is quite common in SQUID measurements on samples with a weak signal (such as copper compounds) to find a more or less strong T/H-dependent deviation of the slope of the $\chi_M T$ plot, that needs specific correction. If the compound is antiferromagnetically coupled the result is an anomalous slope, but if it is ferromagnetically coupled, then a minimum of $\chi_M T$ may be obtained together with unrealistic susceptibility values at high temperature. The differences in the experimental data as a function of the applied magnetic field should be attributable to the same reasons.

In our opinion, the authors have used uncorrected susceptibility data compensating the slope deviation with high TIP values of the same order of magnitude as the paramagnetic contribution of the tetranuclear complex in the fitting procedure.

According to the structural data, we have performed simulations using the analytical expression derived from the Hamiltonian $H = -J(S_1S_2 + S_2S_3 + S_3S_4 + S_4S_1)$ and the fixed parameters $g = 2.14$, $J = 12$ cm^{-1}. A TIP value of 0 was used for plot 1 and of 3.8×10^{-3} emu mol^{-1} for plot 2 (as was introduced by the authors in the fit procedure). As may be expected, plot 2 closely approaches the published data and plot 1 the true magnetic response.



Our conclusion is that the reported compound is a ferromagnetic system, with g and J values close to J_3 and J_4 proposed for the authors and that the apparently ferrimagnetic behaviour derives from the use of uncorrected experimental data, compensated in the fitting process with unrealistic TIP values.

References

1 R. Acevedo-Chavez, M. E. Costas, S. Bernés, G. Medina and L. Gasque, *J. Chem. Soc., Dalton Trans.*, 2002, 2553.

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