Communications

A Novel Water-Bridging Copper(II) Complex Involving Intramolecular Second-Sphere Coordinations

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Although a number of binuclear complexes containing copper(II) centers have been investigated to date, the water-bridging structure is quite uncommon.[1-6] Furthermore, an example for the stabilization of a binuclear structure by hydrogen bonding between a coordinated ligand and bridged water molecule is very little known.[4-6] McCleverty et al.[3] reported that stabilization of coordinated ligands by second-sphere coordination is an essential part of substrate-specific host-guest interactions at metalloenzyme active sites. However, preparation of simple model systems which show this behavior is difficult. In this communication, we report the isolation and the structural characterization of a new binuclear copper(II) complex $[Cu_2(\mu\text{-}H_2O)(O_2CCH_3)_4(phen)_2]$ 1, where phen is 1,10-phenanthroline.

The reaction of $Cu(O_2CCH_3)_2 \cdot H_2O$ with phen in a 3:2 molar ratio in dimethylformamide (DMF) solution at ambient temperature gives a pale blue powder. Pale blue crystals[7] of this complex suitable for an X-ray diffraction study were obtained by allowing low concentration DMF solution of $Cu(OAc)_2 \cdot H_2O$ to react with 1,10-phenanthroline and letting the resulting blue solution stand open in air for several days. Traces of water, which might be generated from the solvent or hydrate of copper-acetate starting material, were essential for getting single crystals of 1.

The initial goal of this work was to synthesize the trinuclear copper-acetate complexes $Cu_3(O_2CCH_3)_6(L\text{-}L)_2$, akin to the Mn^{II} analogue[8] by reaction of $Cu(O_2CCH_3)_2 \cdot H_2O$ with bidentate ligands. Such linear trinuclear Cu^{II} complexes are rare and possess interesting structural and magnetic features.[9] However, the reaction did not yield a trinuclear product. Instead, treatment of $Cu(O_2CCH_3)_2 \cdot H_2O$ with 0.67 equivalents of phen in DMF led to the water-bridging dinuclear copper-acetate complex.

The copper atom is located on a crystallographic two-fold axis and has (4+1+1*) coordination. The two copper centers are in oxidation state +2, which is confirmed by the bond lengths and the ^{1}H NMR silence due to the paramagnetism of $Cu(II)(d^9)$. A list of selected bond distances and angles for this complex is outlined in Table 1. A perspective drawing of the molecular structure of 1 is given in Figure 1.

The two copper atoms with terminal acetate groups, Cu(1) and Cu(1)', are bridged by an oxygen atom O(6) of water. The termini of the $[M(O_2CCH_3)_2(\mu\text{-}H_2O)\text{-}(O_2CCH_3)_2M]$ units are capped by aromatic rings(phen), resulting in highly

distorted pseudo-octahedral geometry at these sites. Of particular interest are the facts that the geometry in the crystal structure is supported by at least two additional intra-

Table 1. Selected Interatomic Distances (Å) and Bond Angles (deg) with Their Estimated Standard Deviations in Parentheses

Cu(1)--O(1)	1.927(5)	Cu(1)···O(5)	4.212(7)
Cu(1)--O(2)	1.961(6)	O(1)--C(13)	1.28(1)
Cu(1)--O(6)	2.292(5)	O(2)--C(15)	1.20(1)
Cu(1)--N(1)	2.019(7)	O(3)--C(15)	1.26(1)
Cu(1)--N(2)	2.033(6)	O(5)--C(13)	1.23(1)
Cu(1)···Cu(1)'	4.317(2)	O(5)--O(5)'	4.69(1)
Cu(1)···O(3)	2.648(7)	O(5)···O(6)	2.624(9)

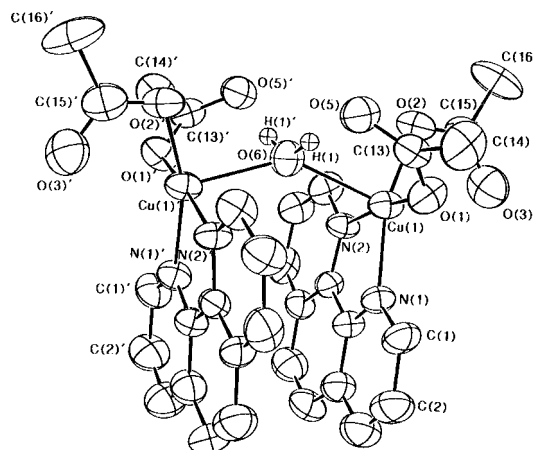|			
Cu(1)--O(6)--Cu(1)'	140.7(7)	O(1)--C(13)--O(5)	125.3(7)
Cu(1)--Cu(1)--O(6)	19.6(4)	O(1)--C(13)--C(14)	115.6(7)
Cu(1)--O(1)--C(13)	126.2(5)	O(2)--Cu(1)--N(1)	160.1(3)
Cu(1)--O(2)--C(15)	109.5(6)	O(2)--Cu(1)--N(2)	93.6(3)
Cu(1)--O(6)--O(5)	80.6(1)	O(2)--Cu(1)--O(6)	91.1(4)
Cu(1)--N(1)--C(1)	128.3(6)	O(2)--C(15)--O(3)	122.3(9)
Cu(1)--N(1)--C(5)	119.4(7)	O(2)--C(15)--C(16)	118.9(9)
Cu(1)--N(2)--C(10)	127.2(6)	O(3)--Cu(1)--O(6)	143.6(4)
O(1)--Cu(1)--O(2)	94.2(2)	O(3)--C(15)--C(16)	119(1)
O(1)--Cu(1)--O(6)	95.1(2)	O(5)--O(6)--O(5)'	126.5(7)
O(1)--Cu(1)--N(1)	90.7(2)	N(1)--Cu(1)--N(2)	81.7(3)
O(1)--Cu(1)--N(2)	172.2(3)		

