Structural and magnetic studies on copper succinate dihydrate single crystals

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Abstract. Single crystals of copper succinate dihydrate were grown in silica gel by slow diffusion of copper chloride to sodium metasilicate gel impregnated with succinic acid. The grown crystal was subjected to single crystal X-ray diffraction studies. In its structure each copper atom is penta co-ordinated to oxygen atoms of four succinate oxygens and oxygen of co-ordinated water molecule. The four bis-bidendate succinate anions form syn–syn bridges among two copper atoms to form a polymeric two-dimensional chain. From room temperature vibrating sample magnetometer (VSM) studies, the magnetic moment of the material is calculated as 1.35 Bohr magneton (BM), indicating anti-ferromagnetic interaction between copper atoms and can be explained as due to the orbital overlap of the bridging ligand and the two copper atoms in syn–syn orientation. A strong bonding of the magnetic orbital of equatorially oriented Cu atom on both sides of the exchange pathway (Cu–O-C-O–Cu) leads to the anti-ferromagnetic interaction.

Keywords. Copper succinate dihydrate; single crystal growth; X-ray diffraction; magnetic moment.

1. Introduction

The design and the development of new metal–organic frameworks (MOFs) is one of the main focuses of crystal engineering since such material possess a broad variety of physical properties, functions and applications such as materials chemistry, heterogeneous catalysis, gas storage, polymer magnets, etc. [1–4]. A larger variety of inorganic and organic components can be used to construct MOFs. Supramolecular organized molecular magnets can be constructed by combining both molecule-based magnetism and supramolecular chemistry [5,6]. Succinate ligand can serve as a versatile ligand to provide several possibilities for creating supramolecular architectures yielding one-, two- and three-dimensional polymeric networks [7–9]. Hydrogen bonding and bridging among metal atoms via carboxylate groups in these systems gives the necessary support for forming such networks. MOFs of copper complexes have attracted special interest due to their magnetic super exchange interactions among copper atoms through bridging ligands [10,11]. Hydrothermal reaction conditions are generally employed for the synthesis of such frameworks. To make an environmentally friendly growth process, we have employed a simple room temperature gel growth technique for the crystallization of copper succinate dihydrate.

2. Experimental

Crystallization of copper succinate was carried out by ionic diffusion in hydro-silica gel. The gelating medium was prepared by titrating aqueous solution of sodium meta silicate of specific gravity 1.04 against 0.5 M succinic acid. Acidic strength and volume were adjusted to maintain the pH at 5. This solution was then introduced into standard test tube and after proper gel setting the supernatant copper chloride solution of molarity 0.5 M was poured over it without tampering the meniscus of the gel. Thin plate-like blue crystals of copper succinate were taken out of the gel solution after a month. The growth details, spectroscopic, thermal and dielectric characterization of the crystal were discussed earlier by the authors [12].

After harvesting the grown copper succinate crystals, structural characterization was performed using the single crystal X-ray diffraction technique. The single crystal X-ray diffraction (XRD) data were collected using a Bruker Kappa Apex II diffractometer, with graphite-monochromator Mo-Kα (λ = 0.71073 Å) radiation. The unit cell dimensions were recorded at 296 K. The magnetic characterization of copper succinate crystals was carried out using a Lakeshore 7404 model vibrating sample magnetometer.

3. Results and discussion

3.1 *Structural studies*

A good single crystal of size $0.35 \times 0.30 \times 0.25$ mm^3 was chosen for the single crystal XRD analysis. The programme SAINT/XPREP was used for data reduction and

Table 1. Crystal data and structure refinement parameters for copper succinate.

