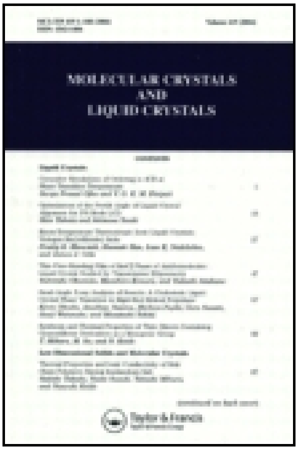

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Structures and Magnetic Properties of 4,6-Diacetylresorcinate-Bridged Dinuclear Copper(II) Complexes

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Structures and Magnetic Properties of 4,6-Diacetylresorcinate-Bridged Dinuclear Copper(II) Complexes

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Dinuclear Cu(II) complexes bridged by 4,6-diacetylresorcinate (dar^{2-}), $[Cu_2(dar)(bpy)_2]X_2$ ($X = ClO_4^-$ (**1**), BF_4^- (**2**)) and $[Cu_2(dar)(phen)_2]X_2$ ($X = ClO_4^-$ (**3**), BF_4^- (**4**)) have been prepared and studied in relation to their crystal structures and magnetic properties. The X-ray crystallography indicates that **1** and **2** have a 1-D network arrangement of the dar-bridged dinuclear units, combined by the 'out-of-plane' bond through the phenolic oxygen, whereas **3** has a discrete dinuclear structure. Cryomagnetic studies indicate a weak antiferromagnetic interaction ($J = -20 \sim -9.9$ cm^{-1}) between Cu(II) ions through the dar bridge.

Keywords: 4,6-diacetylresorcinate bridge; dinuclear complex; 1-D network; antiferromagnetic interaction; crystal structure; magnetic property

INTRODUCTION

The use of bis-chelate ligands is a promising way for constructing metal-assembled compounds of various structures.[1] Oxalate[2], oxamide[3] and dithiooxamide[3] ions are such bis-chelate ligands that bridge two metal ions in a M···M separation of 5.0 ~ 5.5 Å. It is shown that these bridges mediate a strong antiferromagnetic interaction between two Cu(II) ions. Aromatic bis-chelates such as terephthalate[4] or chloranilate[5] are also shown to act as bridges to form polynuclear complexes. Antiferromagnetic interaction between two Cu(II) ions mediated by such aromatic bridges is generally weak because the bridges give rise to a long Cu···Cu separation. 4,6-Diacetylresorcinate (dar^{2-}) can be another example of aromatic bridges, but no dar-bridged polynuclear complex has been reported so far. Because of the topological reason of dar, the Cu-dar-Cu linkages is not linear and has a bite angle of ~ 120°. The topological effect of the dar bridge upon magnetic superexchange between a pair of Cu(II) ions is of great interest. Further, such non-linearity in the Cu-B-Cu linkage leads to an oligomeric assembly of metal ion or an extension of metal centers to afford an unprecedented network structure.

Beginning with this study of dar-bridged polynuclear complexes, it is aimed to see the bridging ability of dar toward Cu(II) ion and to evaluate the role of dar in magnetic exchange between two Cu(II) ions. In this study Dinuclear Cu(II) complexes, $[Cu_2(dar)(bpy)_2]X_2$ ($X = ClO_4^-$ (**1**), BF_4^- (**2**)) and $[Cu_2(dar)(phen)_2]X_2$ ($X = ClO_4^-$ (**3**), BF_4^- (**4**)), end-capped by 2,2'-dipyridyl (bpy) or 1,10-phenanthroline (phen), have been obtained and their crystal structures and cryomagnetic properties are studied.

PREPARATIONS AND GENERAL PROPERTIES

4,6-Diacetylresorcinol (H_2dar) was synthesized according to the literature.[6] Dinuclear copper(II) complexes **1** - **4** were prepared in a similar way. The synthetic procedure of **1** is described in detail.

$[Cu_2(dar)(bpy)_2](ClO_4)_2$ (**1**). 2,2'-Bipyridine (bpy) (156 mg, 1 mmol) was dissolved in methanol (10 ml) and added to an aqueous methanol solution (1:1 in volume; 10 ml) of $Cu(ClO_4)_2{\cdot}6H_2O$ (370 mg, 1 mmol). To this reaction mixture was added a methanolic solution (10 ml) of H_2dar (97 mg, 0.5 mmol), and the resulting deep green solution was stirred for 10 min with heating. After being allowed to stand overnight at room temperature, a dark green microcrystalline precipitate was collected by suction filtration and crystallized from dmf. Yield 320 mg (77 %). Anal. Calcd. for $C_{30}H_{24}N_4Cl_2Cu_2O_{12}$: C, 43.39; H, 2.91; N, 6.75; Cu, 15.3 %. Found: C, 43.51; H, 2.99; N, 6.71; Cu, 14.8 %. **2**: Yield 290 mg (72 %). Anal. Calcd. for $C_{30}H_{24}N_4B_2F_8Cu_2O_4$: C, 44.75; H, 3.00; N, 6.96; Cu, 15.8 %. Found: C, 44.86; H, 3.18; N, 7.06; Cu, 15.5 %. **3**: Yield 280 mg (63 %). Anal. Calcd. for $C_{34}H_{24}N_4Cl_2Cu_2O_{12}$: C, 46.48; H, 2.75; N, 6.38; Cu, 14.5 %. Found: C, 46.40; H, 2.93; N, 6.18; Cu, 14.4 %. **4**: Yield 310 mg (73 %). Anal. Calcd. for $C_{34}H_{24}N_4B_2F_8Cu_2O_4$: C, 47.86; H, 2.84; N, 6.57; Cu, 14.9 %. Found: C, 47.77; H, 2.91; N, 6.54; Cu, 14.6 %.

