# The Formation of a Hydrogencarbonato-bridged Dinuclear Copper(II) Complex by Fixation and Activation of Atmospheric $CO_2$

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The first hydrogencarbonato-bridged dinuclear copper(II) complex $[Cu_2(L)(HCO_3)](BF_4)_2 \cdot 5H_2O$, **1** was obtained by allowing of acetone solution containing a copper(II) complex $[Cu_2(L)(OH)](BF_4)_2 \cdot 6H_2O$, where HL is *N,N,N',N'*-tetrakis-[(1-methyl-2-benzimidazolyl)methyl]-2-hydroxy-1,3-diaminopropane. The crystal structure of **1** was determined by X-ray crystallography and characterized by the magnetic susceptibility and infrared and visible absorption spectrum.

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Studies on di- and trinuclear metal complexes bridged by carbonato or hydrogencarbonato are mainly noted from three areas; i.e.(i) the research for the fixation and activation of $CO_2$ from the viewpoint of environmental protection,[1-6] (ii) the function models for zinc containing carbonic anhydrase,[4,7,8] (iii) the relationship between the bridging modes of carbonato and magnetic properties.[2,4,9-11] In connection with these investigations, the dinuclear copper(II) complex $[Cu(HB(3,5\text{-}iPr_2pz))_3]_2(OH)_2$ bridged by two hydroxo was found to react with $CO_2$ to afford μ-carbonato copper(II) complex $[Cu(HB(3,5\text{-}iPr_2pz)_3]_2(CO_3)$.[1-4] Also the cobalt(II) complex $[Co_2OH(tcoa)](ClO_4)_3$ bridged by one hydroxo trapped $CO_2$ rapidly to give a carbonato-bridged complex $[Co_2CO_3(tcoa)](ClO_4)_2 \cdot 3H_2O$.[10] Recently we reported efficient $CO_2$ uptake by the nickel(II) complex $[Ni_2(L')(OH)(H_2O)_2](ClO_4)_2$.[12] In the system, $CO_2$ is taken up from the air, as monomethyl carbonate in methanol under the presence of urea derivative to give $[Ni_2(L')(OOC\text{-}O\text{-}CH_3)(CH_3OH)_2](ClO_4)_2 \cdot H_2O \cdot CH_3OH$.[12] In this paper, we isolated the first hydrogencarbonato-bridged dinuclear copper(II) complex $[Cu_2(L)(HCO_3)](BF_4)_2 \cdot 5H_2O$, **1** by allowing a dinuclear complex $[Cu_2(L)(OH)](BF_4)_2$ in acetone.[13]

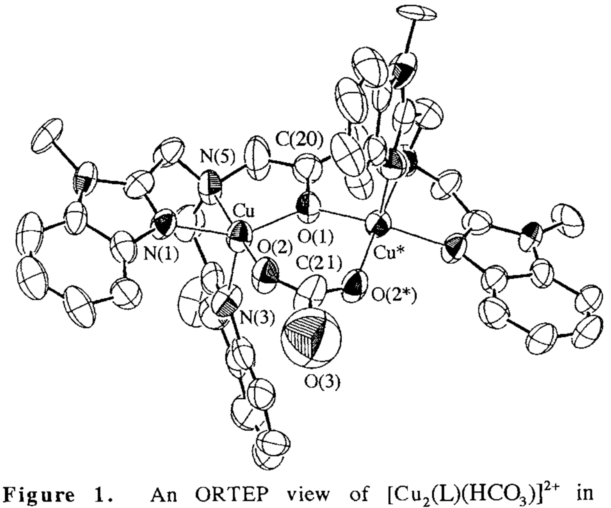

**Figure 1.** An ORTEP view of $[Cu_2(L)(HCO_3)]^{2+}$ in **1**. Selected bond lengths(Å) and angles(°): Cu···Cu* 3.440(4), Cu–O(1) 1.898(6), Cu–O(2) 1.94(1), Cu–N(1) 2.00(1), Cu–N(3) 2.15(1), Cu–N(5) 2.13(1), O(2)–C(21) 1.23(1), O(3)–C(21) 1.52(3) Å; Cu–O(1)–Cu* 130.0(7), Cu–O(2)–C(21) 129(1), O(1)–Cu–O(2) 95.0(4), O(1)–Cu–N(1) 148.8(4), O(1)–Cu–N(3) 104.6(3), O(1)–Cu–N(5) 84.8(5), O(2)–Cu–N(1) 97.5(5), O(2)–Cu–N(3) 102.6(6), O(2)–Cu–N(5) 174.5(5), N(1)–Cu–N(3) 100.5, N(1)–Cu–N(5) 80.1(5), N(3)–Cu–N(5) 82.8(6), O(2)–C(21)–O(3) 115(1), O(2)–C(21)–O(2*) 131(2)°.