Parameter	Copper succinate
Empirical formula	$C_4 H_8 Cu O_6$
Formula weight	215.65
Temperature	296 (2) K
Wavelength	0.71073 Å
Crystal system, space group	Triclinic, P(-1)
Unit cell dimensions	$a = 6.4311(4)$ Å, $\alpha = 76.176(2)°$
	$b = 7.6129(4)$ Å, $\beta = 73.472(2)°$
	$c = 8.0730(5)$ Å, $\gamma = 81.559(2)°$
Volume	366.62 (4) Å^3
Z	2
Calculated density	1.9535 Mg m^{-3}
Theta range for data collection	2.77 to 28.24°
Reflections collected/unique	2865/1769 [R(int)$=0.0142$]
Data/restraints/ parameters	1769/6/116
Goodness-of-fit on F^2	1.114
Final R indices [$I > 2$sigma(I)]	$R_1 = 0.0275$, $wR_2 = 0.0848$

Table 2. Atomic co-ordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å$^2 \times 10^3$) of the non-hydrogen atoms. U (eq) is defined as one-third of the trace of the orthogonalized Uij tensor.

Atom	x	y	z	U(eq)
Cu(1)	9211(1)	6551(1)	438(1)	18(1)
O(4)	10946(3)	5822(2)	2177(2)	28(1)
O(6)	7814(3)	6885(2)	1499(2)	30(1)
O(1)	6934(3)	5032(2)	2019(2)	28(1)
O(5)	11738(3)	7649(2)	1326(2)	27(1)
O(3)	7465(3)	8865(3)	1368(3)	43(1)
O(1S)	2960(4)	1110(3)	2539(4)	49(1)
C(3)	2962(4)	3756(3)	3989(3)	25(1)
C(2)	5041(3)	2484(3)	3674(3)	22(1)
C(1)	6868(3)	3361(3)	2220(3)	20(1)
C(4)	1982(3)	4266(3)	2428(3)	21(1)

Table 3. Selected bond lengths (Å) for copper succinate.

Cu(1)–O(1)	1.9591(17)
Cu(1)–O(4)	1.9646(17)
Cu(1)–O(6)	1.9648(17)
Cu(1)–O(5)	1.9698(17)
Cu(1)–O(3)	2.1211(18)
Cu(1)–Cu(1)#1	2.6062(5)
O(4)–C(4)#2	1.272(3)
O(1)–C(1)	1.249(3)
O(5)–C(1)#1	1.269(3)
C(3)–C(4)	1.510(3)
C(3)–C(2)	1.527(3)
C(2)–C(1)	1.508(3)
C(1)–O(5)#1	1.269(3)
C(4)–O(6)#3	1.254(3)
C(4)–O(4)#4	1.272(3)

Table 4. Selected bond angles (deg) for copper succinate. Symmetry transformations used to generate equivalent atoms: #1($-x+2$, $-y+1$, $-z$), #2($x+1$, y, z), #3($-x+1$, $-y+1$, $-z$), #4($x-1$, y, z).

O(1)–Cu(1)–O(4)	90.11(8)
O(1)–Cu(1)–O(6)	90.63(8)
O(4)–Cu(1)–O(6)	168.80(7)
O(1)–Cu(1)–O(5)	168.91(7)
O(4)–Cu(1)–O(5)	89.68(8)
O(6)–Cu(1)–O(5)	87.45(8)
O(1)–Cu(1)–O(3)	90.18(8)
O(4)–Cu(1)–O(3)	97.08(9)
O(6)–Cu(1)–O(3)	94.09(9)
O(5)–Cu(1)–O(3)	100.85(8)
C(4)#2–O(4)–Cu(1)	122.52(15)
C(4)#3–O(6)–Cu(1)	123.71(15)
C(1)–O(1)–Cu(1)	127.97(15)
C(1)#1–O(5)–Cu(1)	118.43(14)
C(4)–C(3)–C(2)	112.92(17)
C(1)–C(2)–C(3)	112.65(18)
O(1)–C(1)–O(5)#1	124.6(2)
O(1)–C(1)–C(2)	117.25(19)
O(5)#1–C(1)–C(2)	118.16(19)
O(6)#3–C(4)–O(4)#4	124.3(2)
O(6)#3–C(4)–C(3)	118.1(2)
O(4)#4–C(4)–C(3)	117.55(19)

APEX2/SAINT for cell refinement. The structure was solved using SIR92 and refinement was carried out by full-matrix least squares on F2 using SHELXL-97. Based on 2865 reflections and 116 parameters, the residuals converged to R(int) $= 0.0142$.

