

Table I. Orbital Parameters Used in the Calculations

element	orbital	H_{ii} , eV	ζ
Cu	4s	-11.4	2.2
	4p	-6.06	2.2
	3d ^a	-14.0	5.95 (0.5933), 2.30 (0.5744)
Fe	4s	-9.10	1.9
	4p	-5.32	1.9
	3d ^a	-12.6	5.35 (0.5505), 2.00 (0.6260)
Zn	4s	-12.41	2.01
	4p	-6.53	1.70

^a A double- ζ expansion, with coefficients in parentheses.

z^2 orbital, by symmetry the only one of the d set which is stabilized in this way, is doubly occupied for case B and only singly occupied in case A. For the d^{10} configuration then, distortion A is favored since $|\Delta E_2| > |\Delta E_1|$ on the basis of energy gap arguments. Such an argument allows access to the observation of linear two-coordination found for the Hg(II), Ag(I), and Cu(I) systems. These structural features have been described for many years in terms of Orgel's model¹⁹ of s/d mixing. Thus the structure of cinnabar (HgS) may be regarded as one containing octahedral coordination around mercury with two short bonds and four very long ones. The structures of the heavier mercuric halides are of the cadmium halide type, but instead of six-coordination, the geometry with two short plus four long distances is found. Figure 5b shows the extension of the argument to the distortion of the tetrahedron. The distortion (A) toward the trigonal plane (a_1 highest in energy as in Figure 3c) should be energetically favored over the distortion (B) to the structure with one short and three long bonds since, as in the octahedral case, $|\Delta E_2| > |\Delta E_1|$ on the basis of energy gap arguments. Although our calculation (Figure 1) shows this to be true, it is perhaps more appropriate to note that this is the distortion which appears most frequently in the examples we have found in the literature. By calculation, we find an s/d ratio in the a_1 orbital of Figure 3c of 0.18 for $z = 4.33$ and 0.14 for $z = 1.1$, two equal distortions from the tetrahedral geometry to quantitatively support this claim.

Mixing of 4s and 3d orbitals plays a role in influencing coordination number in molecular Cu(I) chemistry, as shown in a recent study⁸ of some cubane type systems. We need only look at some other "unusual" chemistry in this part of the periodic table to find other examples where such orbital effects are important. Interactions between Cu(I) atoms,²⁰ of importance in the assembly

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of many Cu(I) complexes, electronically are very similar to those associated with Pt(0)-Pt(0) interactions.²¹ Mixing between the nd and $(n+1)s$ orbitals is of crucial importance for both. Such effects are doubly important in cuprite, Cu_2O . The structure of this material consists of two interpenetrating Cu_2O lattices each containing linear two-coordinate copper and tetrahedral oxygen atoms in an ice-like arrangement. The Madelung energy is less favorable for the two separate lattices than for the observed structure. The presence of a stabilizing Cu(I)-Cu(I) interaction is sufficient to hold the structure together. (The interaction energy of the two lattices has been calculated²² to be of the order of 1 kcal/mol). Thus s/d interactions are responsible here both for the linear O-Cu-O unit in the ice-like structure of each lattice and for the interaction which holds them together.

Orbital mixing of a related type is also important at the beginning of the transition metal series. It can be used to understand the bent structures²³ of some of the AX_2 molecules ($A =$ group 2 element, $X =$ group 17 element) and also allows access²⁴ to the unusual geometries of several d^0 transition metal systems.

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Appendix

A metal-sulfur distance of 2.30 Å was used for all calculations of the tetrahedral geometry, except where stated. This leads to a distance of 2.169 Å for the corresponding trigonal planar geometry. (See ref 25 for a compendium of Cu(I)-S distances.) From considerations of the bond valence sum, the difference between three- and four-coordinate distances should be 0.106 Å, irrespective of the nature of the atoms. Table I shows the orbital parameters used in the calculations.

Registry No. Cu, 7440-50-8; Ag, 7440-22-4.

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Magnetic Ordering in $[\text{Co}(\text{NH}_3)_6][\text{CuCl}_5]$: Specific Heat Measurements

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The specific heat of $[\text{Co}(\text{NH}_3)_6][\text{CuCl}_5]$ is reported over the temperature interval 1.6-40 K. A λ -feature, characteristic of a magnetic phase transition, is observed at 3.925 ± 0.005 K. Only 23% of the magnetic entropy is acquired below T_c , which is indicative of substantial short-range order.

Introduction

The substance $[\text{Co}(\text{NH}_3)_6][\text{CuCl}_5]$ is one of a series of bimetallic compounds that are of current interest.¹ The various physical properties of this material have been summarized earlier.²

The compound is cubic at room temperature, but it undergoes a structural transition to a tetragonal phase as it is cooled below 280 K.³ We illustrate here the utility of specific heat measurements for the determination of the character of systems with magnetic interactions. This paper marks the first report of the specific heat of a copper-containing bimetallic coordination

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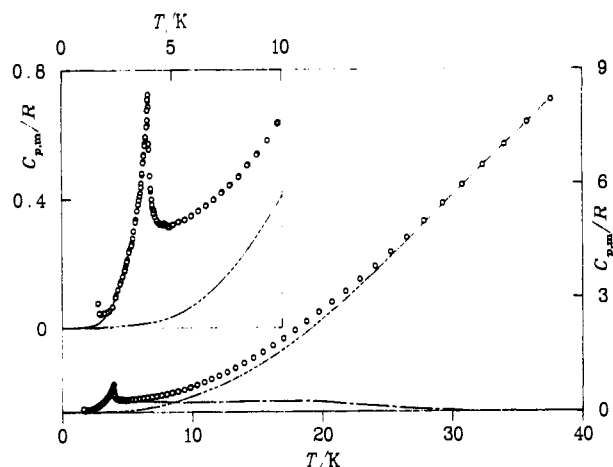


Figure 1. Specific heat of $[\text{Co}(\text{NH}_3)_6][\text{CuCl}_5]$. The points are the experimental data, the solid curve at low temperatures is the extrapolation to 0 K, the lattice specific heat is indicated by ----, and the magnetic contribution is indicated by -·-. The inset shows the transition region on an expanded scale.

compound at low temperatures.

