Magnetic exchange interactions in the heteropoly complexes [M₄(H₂O)₂(PW₉O₃₄)₂]¹⁰⁻ [M≡Co(II) and Cu(II)]

C. J. Gomez-Garcia
Department of Química Inorgánica, University of Valencia, Spain

N. Casañ-Pastor
*Department of Química Inorgánica, University of Valencia, Spain and Department of Chemistry,
University of Georgetown, Washington, DC*

E. Coronado
Department of Química Inorgánica, University of Valencia, Spain

L. C. W. Baker
Department of Chemistry, University of Georgetown, Washington, DC

G. Pourroy
Department of Materials Science, EHICS, Strasbourg, France

The magnetic properties of the heteropolyanions $[M_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ [M = Co(II) and Cu(II)] down to 4 K are reported. Their individual heteropoly molecules contain a rhomblike arrangement formed by four coplanar MO_6 octahedra sharing edges. The magnetic properties support an intramolecular ferromagnetic exchange in the Co(II) tetramer, and antiferromagnetic exchange in the Cu(II) tetramer. These behaviors are discussed assuming anisotropic exchange in the Co(II) compound, and Heisenberg exchange in the Cu(II) compound.

I. INTRODUCTION

Heteropoly complexes resemble discrete fragments of metal oxide structures of definite sizes and shapes, that maintain their identities in solution as well as in solid state.[1,2] In view of their ability to accommodate transition metals at specific sites, and to undergo multiple-electron reduction, heteropolyanions attract current attention as models for the molecule-to-solid-state continuum in catalysis and other interrelated areas.

In magnetochemistry these compounds have been hardly studied, probably due to the weak magnetism of the samples (the magnetic sites are embedded in a giant diamagnetic polytungstate molecule). Nevertheless, they can be especially valuable in this area since they offer an ideal structural support for the study of the interactions between paramagnetic metal atoms[3] as well as between delocalized electrons and paramagnetic metal atoms.[4]

We report a magnetic study of the series $[M_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ [M = Co(II) and Cu(II)] which contains isolated polymetallic entities M_4O_{16}, inbetween two diamagnetic anions $(PW_9O_{34})^{9-}$ [Fig. 1(a)]. The magnetic measurements have been carried out in a variable temperature susceptometer equipped with a SQUID sensor.

II. THE COBALT SYSTEM

In this compound the magnetic moment shows a continuous increase below 30 K and a tendency towards a plateau as T falls below 7 K, which supports an intramolecular ferromagnetic interaction (Fig. 2). Owing to the anisotropy of the Co(II), with EPR g components in the range 2.8–7.0, an anisotropic exchange model is expected to be convenient in the analysis of the magnetic properties.[5] In view of the structural features of the magnetic entity [see Fig. 1(b)], we have

considered five nearest-neighbors exchange interactions, namely J_{12}, J_{23}, J_{34}, J_{14}, and J_{13}. The symmetry of the entity requires the first four interactions to be identical (namely J), while the latter may be different (namely J'). The anisotropy is accounted for by considering two exchange components, namely $J_\parallel$ and $J_\perp$, for the component parallel and perpendic-
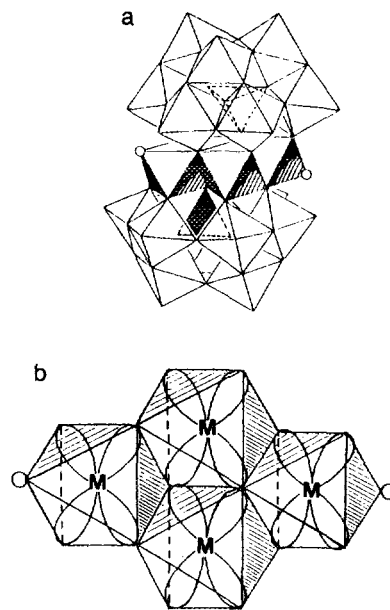

FIG. 1. (a) The structure of the $[M_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ complex. Each vertex of a polyhedron locates the center of an O atom; each white octahedron contains a W atom; each tetrahedron contains a P atom; and each shaded octahedron contains a M atom. (b) Geometry of the M_4O_{16} magnetic moiety showing the orientation of the $d_{x^2-y^2}$ metal orbitals. The circles locate the O atoms of the H_2O molecules coordinated to two of the M's.

