The Magnetic Super-Exchange Coupling in Copper(II) Acetate Monohydrate and a Redetermination of the Crystal Structure

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Abstract

The magnetic properties and redetermination of crystal structure of copper(II) acetate monohydrate have been studied. The copper(II) centers are separated by 2.617(1) Å and antiferromagnetically coupled (-2J = 292.2 cm^{-1}), which follows from temperature-dependent magnetic susceptibility measurements in the temperature range 4.2 to 300 K. The magnetic moment at 300 K is about 2.1 Bohr magnetons while 0.1 Bohr magnetons at 4.2 K. The magnetic susceptibility is at a maximum near 250 K and decreases rapidly as the temperature is lowered to liquid helium temperature.

Key Word: Magnetic Super - Exchange; Antiferromagnetic Coupling; Crystal Structure

1. Introduction

Magneto-structural correlations have been studied extensively in dinuclear copper(II) compounds. Three classes of compounds may be distinguished, namely dinuclear copper(II) halides with salicylaldimines, dinuclear copper(II) halides with pyridine N-oxide, and dinuclear copper(II) carboxylates [1]. Dinuclear copper(II) compounds are of particular interest due to their stability in the dimeric form and their magnetic super-exchange interactions between copper atoms through the bridging ligands.

Bleaney and Bowers [2] proposed direct magnetic exchange coupling between a pair of copper(II) atoms in copper(II) acetate monohydrate on the basis of ESR studies and van Niekerk and Schoening [3] found a binuclear structure for copper(II) acetate monohydrate involving bridging acetate groups and Cu - Cu nearest neighbour distance of 2.64 Å slightly greater than the interatomic distance of 2.556 Å in metallic copper at 20

°C (International Tables for X-ray Crystallography, 1962, p. 278). The crystal structure of copper(II) acetate monohydrate was also determined using neutron-diffraction and Cu - Cu separation was found to be 2.614(2) Å [4]. The question of the mechanism for direct interaction between the adjacent copper atoms in such complexes as Cu(II) acetate monohydrate was the subject of many discussions in the literature [5-7]. The complete MO treatment of exchange interactions in copper(II) acetate monohydrate indicated that the contributions to the singlet-triplet energy splitting, -2J, are of four major types: direct exchange (ferromagnetic); super-exchange, SE (antiferromagnetic); double-spin polarization, DSP (overall antiferromagnetic); higher order effects, SE, SE+P (antiferromagnetic) [8].

I have measured magnetic susceptibilities in the temperature range 4.2-300 K using the Faraday method to investigate the magnetic exchange coupling between a pair of copper(II) atoms in copper(II) acetate monohydrate experimentally. I have also redetermined the crystal structure with the aim of obtaining more accurate structure parameters than those of van Niekerk & Schoening [3].

2. Experimental

Magnetic susceptibility measurements of the powdered sample were performed on a Faraday-type magnetometer consisting of a CAHN D-200 microbalance, a Leybold-Heraeus VNK 300 helium flux crystat and a Bruker BE 25 magnet connected with a Bruker B-Mn 200/60 power supply in the temperature range 4.2-300 K. Details of the apparatus have already been described [9]. The applied field was 1.2 T. Diamagnetic corrections of the molar magnetic susceptibility of the compound was applied using Pascals constants [10]. Magnetic moments were obtained from the relation $\mu_{eff} = 2.828(\chi T)^{1/2}$.

A crystal of dimensions 0.15x0.20x0.20 mm was mounted on an Enraf-Nonius CAD-4 diffractometer equipped with a graphite monochromator. Cell constants were determined by least-squares refinement of diffractometer angles for 25 reflections collected in the range $1.12° < \theta < 25.70°$. Three standard reflections were monitored every 120 min., but no considerable intensity variations were recorded. A total of 1380 reflections were recorded, with Miller indices $h_{min} = 0$, $h_{max} = 15$, $k_{min} = 0$, $k_{max} = 11$, $l_{min} = -17$, $l_{max} = 16$. The structure was solved by direct methods using SHELXS86 [11]. The E-map computed from the phase set with the best combined figure of merit revealed the positions of all non-hydrogen atoms. Full-matrix least-square refinement of the fractional coordinates of the non-hydrogen atoms with anisotropic atomic displacement parameters was performed SHELXL97 [12]. Positions of H atoms were centered at calculated positions and refined using a riding model for both positions and isotropic thermal parameters. Final R and wR factors were 0.032 and 0.093, respectively, for 98 parameters using the I values of 1203 ($I > 2\sigma$ (I)) reflections. The highest and the lowest peaks in the final difference map were 0.532 and 0.536 eÅ^{-3}, respectively. Scattering factors were taken from SHELXL97 [12].