Figure 1. ORTEP drawing showing 50% probability ellipsoids and labeling scheme for the complex 1. Hydrogen atoms are omitted for clarity.

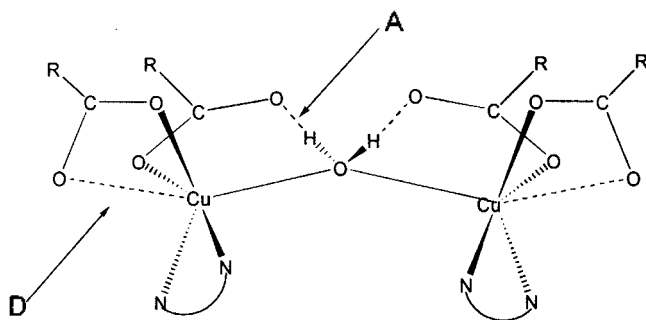*Author to whom correspondence should be addressed.

Figure 2. The general structure of $[Cu_2(\mu\text{-}H_2O)(O_2CCH_3)_4$ (phen)$_2$], showing the dangling (O_d) and the bridging (O_b) oxygen atoms of the monodentate acetates, the central metals, and Cu, which interact with O_d (see, D). The H atoms of bridged water molecule which interact with another monodentate acetate for hydrogen-bonding are also shown (see, A).

molecular coordinations, which are hydrogen-bonding to the acetates of the water bridge, and the interaction to the copper(II) centers of other acetates. (see, Figure 2). Such units are little known in metal carboxylate chemistry.[10-16]

The dangling oxygen atoms of potentially bidentate acetates interact with the metals and block the potential sixth coordination site of the metals. Several factors reveal the existence of a weak interaction between the dangling oxygen atom (O_d, Figure 2) and the metal; (i) the monodentate acetates are oriented such that O_d points toward metal, (ii) the M-O_d separation is relatively short, 2.648(7) Å and (iii) the C-O bonds in the monodentate acetates are relatively symmetric in structure.

On the basis of the X-ray data in some related compounds,[17,18a] the average distances of Cu-O in the oxo-bridging Cu-O-Cu and Cu-OH-Cu species are 1.6-1.9 and 1.9-2.0 Å, respectively. But, the bond length of Cu(1)-O(6) in the present study is a longer distance, 2.292(5) Å, than that observed in typical oxometal complexes, very close to the value at which Cu(II) is bound to the H_2O ligand (Cu-OH_2, 2.234 Å).[17] Also, the Cu(1)···Cu(1)' distance is 4.317(2) Å, which is longer than observed in the μ-OH species, 2.9-3.0 Å. These facts strongly suggest that the bridging ligand is a water molecule. The hydrogen atoms of the water-bridging ligand were directly located in the crystal structure. In addition, the presence of an interaction between the H atom and oxygen atom of acetates is also confirmed by several factors: (i) the average distance of O···O in the compounds involving a hydrogen bond is 2.7 Å[18b] close to the value (O(5)···O(6), 2.624(9) Å) of this study, which is indicative of definite O-H···O hydrogen bonding[19] and (ii) the C-O bonds in the monodentate acetates oriented toward bridging oxygen atoms are relatively symmetric in structure (O(1)-C(13), 1.28(1) and O(5)-C(13), 1.23(1) Å).

Also, the Cu(1)···Cu(1)' distance is 4.317(2) Å, which is much longer than that observed in the π-stacking interacted complexes (*ca.* 3.6 Å).[20,21] But the dihedral angle of phenanthroline fragments is 68.5(5)° which is a deviation from the parallel of planes. Thus, at least a weak π-stacking interaction between the bottoms of a phen plane may be expected.

As noted previously, the additional interactions (*e.g.* hydrogen-bonding, O_d to metal interaction, and π-stacking

interaction) are named as second-sphere coordination, which cause stabilizing of the crystal structure.

The syntheses, structural characterizations, spectral, and electrochemical properties of related complexes including this complex in solid and solution state are currently under investigation.

