Fixation of Atmospheric CO_2 by a Copper(II) Complex

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CO_2 contamination in air is fixed by a binuclear di-μ-hydroxo copper(II) complex to give a corresponding binuclear μ-carbonato complex of which the crystal structure is established by *X*-ray crystallography.

The elimination of atmospheric CO_2 has been receiving increasing attention because of the serious environmental problems resulting from the current increase of CO_2 concentration in air. The fixation of CO_2 by transition metal complexes has been known for several decades,[1] and is expected to be effective for the development of such a process. However, most of the complexes reported so far are air-sensitive and not suitable for CO_2 fixation under atmospheric conditions. Another difficulty is caused by the low concentration of CO_2 in air. Most of the transition metal complexes are not reactive enough to fix CO_2 of such a low concentration. In this communication, we report CO_2 fixation *in air* by a copper complex.

Formation of a binuclear μ-carbonato copper(II) complex upon the reaction of CuCl and a nitrogen-containing ligand such as an amine under an O_2/CO_2 mixture was demonstrated previously.[2] The reaction was suggested to proceed *via* a binuclear μ-oxo intermediate. Recently, we succeeded in isolating a binuclear μ-oxo copper(II) complex $[(Cu\{HB(3,5\text{-}Me_2pz)_3\})_2O]$† (**1**)[3] and found that it reacts with CO_2 to yield a

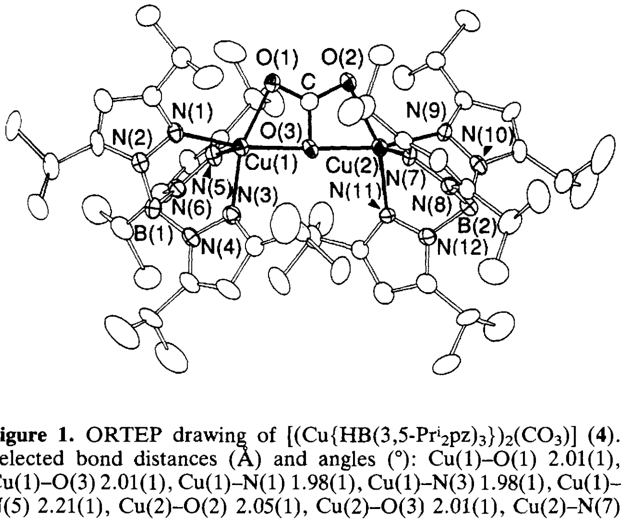

Figure 1. ORTEP drawing of $[(Cu\{HB(3,5\text{-}Pr^i{}_2pz)_3\})_2(CO_3)]$ (**4**). Selected bond distances (Å) and angles (°): Cu(1)–O(1) 2.01(1), Cu(1)–O(3) 2.01(1), Cu(1)–N(1) 1.98(1), Cu(1)–N(3) 1.98(1), Cu(1)–N(5) 2.21(1), Cu(2)–O(2) 2.05(1), Cu(2)–O(3) 2.01(1), Cu(2)–N(7) 2.18(1), Cu–N(9) 2.00(1), Cu(2)–N(11) 1.99(1), C–O(1) 1.23(2), C–O(2) 1.26(2), C–O(3) 1.34(2), Cu(1) · · · Cu(2) 4.017(3), Cu(1)–O(3)–Cu(2) 177.0(6), Cu(1)–O(1)–C 90.4(9), Cu(2)–O(2)–C 90.0(1.0), O(1)–C–O(3) 116.1(1.3), O(2)–C–O(3) 114.9(1.5).

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† $HB(3,5\text{-}Me_2pz)_3$ = hydrotris-(3,5-dimethylpyrazol-1-yl)borate, $HB(3,5\text{-}Pr^i{}_2pz)_3$ = hydrotris-(3,5-di-isopropylpryazol-1-yl)borate.

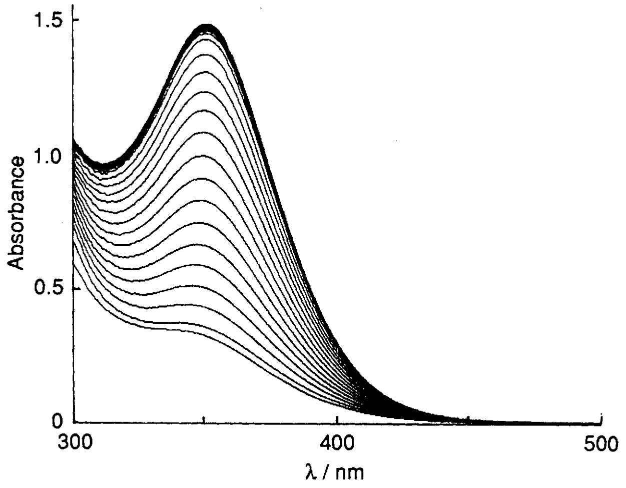
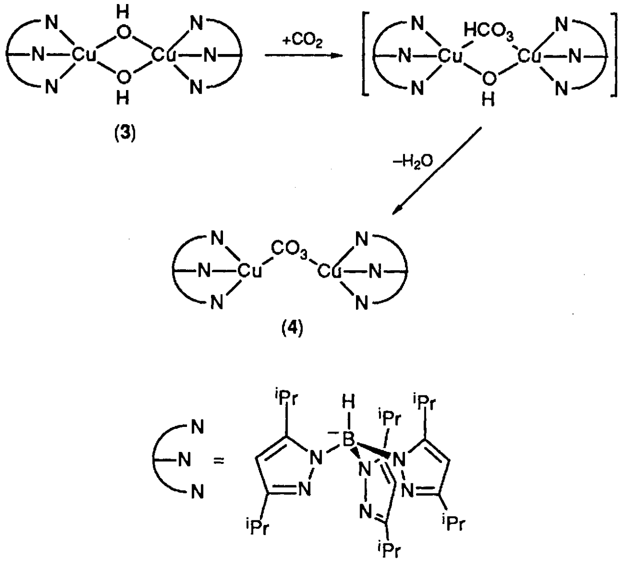


