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Evidence for Large Antisymmetric Superexchange in Tetrameric Copper Complexes

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Transition metal cluster complexes often combine high local symmetry about individual magnetic ions with low spin-pair symmetry. These complexes should therefore enrich greatly the field of study of highly anisotropic, particularly asymmetric, exchange phenomena of low order. We illustrate by presenting evidence indicating strongly that the tetrameric copper complex $Cu_4OCl_6[OP(C_6H_5)_3]_4$ provides the first example in the literature of large (lowest-order) antisymmetric superexchange between orbitally degenerate magnetic ions.

The possible existence of contributions to magnetic insulator exchange asymmetric with respect to the spins involved has long been recognized in the literature. In particular we are familiar with the Dzialoshinski-Moriya antisymmetric bilinear coupling of the form $\vec{S}_1\cdot\overleftrightarrow{K}_A\cdot\vec{S}_2$, where $\overleftrightarrow{K}_A$ is an antisymmetric exchange tensor.[1,2] Such an interaction exists only when spin-pair crystal symmetry is sufficiently low. In simple inorganic magnetic crystals this low spin-pair symmetry seems always, via space-group restrictions, to lead to low local symmetry about individual magnetic ions, producing in turn an orbitally quenched magnetic ground state. Asymmetric exchange contributions then occur only via exchange coupling through excited states and are consequently small; rarely larger than a few percent of the symmetric exchange and usually even smaller.

There has recently been increasing recognition of the value of using organic spacer molecules in crystals to "isolate" chains or planes of magnetically coupled ions and elevate the study of physics in less than three dimensions from the realm of academic interest.[3,4] We wish to point to particular advantages concerning asymmetric exchange to be gained from this principle when taken a step further to "isolate" small clusters of magnetic ions by embedding them in an organic-ligand matrix.

First, the severe geometric restrictions imposed on magnetic ions in simple inorganic crystals by space-group symmetry are removed in cluster-complex crystals where only clusters as a whole are subject to translational symmetry conditions. In particular, high local symmetry (and orbital degeneracy) is not necessarily incompatible with low spin-pair symmetry, enriching greatly the potential field of study of highly anisotropic and particularly asymmetric exchange phenomena of low order. Additional advantages of cluster-complex studies relate to the few-body nature of the associated statistical problem (which is therefore particularly amenable to exact solution) and to the extensive variations of composition which can be generated to enable systematic study of exchange phenomena in terms of bond length, bond angle, ionicity, etc.

As an example of the increased opportunities afforded by these complexes for the study of asymmetric exchange, we present in this Letter evidence from magnetic-susceptibility measurements, which strongly suggests that the tetrameric copper complex $Cu_4OCl_6[OP(C_6H_5)_3]_4$ provides the first example in the literature of large (lowest-order) antisymmetric superexchange between orbitally degenerate magnetic ions.

Conditions under which effective spin-spin interactions may be highly anisotropic and result in spin Hamiltonians grossly different from Heisenberg form have received much attention in recent literature.[5] The *simplest* general class of interactions exhibiting these effects involves orbitally degenerate Kramers doublets, for which the most general operator coupling the two fictitious spins $s=\frac{1}{2}$ is

$$\mathcal{H}_{12}=\sum_{\alpha,\beta} s_{1\alpha}J_{\alpha\beta}s_{2\beta}, \quad \alpha,\beta=x,y,z. \tag{1}$$

In particular, there is no *a priori* reason why asymmetric terms should not be of the same order as symmetric ones if they are not precluded on symmetry grounds. Additional simplification results when the Kramers doublets involve single-electron (or single-hole) wave functions, in which case $J_{\alpha\beta}$ can be directly related to orbital overlaps and simple physical arguments in terms of potential and kinetic exchange.[6]

The molecular structure of an individual copper-tetramer cluster in $Cu_4OCl_6[OP(C_6H_5)_3]_4$ is shown in Fig. 1(a) and consists of a regular tetrahedron of Cu^{2+} ($3d^9$) ions at the center of which is an oxide ion. Six Cl^- ions bridge adjacent coppers giving each Cu^{2+} trigonal bipyramidal coordination and near-regular C_{3v} point symmetry with a local c axis defined by direction $O^{2-}-Cu^{2+}$. At the outer end of each local c axis is a neutral triphenylphosphine-oxide molecule.