Crystal data for the copper(II) acetate monohydrate, $C_8H_{16}O_{10}Cu_2$, M_r= 227.3 g.mol^{-1}, monoclinic C2/c, a = 13.1725(9), b = 8.5675(7), c = 14.1355(15) Å, β = 119.085(8)°, V=1394.1(2) Å^3, Z = 4, D_C=1.902 g.cm^{-3} and $\mu(MoK\alpha)$ = 3.095 mm^{-1}, F(000) = 808, T=293(2) K, R = 0.032 and wR = 0.093 for 1203 observed reflections.

3. Discussion

Magnetic susceptibility measurement for a powdered sample of the investigated compound was performed by the Faraday method in the temperature range 4.2-300 K. Experimental data were corrected for the underlying diamagnetism (estimated as 245.10^{-6} cm^3/mol). The data were fitted to the following expression [13],

$$\chi = \frac{N_Lg^2\mu_B^2}{3kT}\left[1 + \frac{1}{3}exp(-2J/kT))\right]^{-1}(1-x_p) + \frac{N_Lg^2\mu_B^2}{4kT}x_p + N\alpha$$

using the isotropic (Heisenberg) exchange Hamiltonian ($\mathbf{H= -2J\ S_1.S_2}$) for two interacting S=1/2 centers. Nα (60.10^{-6} cm^3/mol for each copper atom) is the temperature independent paramagnetism, χ_p is the molar fraction of monomeric impurity. Least-squares fitting of the data displayed in Figure 1 with the corrected above equation leads to -2J= 292.2 cm^{-1}, g= 2.16 and χ_p= 3.7%. The magnetic moment at room temperature is about 2.1 Bohr magnetons, more than the theoretical spin-only value of 1.73. The magnetic moment at 4.2 K is about 0.1 Bohr magnetons and increases rapidly as the temperature increases.
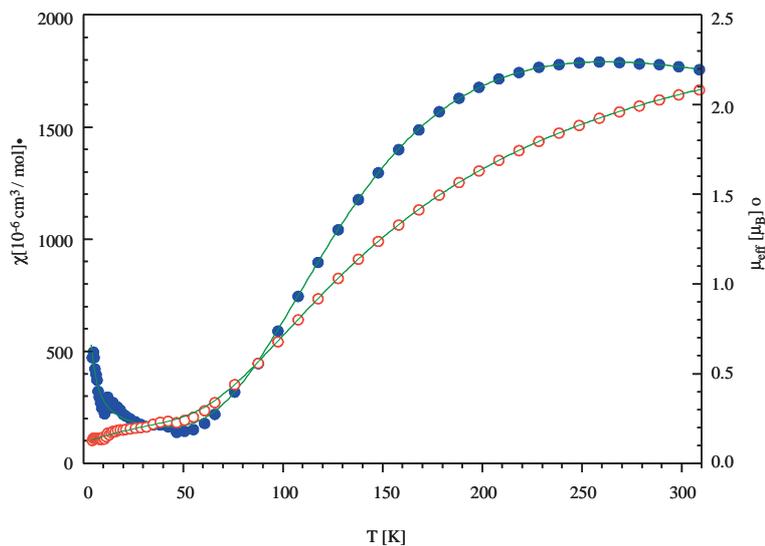
Figure 1. Molar susceptibility and effective magnetic moment per copper vs. temperature curves for copper(II) acetate monohydrate.

In the copper(II) carboxylate dimers, an antiferromagnetic super-exchange interaction exists between the two copper(II) atoms through the four bridging carboxylate ions. The magnitude of the exchange interaction is given by 2J, the separation energy between the singlet ground state and the triplet state. The $-2J=292.2$ cm^{-1} in the investigated compound indicates antiferromagnetic coupling. The main factor which determines the magnitude of the antiferromagnetic interaction in the dimeric copper(II) carboxylates is the electronic structure of the bridging OCO moiety. The unpaired electrons in the $d_{x^2-y^2}$ orbital of the Cu^{+2} cations interact with each other through the molecular orbitals of the bridging ligands. The spin super-exchange interaction of the binuclear copper(II) complexes can be understood in terms of the natural (non-orthogonalized) magnetic orbitals [14]. The natural magnetic orbital (NMO) of the Cu atom in the cage structure is mainly the $d_{x^2-y^2}$ orbital and has tails on the bridges. The spin super-exchange interaction increases along with the overlap integral of two NMOs. When the Cu-O-C-O-Cu bridge bends, the overlap between the $d_{x^2-y^2}$ orbital of the Cu^{+2} ion and the $2p_x$ orbital of the oxygen atoms in the symmetric decreases and the tails of the NMO on the bridge decrease. A previous study also revealed that differences in the 2J values are not mainly the result of any geometrical features, but result from the different electronic structures of the bridging ligands [15]. The 2J value differs between copper(II) tricholoroacetates (ca 200 cm^{-1}) [16], copper(II) benzoates (ca 300 cm^{-1}) [17] and triorganosilanecarboxylate dimers (ca 1000 cm^{-1}) [18]. The key point which determines the strength of the spin-exchange interaction is the $2p_x$ orbital population of the carboxylate C atom.