The ν(C=O) band is seen at 1600 cm^{-1} for **1** and **2** and at 1590 cm^{-1} for **3** and **4**. The appearance of ν(C=O) vibration at a lower frequency relative to that of H_2dar (1650^{br} cm^{-1}) means the coordination of the acetyl group in these complexes. The IR spectra of **1** and **2** are similar to each other and those of **3** and **4** are similar to each other, except for the vibration of the respective counter anion. In the solid state, the reflectance spectra of **1** and **2** show an absorption at 575 nm attributable to the superposed d-d transition band of copper(II). The corresponding absorption for **3** and **4** is seen at 600 nm. In dmf solution **1** and **2** show the d-d band maximum at 615 nm ($\varepsilon = 203$) and **3** and **4** show the maximum at 620 nm ($\varepsilon = 215$). Electronic conductivity studies in dmf indicate that all the compounds behave as 1 : 2 electrolytes. It appears that the bpy complex (**1** and **2**) and the phen complexes (**3** and **4**) differ in bulk structure but all the complexes have the same monomeric structure in dmf solution.

CRYSTAL STRUCTURE

The crystal data of $[Cu_2(dar)(bpy)_2](ClO_4)_2$ (**1**), $[Cu_2(dar)(bpy)_2](BF_4)_2$ (**2**) and $[Cu_2(dar)(phen)_2](BF_4)_2$ (**4**) are as follows. **1**: triclinic, space group = $P\bar{1}$ (No. 2), a = 12.493(4), b = 13.295(7), c = 11.207(5) Å, α = 105.06(5), β = 100.79(3), γ = 111.30(3)°, V = 1590(1) Å^3, Z = 2 and the refinement converges with R = 0.076 and Rw = 0.048 based on 1597 observed reflections with $I > 2.50\sigma(I)$. **2**: triclinic, space group = $P\bar{1}$ (No. 2), a = 12.452(4), b = 13.175(5), c = 11.116(4) Å, α = 104.91(3), β = 100.91(3), γ = 110.79(2)°, V = 1566(1) Å^3, Z = 2 and R = 0.051 and Rw = 0.035 based on 3283 observed reflections with $I > 3.00\sigma(I)$. **4**: and orthorhombic, space group = $Pccb$ (No. 56), a = 8.449(3), b = 16.617(4), c = 24.039(3) Å, V = 3375(2) Å^3, Z = 4 and R = 0.056 and Rw = 0.041 based on 1468 observed reflections with $I > 3.00\sigma(I)$.

The X-ray crystallography confirms that compounds **1** and **2** have the same dinuclear core structure bridged by dar^{2-}. Two copper(II) ions Cu(1) and Cu(2) are crystallographically independent. The geometry around each copper atom is regarded as a square-pyramid, where the equatorial plane is defined by two oxygen atoms of dar^{2-} and two nitrogen atoms of bpy and the apical position is occupied by a phenolic oxygen atom of the nearest dinuclear unit. The Cu(1)···Cu(2) separation through dar-bridge is 8.150(3) Å for **1** and 8.145(3) Å for **2**. The average basal Cu-O and Cu-N bond distances are 1.91 and 1.97 Å, respectively, for **1** and 1.906 and 1.978 Å, respectively, for **2**, respectively. The plane defined by O(1), O(2), Cu(1), N(1) and N(2) and the plane defined by O(3), O(4), Cu(2), N(3) and N(4) form a dihedral angle of 12.57° for **2** and 12.43° for **3**. The deviation of Cu(1) and Cu(2) from the basal plane is 0.022 and 0.104 Å, respectively, for **1** and 0.004 and 0.095 Å, respectively, for **2**.

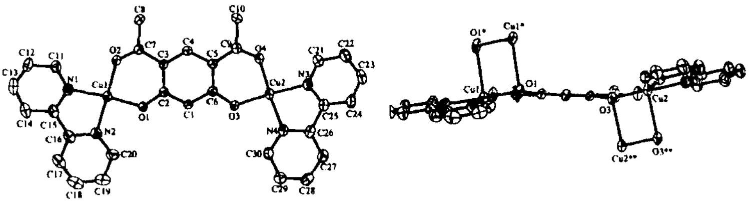

FIGURE 1. ORTEP drawing for the asymmetric unit of $[Cu_2(dar)(bpy)_2](BF_4)_2$ (**2**): top view (left) and side view (right).