The magnetic susceptibilities of single crystals of $[\text{Co}(\text{NH}_3)_6][\text{CuCl}_5]$ were recently reported.² The data were shown to be consistent with the compound behaving as a three-dimensional (simple cubic lattice), spin $S = 1/2$, Heisenberg antiferromagnet, with $T_c = 3.8$ K. Note that the Co(III) cation is diamagnetic and that all the magnetism in this material arises from the copper(II) moiety. One of the curious aspects of these data is that no easy axis of antiferromagnetic alignment is evident. It was concluded that a three-domain structure, arising from tetragonal distortions, effectively prevents the establishment of a macroscopic easy axis. This conclusion is consistent with the EPR study.³

The sample was prepared and analyzed as earlier.⁴ Heat capacity measurements were conducted in the adiabatic calorimetric cryostat whose detailed description is provided elsewhere.⁵

Results and Discussion

The specific heat of $[\text{Co}(\text{NH}_3)_6][\text{CuCl}_5]$ is presented in Figure 1. As anticipated, a λ -type phase transition is found at 3.925 ± 0.005 K, which is identified as the critical temperature. The critical temperature is insignificantly higher than the 3.8 K previously reported.² The small shoulder in the data just below 5 K is attributed to a small impurity of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$.

Resolution of the heat capacity due to the magnetic transition requires separation of the lattice specific heat from the experimental results. This task is accomplished by employing the enhanced Komada–Westrum phonon distribution model in a method that was described previously.^{5,6} The parameter Θ_{KW} , representing the approximated phonon density of states which the model calculates, is presented in Figure 2. The constant value of the characteristic temperature at higher temperatures, $\Theta_{\text{KW}} = 50$ K, was used for the calculation of the lattice specific heat (Figure 1) between 0 and 38 K.

The specific heat associated with the magnetic ordering may be readily calculated once the lattice heat capacity is determined,

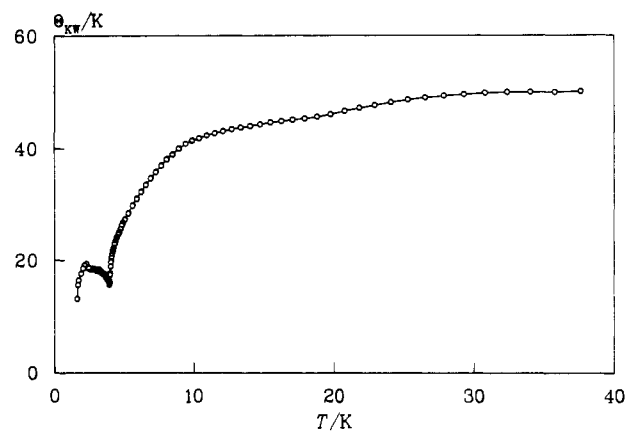


Figure 2. Apparent characteristic temperature Θ_{KW} for $[\text{Co}(\text{NH}_3)_6][\text{CuCl}_5]$.

and is also presented in Figure 1. Although the transition takes place at the relatively low temperature of 3.9 K, the magnetic contribution to the specific heat extends up to about 30 K. The same phenomenon is mirrored in Figure 2, where Θ_{KW} displays a broad minimum over the transition region, and remains constant above that region where no magnetic contribution to the specific heat is present.

The magnetic entropy is found to be $0.66R$ between 0 and 30 K, in excellent agreement with the theoretical value of $R \ln 2 = 0.69R$. Only 23% of the entropy associated with the magnetic ordering originates below the critical temperature, 3.925 K. This indicates that short-range order plays an important role in the magnetic interactions. The susceptibility data exhibit a broad maximum at 7.5 K, 3.6 K above the critical temperature, and the experimental results deviate from theoretical predictions for a simple Heisenberg antiferromagnet, below that maximum. The tetragonal distortion and the three-domain structure it may cause³ are probably the source of this phenomenon.

Short-range order is common in copper(II) compounds. This is usually the result of lower-dimensional magnetic interactions, mainly in one dimension.⁷ One-dimensional order will usually be accompanied by a broad maximum in the magnetic heat capacity above the critical temperature,⁸ and such a maximum has been observed in the present study. Several attempts have been made to fit the data to a likely model; in particular, a fit was attempted with the Bonner–Fisher model for spin $1/2$ Heisenberg linear chains.⁹ Neither the shape of the curve nor the slope above the maximum agrees with the model. This is not surprising, for with more than 23% of the magnetic ordering (i.e., magnetic entropy) associated with the λ -anomaly, the material would be at best a poor example of a magnetic linear chain. We nevertheless conclude that short-range order is of prime importance in this material. The nature of this short-range order is not yet clear, but the analysis of the susceptibility data in terms of a simple-cubic lattice appears to be unjustified.

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