The molecular structure of the investigated compound is shown in Figure 2 with the atom-numbering schemes. Fractional atomic coordinates and equivalent isotropic displacement parameters for non-hydrogen atoms are given in Table 1. Bond distances and bond angles are listed in Table 2. From the point of symmetry, the two monomeric units are connected by a center of inversion. The six nearest neighbours of a copper atom are comprised of four oxygen atoms belonging to four different acetate groups, a copper atom and a water molecule. The six atoms form a distorted octahedral configuration about each of the two copper atoms. The Cu-Cu distance is 2.617(1) Å. In each molecule the two planar rings [C(1), O(4a), Cu(1a), O(3a), C(1a), O(4), Cu(1), O(3) and C(2), O(2a), Cu(1a), O(1a), C(2a), O(2), Cu(1), O(1)] are perpendicular to one another [89.91(6)°].

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters [Å^2]. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	x/a	y /b	z/c	U_{eq}
Cu(1)	0.15511(3)	0.16601(4)	0.45500(2)	0.0201(2)
O(1)	0.1666(2)	0.1615(2)	0.6005(2)	0.0283(5)
O(2)	0.1745(2)	0.1896(2)	0.3242(2)	0.0288(5)
O(3)	0.0803(2)	0.3707(3)	0.4252(2)	0.0330(5)
O(4)	0.2579(2)	-0.0145(2)	0.4999(2)	0.0330(5)
O(5)	-0.0073(2)	0.0427(3)	0.3674(2)	0.0386(6)
C(1)	0.1344(3)	0.4984(4)	0.4498(2)	0.0265(6)
C(2)	0.2479(2)	0.2291(3)	0.6804(2)	0.0245(6)
C(3)	0.2547(3)	0.2139(5)	0.7889(3)	0.0447(8)
C(4)	0.0622(3)	0.6457(4)	0.4161(3)	0.0413(9)
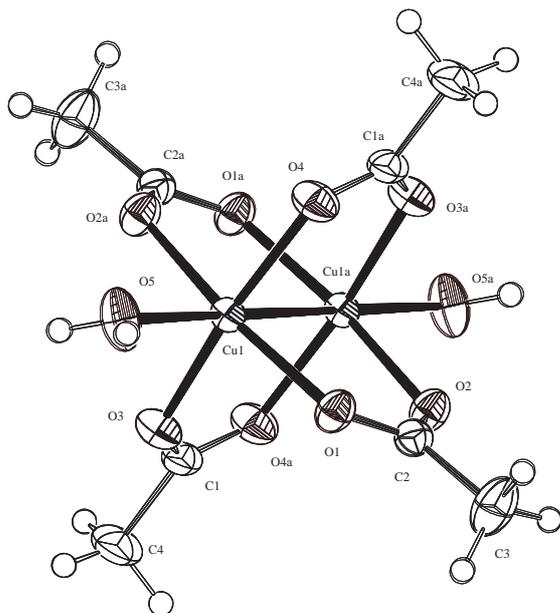
Figure 2. Molecular structure copper(II) acetate monohydrate and crystallographic numbering scheme. Displacement ellipsoids are plotted at the 50% probability level [19].

Table 2. Bond lengths [Å] and angles [°] (Atoms labelled with an "a" are related to those without by a centre of inversion).

Cu(1) − Cu(1a)	2.617(1)	O(1) - Cu(1) - O(2)	168.7(1)
Cu(1) − O(1)	1.987(2)	O(1) - Cu(1) - O(5)	98.1(1)
Cu(1) − O(2)	1.996(2)	O(2) - Cu(1) - O(5)	93.2(1)
Cu(1) − O(3)	1.954(2)	O(3) - Cu(1) - O(2)	89.3(1)
Cu(1) − O(4)	1.947(2)	O(3) - Cu(1) - O(1)	91.0(1)
Cu(1) − O(5)	2.157(2)	O(3) - Cu(1) - O(5)	93.5(1)
O(1) − C(2)	1.258(4)	O(4) - Cu(1) - O(1)	87.4(1)
O(2) − C(2a)	1.263(4)	O(4) - Cu(1) - O(2)	90.1(1)
O(3) − C(1)	1.259(4)	O(4) - Cu(1) - O(5)	97.9(1)
O(4) − C(1)	1.248(4)	O(4) - Cu(1) - O(3)	168.7(1)
C(1) − C(4)	1.512(4)	O(1) - C(2) - O(2a)	124.4(3)
C(2) − C(3)	1.499(4)	O(4) - C(1) - O(3a)	126.0(3)
		C(2) - O(1) - Cu(1)	121.5(2)
		C(1) - O(3) - Cu(1)	124.2(2)
		O(3) - C(1) - C(4)	117.0(3)
		O(1) - C (2) - C(3)	118.7(3)

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