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Through space magnetic exchange in tetrabromocuprates: theoretical considerations

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Abstract

The temperature dependence of the magnetic susceptibility of a two-dimensional Heisenberg antiferromagnet [bis(2-amino-5-chloropyridinium) tetrabromocuprate] is calculated via ab initio electronic structure methods. Individual pair-wise exchange values are used to determine the magnetic structure of the crystal and then to compute its magnetic susceptibility using a recently proposed method (J. Phys. Chem. A 106 (2002) 1299). Comparison of the calculated susceptibility to the experimental values shows excellent agreement.

Keywords: Tetrabromocuprates; Two-dimensional Heisenberg antiferromagnet; Magnetic susceptibility; Ab initio

1. Introduction

The study of magnetism in low-dimensional systems has been of major interest for nearly three decades and this interest has increased in the past decade due to the discovery of the copper oxide-based superconductors. The need to understand the nature of the magnetic interactions in these systems has become paramount and there has been a great deal of both theoretical [1] and experimental [2] work in the area, especially in two-dimensional Heisenberg systems. We have been interested in the use of the techniques of *Molecular Magnetism* [3] to study the effects of changes in packing, bond lengths and angles on magnetic exchange in low-dimensional systems. Complexes of tetrahalocuprates (as the source of the magnetic moment) with differing organic cations provide a wealth of structural types, as the packing of the CuX_4^{2-} ions is highly dependant upon the size and shape of the organic cations. A wide variety of materials have been prepared and studied by ourselves and others [4]. It is well known from this literature that the interactions between the CuX_4^{2-} ions in such compounds are dependant upon a number of factors including the distortion of the CuX_4^{2-} ion, distances between the species and the associated bond and torsion angles.

We have recently developed a system for calculating the magnetic exchange constants in magnetic materials based upon the structure of the solid and for calculating the temperature dependence of the magnetic susceptibility and heat capacity in such materials. We initially applied the technique to the analysis of ferromagnetic and antiferromagnetic interactions in organic systems [5]. We are interested in applying the technique to inorganic systems as well and thus undertook the present study of the two-dimensional Heisenberg antiferromagnet, bis(2-amino-5-chloropyridinium) tetrabromocuprate, $(5CAP)_2CuBr_4$.

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2. Experimental

2.1. Synthesis and magnetic studies

The preparation and magnetic data for the complex have been previously reported [4a].

2.2. Calculations

The method employed to compute the macroscopic magnetic properties of a crystal is based on the ab initio determination of the magnetic interaction between all unique pairs of radicals found in the crystal (the so-called J_{AB}) and then using these pairs in the Heisenberg Hamiltonian to find its matrix form **H** on a finite spin basis, obtained by defining the minimal magnetic model space (a finite space containing all different interactions and capable of regenerating the whole crystal by translations along all directions in space). The diagonalization of this **H** matrix gives the spectrum of spin states for the crystal, which is the only information needed to compute the macroscopic properties using Statistical Mechanics (see Ref. [5] for details and an accompanying paper in this issue illustrating the principles of this method on *p*-nitro-phenylnitronyl nitroxide). Therefore, there is no external intervention by the user: the process is rigorous, and based on knowledge of the microscopic J_{AB} magnetic interactions between the pairs.

The computation of the J_{AB} pair interactions has been done at the CAS(6,6)/LANL2DZ* level, where some extra functions have been added to the standard LANL2DZ basis set to extend its flexibility: on the Br atoms, we have added one each diffuse s, p and d function (exponents 0.00396, 0.00240 and 0.038878, respectively), plus one set of p polarization functions (exponent 0.155065); on the Cl atoms we added one diffuse s, p and d function (exponents 0.01905, 0.015702759, and 0.3890) and two sets of polarization d functions (the first contracted from four primitives, while the second is a single function of exponent 1.32408768). With these extra functions, the basis set is flexible enough to take into account the anionic nature of the fragments as well as the possible polarization of each of the atoms by the presence of the second fragment. The CAS space was built by adding the two CAS(3,3) spaces in each $CuBr_4^{2-}$ fragment, designed to allow for the presence of polarization on each of these fragments. All calculations where done using the GAUSSIAN-98 package [6].