In local C_{3v} symmetry, the d-hole eigenfunctions for Cu^{2+} (quantized along a local c axis) are

$$|0\rangle, \quad |\pm 1'\rangle \sim |\pm 1\rangle \pm \gamma_0 |\mp 2\rangle, \\ |\pm 2'\rangle \sim |\pm 2\rangle \pm \gamma_0 |\mp 1\rangle, \tag{2}$$

where $|\gamma_0|<1$. Simple qualitative arguments dictate that $|\pm 1'\rangle$, involving primarily electron motion in d orbitals d_{xz} and d_{yz} which are directed between the ligands, should have the highest hole energy. The ground orbital state could thus be $|0\rangle$ or $|\pm 2'\rangle$. In the former case superexchange within the tetramer would be Heisenberg-like in lowest order; in the latter case an orbitally degenerate theory would result.

We have measured the magnetic suceptibility χ $(=\mu_{\rm eff}^2/3kT)$ per copper ion for $Cu_4OCl_6[OP(C_6H_5)_3]_4$ as a function of temperature T between 1.6 and 294°K with results, corrected for diamagnetism, shown in Fig. 2. The results cannot even qualitatively be accounted for in terms of quasi Heisenberg interactions. Even if we allow for grossly unrealistic intercluster interactions (the largest yet measured for cluster compounds corresponds to a Curie-Weiss constant $\theta \sim 2$°K),[7] a *qualitative* discrepancy remains. For example, from high-temperature results (Fig. 2) the dominant interaction is ferromagnetic. If antiferromagnetic intercluster forces are invoked to explain the maximum in $\mu_{\rm eff}$ at $T\sim 50$°K, not only are they required to be an order-of-magnitude larger than ever observed before but also, to produce the qualitative behavior of χ at low temperatures shown in the inset of Fig. 2, they need to be of linear-chain form whereas the cluster coordination is cubic with intercluster distances of over 12 Å.[8]

Also pertinent is the existence of the closely related anionic cluster complex $[Cu_4OCl_{10}]^{4-}$ in which the *neutral* triphenylphosphine-oxide lig-

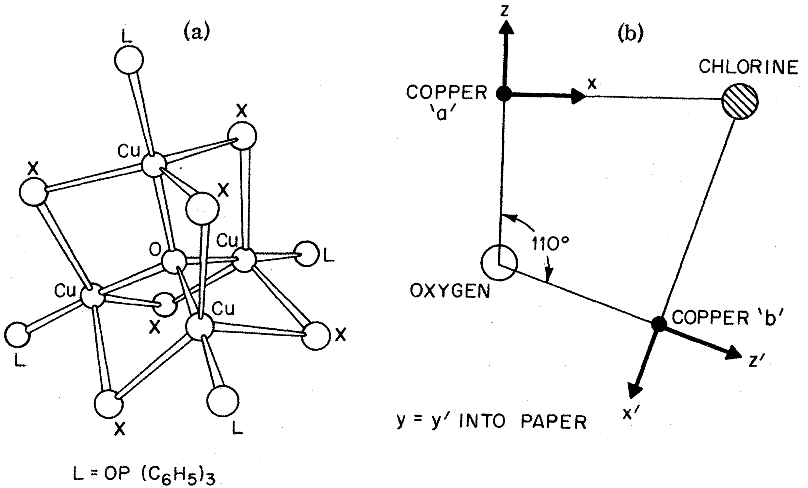

FIG. 1. (a) Molecular structure of an individual copper tetramer cluster in $Cu_4OCl_6[OP(C_6H_5)_3]_4$. (b) The relative spatial relationship of Cartesian coordinate systems (xyz) and ($x'y'z'$) used in the text to discuss orbitally degenerate spin-pair interaction between adjacent copper ions a and b.

ands in Fig. 1(a) are replaced by chlorine *ions*. From a point-charge theory this anionic cluster should definitely have copper ground state $|0\rangle$. In accord with this expectation the magnetic properties of $[Cu_4OCl_{10}]^{4-}$ are grossly different from those of $Cu_4OCl_6[OP(C_6H_5)_3]_4$ and are wholly consistent with a Heisenberg interpretation.[9]