Single crystal XRD studies reveal the triclinic structure for copper succinate dihydrate and the measured cell parameters are $a = 6.4311(4)$ Å, $b = 7.6129(4)$ Å, $c = 8.0730(5)$ Å, $\alpha = 76.176(2)°$, $\beta = 73.472(2)°$, $\gamma = 81.559(2)°$. Table 1 gives the details of the crystal and structure refinement data. The atomic co-ordinates and equivalent thermal parameters for all the non-hydrogen atoms are given in table 2. Tables 3 and 4 give the selected bond lengths and bond angles.

Figure 1 represents a molecular drawing of the crystal with the atom numbering and figure 2 depicts the packing of the molecules down *b*-axis.

In the structure each copper (II) ion exhibits a CuO_5 co-ordination environment with four oxygen atoms from four

different succinate groups in the basal position and the co-ordination geometry is a distorted square-pyramidal.

The corresponding bond lengths are $Cu-O_1 = 1.9591(17)$ Å, $Cu-O_4 = 1.9646(17)$ Å, $Cu-O_5 = 1.9698(17)$ Å, $Cu-O_6 = 1.9648(17)$ Å. The oxygen atom of water remain in the apical position with a bond length $Cu-O_3 = 2.1211(18)$ Å. The copper (II) atom is shifted to a distance of 0.189 (4) Å from the mean plane formed by the succinate oxygen atoms towards the apical oxygen atom.

The succinate group acts as a bidentate ligand towards each copper (II) ion. The four bis-bidendate succinate anions form syn–syn bridges among two copper atom groups to form a polymeric two-dimensional chain with an intra-molecular
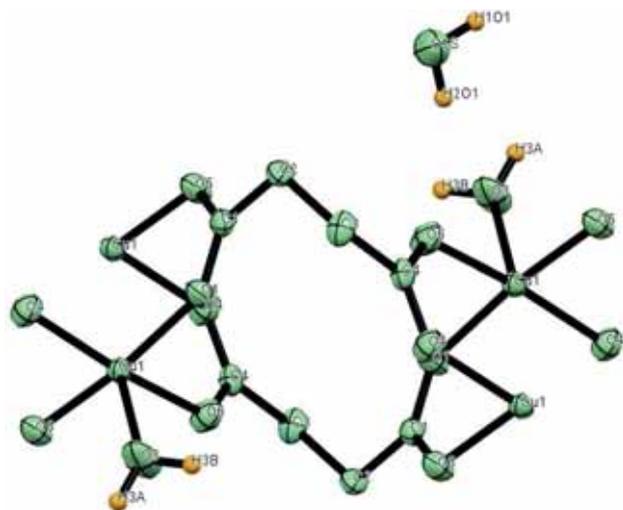