3. Results and discussion

The complex $(5CAP)_2CuBr_4$ (**1**) is a member of a family of isomorphous complexes that are good representations of the two-dimensional Heisenberg antiferromagnetic model. Five such compounds are known at present (where the 5-substituent on the pyridine ring is methyl, chloro, or bromo and the copper halide is chloride or bromide) [4a,4b,7]. The complexes crystallize in the monoclinic space group *C*2/*c* and the $CuBr_4^{2-}$ ions occur as highly distorted tetrahedra (the mean trans Br–Cu–Br angles are typically 135–145°) (Fig. 1).

This family was chosen for initial study due to the high symmetry of the lattice which limits the number of potentially unique interactions between $CuBr_4^{2-}$ units. The complex packs in alternating layers of $CuBr_4^{2-}$ ions and $5CAP^+$ ions parallel to the C-face (Fig. 2).

The structure and properties of **1** were analyzed via a four-step procedure. First, all possible magnetic interactions, J_{AB}, were identified based upon the inter-site distances between $CuBr_4^{2-}$ ions in the crystal lattice.

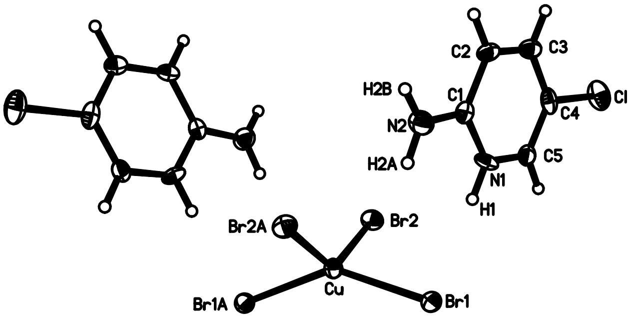

Fig. 1. Thermal ellipsoid plot of **1** showing the distortion of the $CuBr_4^{2-}$ ion. Only the asymmetric unit and the Cu coordination sphere have been labeled.

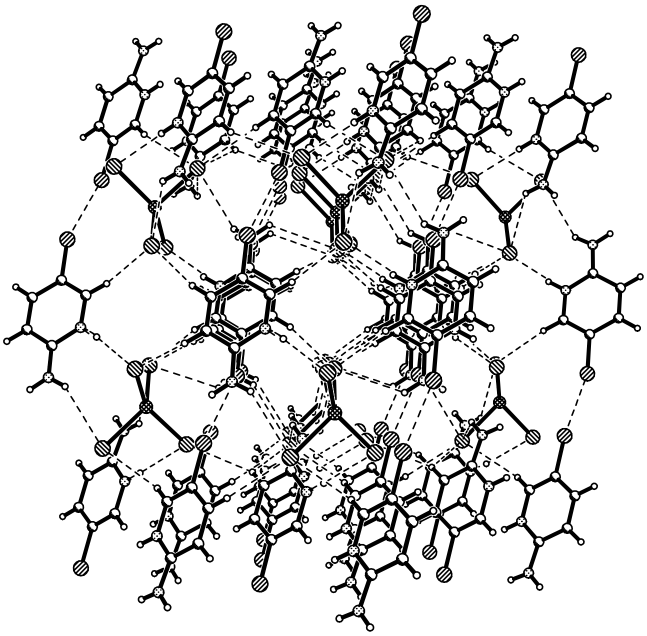

Fig. 2. Packing diagram showing the layer structure of **1** viewed parallel to the C-face diagonal.

Four such pairs were considered based on distance. Within the $CuBr_4^{2-}$ layers (parallel to the C-face) two possible exchange pairs were considered. The C-centering generates a rhombic pattern where each Cu ion has four nearest neighbors with a Br···Br distance of 4.29 Å (Fig. 3). Its pair interaction is identified as J_1. The symmetry ensures that all structural parameters (Br···Br distances, Cu–Br···Br angles, Cu–Br···Br–Cu torsion angles) are identical. The next-nearest neighbor contacts within the plane are the short diagonals of the rhombus (hence two for each Cu) and have a Br···Br separation of 7.71 Å. The long diagonal has a Br···Br separation of 10.18 Å and, in a first approximation, was not considered.