We therefore examine the consequences of having ground orbital states $|\pm 2'\rangle$. Under the influence of spin-orbit coupling we find a ground Kramers doublet

$$\varphi^{\pm}(\pm 2) \sim [|\pm 2\rangle^{\pm} \pm \gamma |\mp 1\rangle^{\pm} \pm \epsilon |0\rangle^{\mp}], \tag{3}$$

in which γ and ϵ are real numerical constants, and superscripts ± refer to spin quantum numbers $\pm\frac{1}{2}$. To discuss magnetic exchange in lowest order we put $\epsilon = 0$, thereby neglecting spin-orbital contributions to exchange itself. The cation orbitals involved are

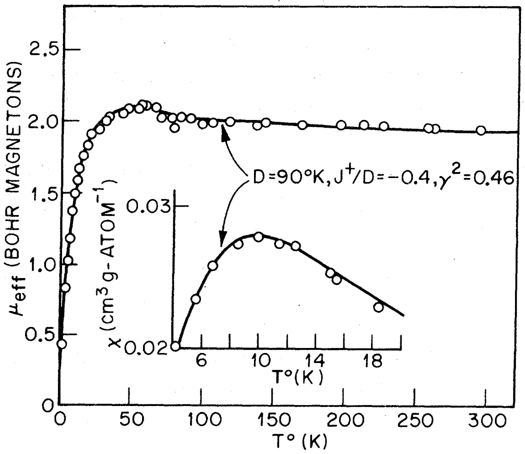

FIG. 2. Temperature dependence of effective magnetic moment μ_{eff} per copper ion in $Cu_4OCl_6[OP(C_6H_5)_3]_4$ comparing the best-fit theoretical curve from orbitally degenerate theory (full curve) with experimental data (circles). Inset is the equivalent comparison at low temperatures in terms of magnetic susceptibility itself and with an expanded temperature scale.

$$\varphi(\pm 2) = 2^{-1/2}(1+\gamma^2)^{-1/2}[d_{x^2-y^2} + \gamma d_{xz} \pm i(d_{xy} - \gamma d_{yz})], \tag{4}$$

where Cartesian coordinates (xyz) are defined *locally for each* copper site.

Forming Slater determinantal wave functions Φ_i $(i = 1, 2, 3, 4)$ for two holes, one in a $\varphi^+(+2)$ or $\varphi^-(-2)$ xyz orbital on site a and the other in an equivalent $x'y'z'$ orbital on site b [Fig. 1(b)], we examine the 4×4 matrix $\langle \Phi_i | \mathcal{H}_{ex} | \Phi_j \rangle$, where $\mathcal{H}_{ex}$ is the exchange operator[6] (kinetic plus potential) defined by Anderson.[10] Writing the dominant exchange contributions,

$$\langle [x^2-y^2, xz]_1 [x'^2-y'^2, x'z']_2 | \mathcal{H}_{ex} | [x^2-y^2, xz]_2 [x'^2-y'^2, x'z']_1 \rangle = 2J_1, \tag{5}$$

$$\langle [xy, yz]_1 [x'y', y'z']_2 | \mathcal{H}_{ex} | [xy, yz]_2 [x'y', y'z']_1 \rangle \equiv 2J_2, \tag{6}$$

where subscripts 1 and 2 refer to hole designation and

$$[xy, yz] = (1+\gamma^2)^{-1/2}(d_{xy} - \gamma d_{yz}), \tag{7}$$

$$[x^2-y^2, xz] = (1+\gamma^2)^{-1/2}(d_{x^2-y^2} + \gamma d_{xz}), \tag{8}$$

the resulting exchange matrix can be written in terms of fictitious spins $\vec{s}_a$ and $\vec{s}_b$ $(s = \frac{1}{2})$ as[9]

$$\mathcal{H}_{ab} = \tfrac{1}{3}J^+(s_{az}s_{bz'} + s_{ax}s_{bx'}) - J^+ s_{ay}s_{by'} + D(s_{az}s_{bx'} - s_{ax}s_{bz'}), \tag{9}$$

in which $J^+ = J_1 + J_2$ and $D = 2\sqrt{2}(J_1 - J_2)/3$.