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Supporting Information Available. Tables giving structure determination summaries, atomic coordinates, bond lengths, bond angles, and anisotropic thermal parameters for non-hydrogen atoms and an ORTEP drawing with complete atomic numbering of 1 is available. Supplementary materials are available from B. K. Koo.

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Vibrational Spectroscopy of C≡N Stretch in Mixtures of Deuterated Acetonitrile and Methanol

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The general spectral characteristics of hydrogen-bonded molecules have been studied since 1930's.[1] Yet, hydrogen bonding still remains as an intriguing subject, particularly in vibrational spectroscopy, related to aggregation,[2] molecular structure,[3] bond energy,[4] etc. While the effects on the frequency and the intensity of hydrogen stretch have been systematically studied,[5] the effects on the electron-donor are relatively less understood. Recently unusual hypsochromic shifts of C≡N stretch of acetonitrile in aqueous solution have been observed as results of hydration and co-solvation of metallic cations.[6,7] The large shifts (up to 50 cm^{-1}) are attributed to electrophilic coordination of cations to the lone pair electrons of nitrogen of acetonitrile,[7] and the hydrogen bond formed between the nitrile group and water molecule results in a hypsochromic shift of about 4 cm^{-1}.[6] In this communication, we report the hypsochromic shift of the v_2 band of acetonitrile in methanol and ab initio results elucidating the causes of the shift.

The v_2 band of acetonitrile, better known as C≡N stretch, is located at 2254 cm^{-1}, and another band shifted by about 40 cm^{-1} toward higher frequency is a combination band $v_3 + v_4$ (CH$_3$ bending and C—C stretching modes) with enhanced intensity due to Fermi resonance.[7] To avoid possible interference in observation of hypsochromic shift of the v_2 band, deuterated acetonitrile was used instead for this study. Deuterated acetonitrile (99.6%, spectroscopic grade) was purchased in ampule from Merck and used without any additional treatment. Methanol was distilled over CaH$_2$ to remove moisture. Mixtures of CD$_3$CN and CH$_3$OH were prepared with mole fractions of CD$_3$CN ranging from 0.01 to 1. The sample was sandwiched with CaF$_2$ or ZnSe windows, and in order to obtain suitable absorption intensity of the v_2 band, the sample thickness was adjusted using spacers or a variable pathlength liquid cell depending on the needed thickness. The spectra were recorded on a Biorad FTS-175C FT-IR spectrometer, which was continuously circulated with filtered air free of moisture and CO$_2$.

The v_2 band of CD$_3$CN is situated at 2262 cm^{-1} (Figure 1) and shows a slightly asymmetric lineshape due to overlap with two hotbands ($v_2 + v_8 - v_8$ and $v_2 + 2v_8 - 2v_8$) where v_8 denotes the C—C≡N bending mode. Evidently

moderate intensity borrowing occurs between the hotbands and a C—D stretching band located at 2250 cm^{-1}.[6] Figure 1 shows the spectral change in the region of the v_2 band with mole fraction of CD$_3$CN. While a new band emerges at about 2269 cm^{-1} as the mole fraction lowers, the intensity of the v_2 band at 2262 cm^{-1} decreases. The newly observed band has been assigned to the v_2 band of hydrogen-bonded
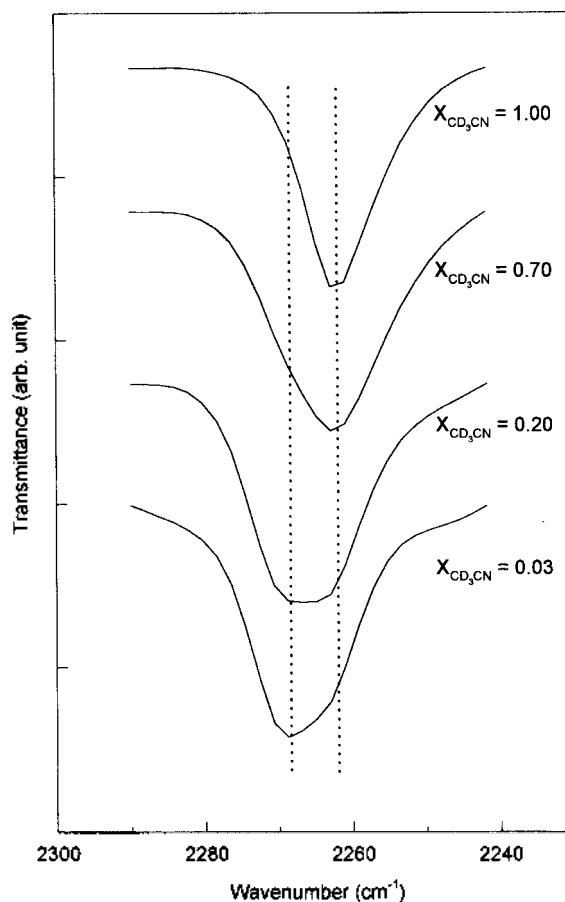

Figure 1. Variation of the v_2 band of CD$_3$CN as a function of mole fraction. All the spectra are taken at 4 cm^{-1} resolution and at room temperature.