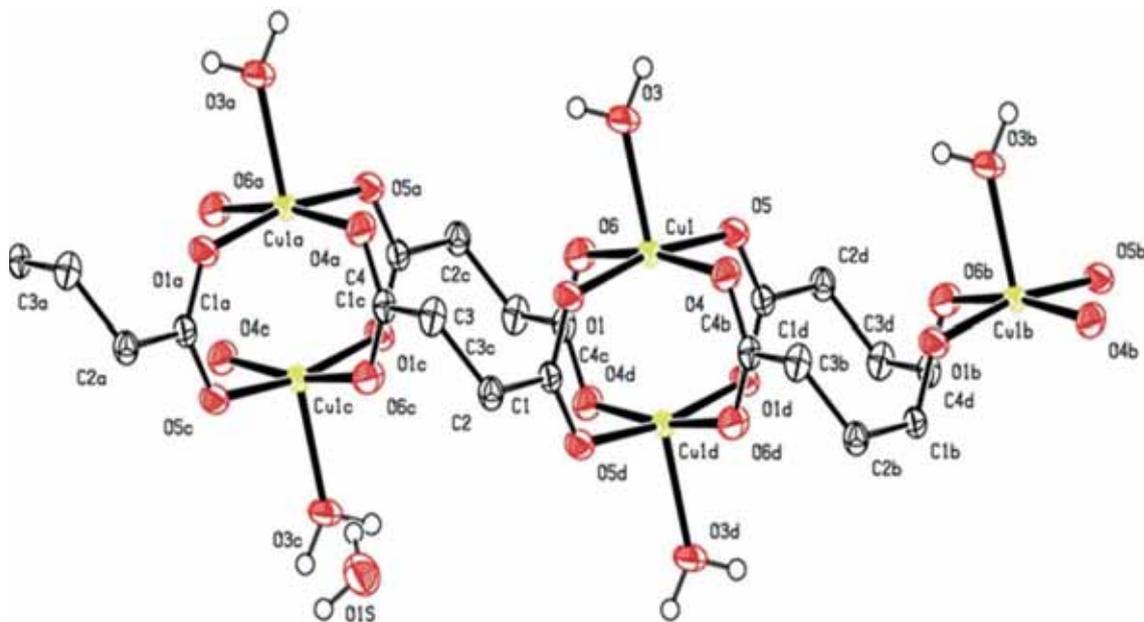**Figure 1.** ORTEP of the molecule at 50% probability.

Cu–Cu distance of 2.6062 (5) Å. The two carboxylate planes are almost perpendicular to each other with a dihedral angle of 81.4°.

In each asymmetric unit there are two water molecules; one co-ordinated and the other lattice water. This lattice water molecule serves as receptors or donors of the O H···O hydrogen bond and is hydrogen bonded to oxygen of the co-ordinated water molecule (O3) and carboxylate oxygen of the succinate group (O4). The co-ordinated water molecule (O3) acts as the donor and gets hydrogen bonded to O(3) and another carboxylate oxygen O(5). Thus, these two water molecules in the structure of copper succinate are involved in the extensive network of hydrogen bonds among themselves and are responsible for the stability of the structure. The parameters of hydrogen bonding are depicted in table 5.

3.2 *Magnetic studies of copper succinate*

The variation of the magnetic moment of copper succinate dihydrate with an external field is depicted in figure 3. The observed hysteresis curve with changing field strength is due to the ferromagnetic or anti-ferromagnetic behaviour of the crystal. The initial increase in the susceptibility may be attributed to relatively faster alignment of dipoles in the beginning. The saturation magnetization of the material is found as 0.00925 emu g^{-1}, the retentivity is 1.2997×10^{-3} emu g^{-1} and coercivity is 141.13 G. The magnetic moment of hydrated copper succinate is calculated as 1.35 BM at room temperature, which is less than the spin-only value of 1.73 BM for one unpaired electron (d^9 system). This value is similar to the values reported earlier for anti-ferromagnetic di-nuclear

Figure 2. The packing of the molecules down *b*-axis.

Table 5. Geometries of the H-bonds in copper succinate. Symmetry transformations used to generate equivalent atoms: #1[$x-1$, $y-1$, z], #2[x, $y+1$, z], #3[$-x+2$, $-y+2$, $-z$]; D = donor, A = acceptor.