ular to the spin direction, respectively. The exchange Hamiltonian is written as

$$H = 2J_{\parallel}(S_{1z}S_{2z} + S_{2z}S_{3z} + S_{3z}S_{4z} + S_{1z}S_{4z})$$
$$- J_{\perp}(S_1^+ S_2^- + S_1^- S_2^+ + S_2^+ S_3^- + S_2^- S_3^+$$
$$+ S_3^+ S_4^- + S_3^- S_4^+ + S_1^+ S_4^- + S_1^- S_4^+)$$
$$- 2J_{\parallel}'S_{1z}S_{3z} - J_{\perp}'(S_1^+ S_3^- + S_1^- S_3^+).$$

Further, taking into account that the tetrameric entities contain two types of metallic sites, two different g tensors g_a (for sites 1,3) and g_b (for sites 2,4), are to be expected. Considering both anisotropic exchange and anisotropic Landé factors, the magnetic properties have been fitted from the following set of parameters: $J_{\perp} = 19 \pm 1$ cm^{-1}, $J_{\perp}/J_{\parallel}$ ≈ 0.1–0.4, $g_{\parallel a} = 7.9$, $g_{\parallel b} = 6.15$, $g_{\perp a} = 2.04$, and $g_{\perp b} = 5.1$. Notice that in order to reduce the number of parameters, we have assumed five identical exchange constants. We observe that this set of parameters gives a very good description of the experiment only when considering anisotropic exchange interactions. A poor fit results when an isotropic exchange model is assumed, despite the large number of adjustable parameters. This result shows the sensitivity of the magnetic susceptibility with respect to the exchange anisotropy.

III. THE COPPER SYSTEM

The product $\chi_m T$ shows, upon cooling, a continuous decrease, reaching a minimum value of 0.86 emu mol^{-1} K around $T = 6$ K (Fig. 3). This behavior is indicative of antiferromagnetic exchange interactions and, owing to the ground state of the interacting copper ions, may be conveniently analyzed by the fully isotropic Heisenberg exchange model ($J_{\perp}/J_{\parallel} = 1$).

Table I reports the energy levels of a rhomblike entity formed by four spins $\frac{1}{2}$ magnetically coupled by two different exchange constants J and J', where J refers to the exchange on the sides of the rhomb ($J = J_{12} = J_{23} = J_{34} = J_{14}$), and J'
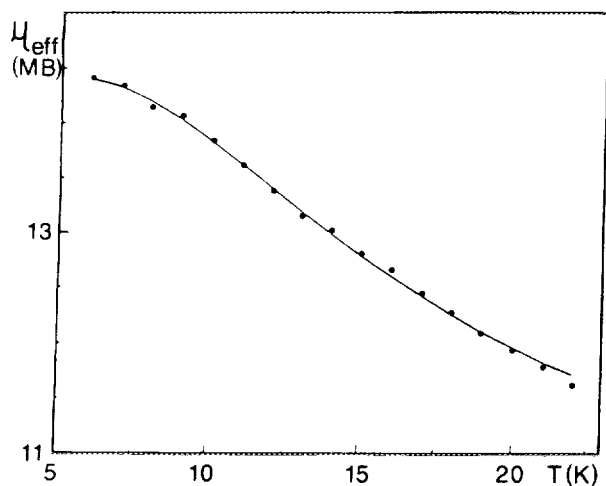

FIG. 2. Plot of corrected effective magnetic moment vs T in the low-temperature region for the cobalt compound. The solid line represents the best fit from the anisotropic exchange model.
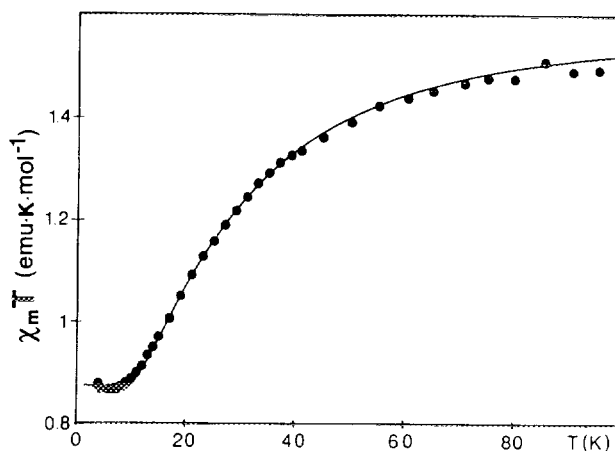