$[Cu_2(L)(OH)](BF_4)_2$ was prepared by a similar method to that for $[Cu_2(L)(OH)](ClO_4)_2$ using $Cu(BF_4)_2$ aqueous solution (45%) instead of $Cu(ClO_4)_2 \cdot 6H_2O$.[14] The acetone solution of $[Cu_2(L)(OH)](BF_4)_2 \cdot 6H_2O$ was allowed to eveporate to bring about a pale green crystals $[Cu_2(L)(HCO_3)](BF_4)_2 \cdot 5H_2O$, **1**.[15] A crystal suitable for X-ray study was sealed in a capillary tube.[16]

The structure consists of one discrete dinuclear $[Cu_2(L)(HCO_3)]^{2+}$ unit, two tetrafluoroborate ions, and five water molecules.

An ORTEP[17] view of $[Cu_2(L)(HCO_3)]^{2+}$ in **1** is shown in Figure 1 with selected bond lengths and angles. The cation in **1** consists of two copper(II) ions bridged by one alkoxo group of L and one bidentate hydrogencarbonato. The Cu-O(1)-Cu* angle is 130.0 (7)°, which is similar to that of the corresponding acetato-bridged complex $[Cu_2(L')(OAc)](ClO_4)_2$.[18] The Cu(1)-O(1) distance of 1.898(6) Å, is also similar to that of $[Cu_2(L')(OAc)](ClO_4)_2$.[18] The coordination around copper(II) exhibits distorted square pyramidal $N_3O_2$ coordination with two nitrogen atoms of L and two oxygen atoms of L and hydrogencarbonato in the basal plane and one nitrogen of L at the apical position. The plane defined by N(1), N(5), O(1) and O(2) is nearly planar: maximum deviation of the atom is 0.341 Å of N(5). The basal

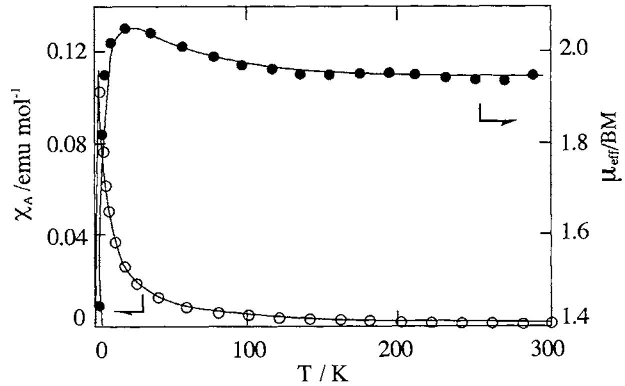

**Figure 2.** Temperature dependence of the magnetic susceptibility and magnetic moment per copper for **1**. The solid line shows the theoretical susceptibility calculated by the Bleaney-Bowers equation.[18]

planes make an angle of 164.7°. The Cu···Cu* distance in the dinuclear complex is 3.440(4) Å.

The complex **1** gave the characteristic IR band due to the bridging hydrogencarbonato at 1556 $cm^{-1}$. The electronic absorption spectrum of **1** exhibits the broad d-d band at 810 nm in a powder state.

The magnetic moment of **1** at room temperature is 1.94 BM. The data of temperature-dependence magnetic moment show a peak near 25 K, indicating a ferromagnetic interacion between two copper(II) ions (Figure 2). This agreed with the magnetic behavior of $[Cu_2(L')(OAc)](ClO_4)_2$.[18] The magnetic parameters can be estimated as $g$ = 2.16, $2J$ = +36.3 $cm^{-1}$, and $N\alpha$ = $450\times10^{-6}$ cgs emu $mol^{-1}$ from best fit of the $\chi_A$ values to the Bleaney-Bowers equation.[19] The $2J$ value is much larger than that ($2J$ = +24 $cm^{-1}$) of $[Cu_2(L')(OAc)](ClO_4)_2$.[18] Studies on the mechanism for the formation of hydrogencarbonato-bridged complex are now in progress.

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## References and Notes

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15 Found: C, 43.35; H, 4.77; N, 12.44 %. Anal. Calcd. for $C_{40}H_{42}N_{10}O_4B_2F_8Cu_2\cdot5H_2O$: C, 42.98; H, 4.70; N, 12.53 %.
16 Crystal data for **1**: $F_W$ = 1117.72, monoclinic, space group $C2/m$ (No.12), $a$ = 20.181(6), $b$ = 22.67(1), $c$ = 13.456(5) Å, $\beta$ = 125.43(2)°, $V$ = 5015(7) $Å^3$, $Z$ = 4, $D_m$ = 1.47 g $cm^{-3}$, $D_C$ = 1.480 g $cm^{-3}$, $\mu(MoK\alpha)$ = 0.936 $mm^{-1}$. A total of 10618 refrections with $3.0 < 2\theta < 52.0°$ was collected on a Rigaku AFC5R diffractometer using $MoK\alpha$ radiation ($\lambda$ = 0.71073 Å). Absorption correction was applied. The structure was solved by use of MITHRIL and DIRDIF and refined by full-matrix least-squares by assuming two fold symmetry for the dinuclear unit; positions of O(1), O(3), C(20), and C(21) were fixed on 4h. Positions of two B atoms of two $BF_4^-$ and O atoms of five water molecules were fixed on 4i. The final $R$ / $R_W$ were 0.098 / 0.084 for 2064 reflections with $I > 3.0\sigma(I)$ and 287 variables. The $\Delta\rho_{max}$ / $\Delta\rho_{min}$ were 0.76 / -0.52 $eÅ^{-3}$.
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