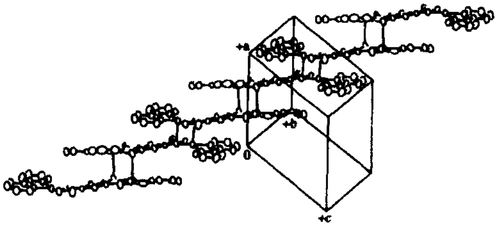

FIGURE 2. ORTEP drawing for the 1-D chain structure of **2**.

The dinuclear units are weakly combined at the axial position of copper(II) center, with the axial Cu(1)-O(1)* (* denotes the symmetric operation -x, -y, -z) and Cu(2)-O(3)** (** denotes the symmetric operation -x+1, -y+1, -z+1) bond distances of 2.65(2) and 2.54(1) Å, respectively, for **1** and 2.708(5) and 2.527(4) Å, respectively, for **2**. In the lattice, the dinuclear units form a 1-D chain structure with Cu(1)-O(1)*-Cu(1)*-O(1) and Cu(2)-O(3)**-Cu(2)**-O(3) four-membered rings. The chain runs along the origin to the (1,1,1) direction.

Complex **4** shows a discrete dar-bridged dinuclear structure. Two coordination geometries of the copper(II) centers are crystallographically the same (square-planar with dar^{2-} and phen). The Cu···Cu interatomic separation is 8.160(3) Å. The average basal Cu-O and Cu-N bond distances are 1.903 and 1.992 Å, respectively. The dihedral angle between the plane defined by O(1), O(2), Cu(1), N(1) and N(2) and the plane defined by O(1)*, O(2)*, Cu(1)*, N(1)* and N(2)* is 5.32°. The deviation of the copper(II) center from the basal least-squares plane is 0.050 Å .

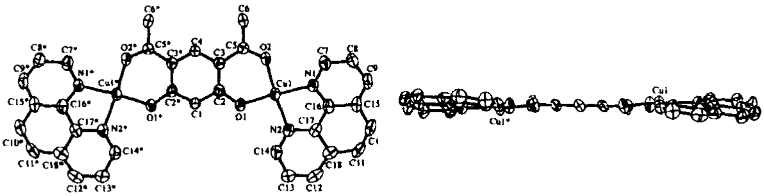

FIGURE 3. ORTEP drawing for the discrete dinuclear structure of $[Cu_2(dar)(phen)_2](BF_4)_2$ (**4**): top view (left) and side view (right).

MAGNETIC PROPERTIES

The cryomagnetic properties of **1** - **4** have been studied in the temperature range of 4.2 - 300 K. The $\chi_A T$ *vs.* T and χ_A *vs.* T plots of **1** are given in Fig. 4, where χ_A is the magnetic susceptibility per copper(II) ion. Complexes **1** and **2** are similar in magnetic behavior to each other.

The $\chi_A T$ value of **1** at room temperature is 0.389 cm^3 K mol^{-1} (1.77 μ_B) which decreases with the lowering of temperature to the value of 0.011 cm^3 K mol^{-1} (0.29 μ_B) at 4.2 K. The magnetic behavior is simulated by the Bleaney-Bowers equation by the least-squares method.[1,7] The best-fit parameters of **1** and **2** are listed in TABLE 1. Crystal structures of **1** and **2** show a 1-D chain structure comprised of the dinuclear units, weakly bonded at the axial position of the copper(II) centers, but the magnetic behavior is interpreted as discrete dinuclear compound because of the long bond distance between dinuclear unit (2.54 - 2.70 Å) and no overlap between $d_{x^2-y^2}$ (equatorial) and d_{z^2} (axial) magnetic orbitals. Complexes **3** and **4** show an antiferromagnetic interaction. The magnetic behavior is well simulated as a discrete dinuclear copper(II) complex. The best-fit parameters of **3** and **4** are listed in TABLE 1. The magnitudes of the antiferromagnetic interaction of **1** - **4** are similar to those of copper(II) complexes having Schiff-base ligand derived from H_2dar (θ = -10 ~ -34 K).[8]

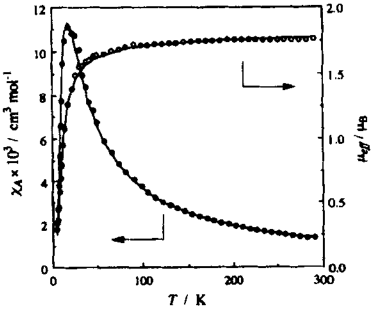

FIGURE 4. The temperature-dependences of $\chi_A T$ (○) and χ_A (●) for **1**: theoretical curves are shown by solid lines.

The magnitudes of the antiferromagnetic exchange interaction of **3** and **4** are larger than those of **1** and **2**. This can be explained by the dihedral angle between the two planes around the copper centers. The phen complexes (**3** and **4**) have a discrete dinuclear core where the two {CuN_2O_2} chromophores form a good coplane with a small torsion between the dar^{2-} and the external ligand (phen) relative to the bpy complexes (**1** and **2**). This situation give rise to a better overlap between the magnetic orbitals for **3** and **4**, giving a larger -J value for these complexes.