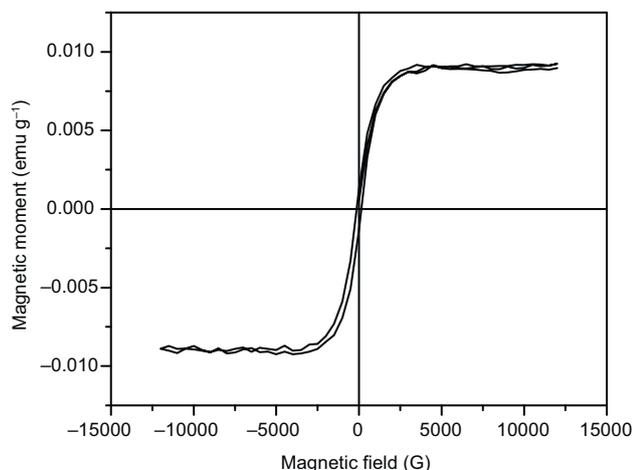| D–H....A	d(D–H) Å	d(H–A) Å	d(D..A) Å	<(D–H....A)°
O(1S)–H(1O1)....O(4)#1	0.853	2.108	2.94	165.27
O(3)–H(3B)....O(1S)#2	0.833	1.965	2.779	165.33
O(3)–H(3A)....O(5)#3	0.851	1.918	2.767	175.49

Figure 3. Variation of magnetic moment with the applied field.

or poly-nuclear complexes, where the carboxylate group acts as a bridge among two metal ions in syn–syn confirmation [13].

Super exchange interaction occurs when two magnetic ions are separated by a non-magnetic ion and hence direct exchange is not possible by overlapping of d-electron wavefunction. Thus an exchange interaction mediated by a non-magnetic ion leads to super exchange interaction. Hybridization of 2p orbital electrons with d orbital at either side causes a minimum energy configuration of the spin arrangement. If the orbital overlaps, the interaction will be negative and the material becomes anti-ferromagnetic and with no overlap the interaction will be positive and ferromagnetic behaviour is exhibited by the material [14].

Each Cu centre is in d^9 electronic configuration and therefore has one unpaired electron each. Direct exchange among the orbitals of these two Cu atoms is not possible in the above complex since the orbitals are too far apart (2.6062 Å). Two spins $S = 1/2$ of two adjacent copper (II) ions are coupled via the succinate ligand, which can result in either a ferromagnetic or an anti-ferromagnetic behaviour. In the present case, the anti-ferromagnetism of copper succinate dihydrate can be described by an orbital overlap of the bridging ligand and the two copper ions in syn–syn confirmation. The anti-ferromagnetic exchange pathway can be explained in terms of the super-exchange mechanism through the ligand bridge.

From the single crystal X-ray data it is known that in the square pyramidal co-ordination sphere, the equatorially co-ordinated oxygen atoms are closer than the axially co-ordinated oxygen atom of the water molecule. Hence, the equatorially oriented Cu orbital is the magnetic, whereas the axially oriented one is not. A strong bonding of the magnetic orbital of equatorially oriented Cu atom on both sides of the exchange pathway (Cu–O-C-O–Cu) leads to the anti-ferromagnetic interaction [15,16].

4. Conclusions

The growth of copper succinate dihydrate crystal was accomplished using the silica gel technique, by the controlled reaction of copper chloride with succinic acid. The material crystallizes in triclinic structure with space group P (–1). Single crystal XRD studies show that in the structure of copper succinate each copper ion exhibits a CuO_5 co-ordination environment with four oxygen atoms of four succinate groups in the basal position and oxygen atom of water in the apical position with distorted square–pyramidal co-ordination geometry. The four bis-bidendate succinate anions form syn–syn bridges among two copper atoms to form a polymeric two-dimensional chain with an intramolecular Cu–Cu distance of 2.606 Å. The magnetic properties of the material are studied using the VSM method and the material is found to exhibit anti-ferromagnetic interaction among copper atoms. The exchange interaction among the copper (II) ions propagated through the succinate bridge is strongly dependent on the geometry around the copper ions and the bridging mode of the succinate group.

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