FIG. 3. Plot of $\chi_m T$ vs T for the copper compound. The solid line represents the best fit from the Heisenberg exchange model.

to the shortest diagonal of the rhomb ($J' = J_{13}$). Notice that in the antiferromagnetic case, due to the crossing of levels $S = 0$ and $S = 1$ for a ratio $J'/J = 2$, the ground state of the system varies from $S = 0$ (for $J'/J < 2$) to $S = 1$ (for $J'/J > 2$). Accordingly, in the former case, $\chi_m T$ would continuously decrease upon cooling. In the latter, the system exhibits an irregular spin-state structure[6] since the spin multiplicity does not vary monotonically versus the energy: The ground state is a triplet, but there are excited states with either lower ($S = 0$) or higher ($S = 2$) spin multiplicities. As a consequence, the magnetic moment would exhibit a minimum at a nonzero temperature, and a plateau at lower temperature, when only the triplet ground state is populated. The copper compound does exhibit this type of behavior. Thus, a very satisfying description of the experiment over the whole temperature range is obtained with the following set of parameters: $J = -3.5$ cm^{-1}, $J' = -12.5$ cm^{-1}, and $g = 2.16$.

The reason J' is stronger than J may be understood from the structural features of the tetramer. In this way, according to the distortions of the octahedral sites, we may assume that the magnetic orbitals of Cu(II) are disposed as schematized in Fig. 1(b). This situation favors the exchange interaction J_{13} ($= J'$), with respect to the other interactions, since in this case the two orbitals are pointing toward the bridging atoms, allowing for a larger overlap integral.

IV. CONCLUDING REMARKS

We have reported two examples of tetrametallic exchange-coupled systems isolated in heteropoly molecules.

TABLE I. Energy levels of Cu$_4$O$_{16}$ (at zero field).

Spin state	Multiplicity	Energy
0	1	$4J-J'/2$
		$3J'/2$
1	3	$2J-J'/2$
		$3J'/2$
		$-J'/2$
2	5	$-2J-J'/2$

The ideal isolation provided by the heteropolytungstate framework has guaranteed the intramolecular nature of the exchange interaction. Thus, although in both cases the ground state of the molecule is magnetic, no sign of intermolecular exchange has been detected. Thus, very good agreements of the experimental data over the whole temperature range has been obtained by assuming anisotropic (cobalt system) or isotropic (copper system) exchange within the molecular entities. An unexpected result deals with the different sign of the exchange interactions in both compounds. We observe that the M-O-M angles of the tetrameric entity, being 90° and ~ 100°, may present a situation for accidental orthogonality of some of the magnetic orbitals involved in superexchange. Nevertheless, such a source of ferromagnetic coupling is unlikely to be at the origin of the behavior observed in the cobalt system, since the copper system shows antiferromagnetic coupling. Our opinion is that the reason for this difference is rather related with the orbital degeneracy of the cobalt. In the framework of the Anderson model, this degeneracy could allow electronic transfers within the t_{2g} orbitals of two interacting cobalts, keeping a parallel spin alignment on the virtual Co(III)-Co(I) excited state, which results in a stabilization of the ferromagnetic state. We expect to give a quantitative explanation of this result soon.

[1] L. C. W. Baker, in *Advances in the Chemistry of the Coordination Compounds*, edited by S. Kirschner (Macmillan, New York, 1961), p. 608.

[2] M. T. Pope, *Heteropoly and Isopoly Oxometalates* (Springer, Berlin, 1983).

[3] L. C. W. Baker, V. E. S Baker, S. H. Wasfi, G. A. Candela, and A. H. Kahn, J. Am. Chem. Soc. **94**, 5499 (1972); J. Chem. Phys. **56**, 4917 (1972).

[4] N. Casañ-Pastor, Ph.D. thesis, Georgetown University, 1988.

[5] N. Casañ-Pastor, J. Bas-Serra, E. Coronado, G. Pourroy, and L. C. W. Baker, J. Am. Chem. Soc. (in press).

[6] O. Kahn, Struct. Bonding (Berlin) **68**, 89 (1987).