Nearest neighbors between the layers (parallel to the c-axis) are made via double Br···Br contacts (J_2) of 4.83 Å (Fig. 4). Each $CuBr_4^{2-}$ ion has two of these nearest neighbors and also has four next-nearest neighbors between layers at a distance of 6.17 Å (double dashed line in Fig. 4). The values for J_1 and J_2 (nearest neighbors within and between planes) calculated at the CAS(6,6) level are -0.88 and -0.29 cm^{-1}, respectively. That is, both are antiferromagnetic and small. The experimental value for J_1 is -4.25 K obtained from a fit to the 2D-Heisenberg model [4a] and ~ -0.5 K for J_2 obtained via mean field theory or the magnetic specific heat (see Hamiltonian below) [4d].

$$\hat{H} = -2\sum_{AB}^{N} J_{AB}\hat{S}_A\cdot\hat{S}_B$$

The dominant interaction in the system is the exchange within the plane, J_1, which is three times that between planes (J_2) and thus the magnetic structure is taken as a two-dimensional set of planes, connected with weaker interactions between the layers. Using this magnetic structure, it is possible to select as minimal magnetic minimum space the 8 site model shown in the inset to Fig. 5, formed by two squares linked by their corners. With the set of spin eigenfunctions defined by this space, the matrix representation of the Heisenberg Hamiltonian is computed using the J_1 and J_2 values in the right places. From there, we obtain the electronic energy levels. The energy levels so obtained were used to calculate the magnetic susceptibility with statistical mechanics methods [8] as we have done previously [5]. The magnetic susceptibility is shown as a function of temperature in Fig. 5.

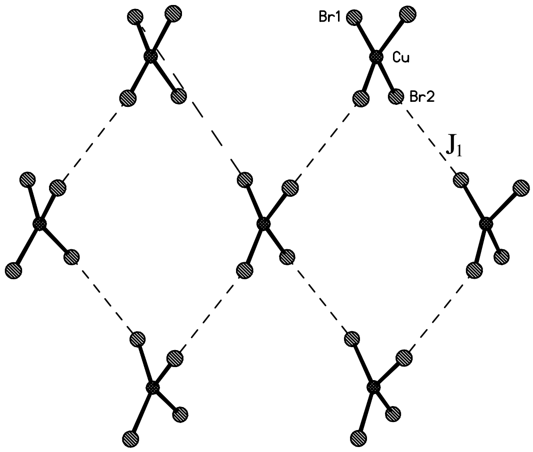

Fig. 3. Packing of the $CuBr_4^{2-}$ units parallel to the face. Dashed lines represent the nearest neighbor contacts between bromide ions.

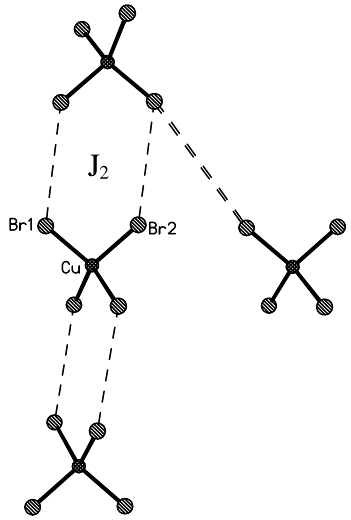

Fig. 4. Packing of $CuBr_4^{2-}$ units C-showing nearest neighbors between layers (dashed lines) and one next-nearest neighbor (double dashed line).

It is readily apparent from Fig. 5 that a scaling factor of $\sim$4 is necessary for agreement between the experiment and the calculated susceptibilities. The deviation seen at low temperatures (below 7 K) arises because the experimental data is from a powder sample, rather than from an aligned single crystal. The good agreement between the calculated and experimental values above 7 K shows that this new method for predicting magnetic interactions from the crystal structure data is valid for transition metal complexes as well as for organic crystals.