The resulting tetramer Hamiltonian (with six spin-pair interactions) can now be expressed as a 16 ×16 matrix in the product spin space $\vec{s}_1 \times \vec{s}_2 \times \vec{s}_3 \times \vec{s}_4$ and diagonalized numerically. There are in general five different energy levels, one sixfold degenerate, two threefold, and two twofold, with a nonmagnetic doublet lowest. Including an applied field term in the Hamiltonian we again diagonalize numerically, sampling the field dependence of the levels, and formally calculate magnetic susceptibility as a function of temperature and of the relevant parameters. It is isotropic, and a quantitative fit of theory with experiment is found (Fig. 2) for $\epsilon = 0.4$, $\gamma^2 = 0.46$, $J_1 \sim 28$°K, and $J_2 \sim 67$°K.

The solution is not unique with respect to spin-orbital admixture ϵ [which enters through (3) via the g factors; equally good solutions can be obtained for smaller ϵ, but not in the limit $\epsilon \to 0$]. Although, for this reason, no great quantitative significance can be attached to the above values J_1 and J_2, their signs are relevant and it is pleasing to see them conform with physical expectations. From (5) the dominant contribution to J_1 would seem to be potential exchange via near-orthogonal (relevant angle 81.5°) x^2-y^2-type orbitals σ bonded to Cl^- anions while from (6), J_2 is π-bonded kinetic exchange via both Cl^- and O^{2-}. Expressed in the *common* coordinate system (xyz) we find, via (9), a spin-pair exchange

$$\mathcal{H}_{ab} \sim -80(s_{ax}s_{bx}+s_{az}s_{bz})+40s_{ay}s_{by}+40(s_{ax}s_{bz}-s_{az}s_{bx}), \tag{10}$$

with coefficients in degrees Kelvin.

Further measurements have been made on closely related complexes $Cu_4OBr_6[OP(C_6H_5)_3]_4$ and $Cu_4OCl_6(C_5H_5N)_4$ with qualitatively similar findings.[9] Agreement with orbitally degenerate theory can again be obtained with exchange parameters conforming qualitatively with physical expectations.

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Delayed Neutron Emission from ^{137}I

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The β-delayed neutron energy spectrum from ^{137}I has been studied with a high-resolution neutron spectrometer. The neutron energy distribution is found to exhibit prominent line structure. The overall shape of the distribution indicates that γ-ray emission strongly competes with d-wave neutron emission over a large excitation energy interval. The line structure is shown to be in general agreement with spin-dependent level-density calculations.

Delayed neutron spectrometry is a potentially fruitful technique for precise level-density measurements above the neutron binding energy. No work has been reported previously on this subject because of the difficulty of producing delayed neutron precursors in sufficient strength, and the limited energy resolution of most fast neutron spectrometers. The recent development of a ^3He ionization chamber[1] with high detection efficiency and superior energy resolution for fast neutrons, in combination with an on-line mass spectrometer, has permitted the investigation of neutron-emitting energy levels in ^{137}Xe following β decay from ^{137}I.

The OSIRIS on-line isotope separator[2] was used to separate by mass the fission products from a ^{235}U sample located near the core of a 1-MW reactor. Ions with mass 137 were collected on magnetic tape and transferred to the remote neutron spectrometer, giving an initial source strength of about 3 μCi and a fast neutron counting rate of more than 1 count/sec. Fresh samples were collected simultaneously with the measurement and transferred to the counting station at 60-sec intervals.

The experimental pulse-height distribution is shown in Fig. 1 for delayed neutrons emitted from excited levels in ^{137}Xe. The prominent line structure seems to suggest neutron emission from widely spaced levels, particularly towards the low-energy end of the spectrum. An interpretation of the structure as arising from statistical fluctuations[3] would appear to be less probable. Analysis of the pulse-height distribution in terms of the energy-dependent spectrometer response function gives the individual energy components, shown in Fig. 1 by vertical lines with appropriate relative amplitudes. Two series of peaks are