Calculations including the next-nearest neighbor interactions both within and between layers are in progress. While we anticipate that these values will be nearly zero, finite values for these exchange pathways may have a significant effect when summed over the lattice. Once these final values are known, direct fitting of the calculated values to the single crystal data will be possible. Finally, we intend to analyze the two additional members of this family (the 5-methyl-, and 5-bromo-substituted compounds) to determine the generality of the scaling factor.

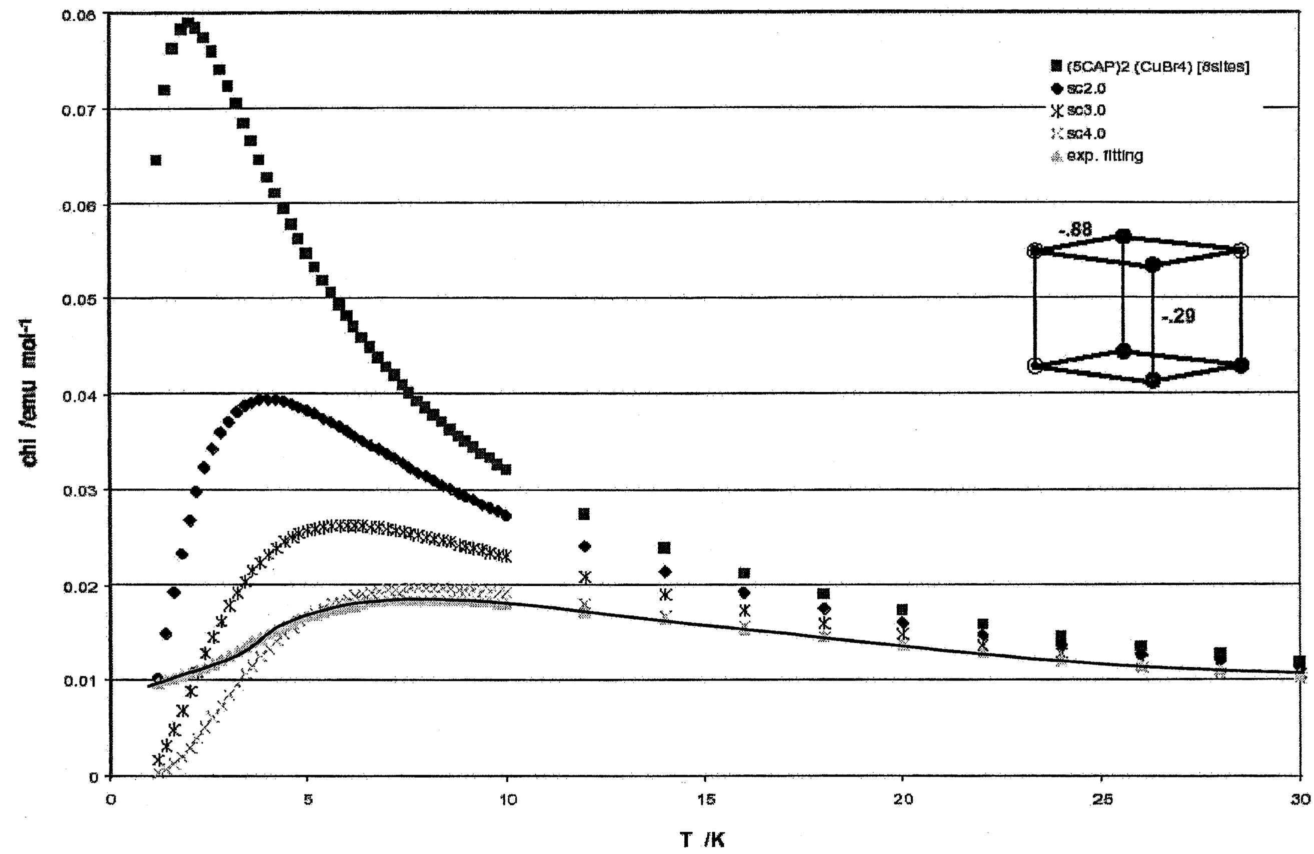

Fig. 5. Calculated magnetic susceptibility of **1** as a function of temperature. Four different scaling factors are shown along with the experimental powder susceptibility (black line).

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