Figure 2. Electronic spectral change in the reaction of (**4**) with CO_2 in the air (in toluene, 1.28×10^{-4} M). The bottom line indicates the spectrum of (**3**) under argon. Immediately after the solution was exposed to the air, repeated scans were initiated with a cycle time of 20 min.

binuclear μ-carbonato complex $[(Cu\{HB(3,5\text{-}Me_2pz)_3\})_2(CO_3)]$ (**2**).‡ However, the complex is not reactive enough to react with atmospheric CO_2.

We have already reported the synthesis and structure of the binuclear di-μ-hydroxo copper(II) complex $[(Cu\{HB(3,5\text{-}Pr^i_2pz)_3\})_2(OH)_2]$ (**3**).[4] The deep blue colour of a toluene solution of (**3**) changes to green instantaneously under a CO_2 atmosphere, and from the resulting solution $[(Cu\{HB(3,5\text{-}Pr^i_2pz)_3\})_2(CO)_3]$ (**4**)§ may be isolated as green crystals in quantitative yield. The crystal structure of (**4**) is shown in Figure 1. The complex has a binuclear structure bridged by a carbonate group; one oxygen atom from the carbonate sits between the two copper ions and the two other oxygen atoms co-ordinate to the other sides of the copper ions respectively. Several binuclear μ-carbonato copper(II) complexes containing a similar co-ordination structure have been reported.[5] Complex (**4**) exhibits a characteristic absorption band at 349 nm ascribed to the ligand to metal charge transfer band ($CO_3^{2-} \rightarrow Cu^{II}$) and a strong IR band at 1593 cm^{-1} due to ν_{CO}.



Scheme 1

Complex (**3**) reacts even with atmospheric CO_2 to afford (**4**) as shown in Figure 2, in which the time dependent development of the characteristic band at 349 nm due to (**4**) is presented. The intensity of the band reaches a maximum within 5 h, and indicates that (**4**) is formed from (**3**) quantitatively in air. IR and ^{1}H NMR analyses of the resulting solution also support the quantitative formation of (**4**). Accordingly, (**3**) is at least 10^3 times more active than (**1**) for CO_2 fixation.

It seems unlikely that a binuclear μ-oxo complex formed by the dissociation of water from (**3**) is responsible for the fixation of CO_2, because there is no spectroscopic indication for involvement of such a complex. The mechanism of CO_2 fixation by (**3**) is rather explained in terms of the nucleophilic attack of the hydroxo group on the electrophilic carbon of CO_2 followed by water dissociation. The unusually high reactivity of (**3**) towards CO_2 is, thus, ascribed to the high basicity of the hydroxo group owing to the strong electron donation property of the present ligand.[6]

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‡ The structure of (**2**) was established by *X*-ray crystallography. Complex (**2**) also has a binuclear structure containing the same co-ordination mode of the carbonate group as in (**4**). The details will be described elsewhere.

§ Satisfactory elemental analyses were obtained for (**4**). UV–VIS (CH_2Cl_2): λ_{max} 670 (ε, 440 mol^{-1} dm^3 cm^{-1}) and 349 nm (12 400); IR (KBr), ν_{BH}, 2533; ν_{CO}, 1593 cm^{-1}. *Crystal data* for (**4**): $M = 1118.12$, monoclinic, space group $P2_1/a$, $a = 26.652(2)$, $b = 12.973(2)$, $c = 19.426(2)$ Å, $\beta = 99.32(1)°$, $U = 6628(1)$ Å^3, $Z = 4$, $D_c = 1.12$ g cm^{-3}, $F(000) = 598$, $\mu(\text{Mo-}K_\alpha) = 3.4$ cm^{-1}. The structure was solved by direct methods and refined by full-matrix least-square methods for anisotropic thermal parameters for all non-hydrogen atoms. No hydrogen atoms were included in the calculations because of the limit of computer capability. Thus, the refinement converged with a slightly high R value: 0.099 (R_w 0.099) for 5186 reflections [$2 < 2\theta < 50°$, $F_o > 3\sigma(F_o)$]. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

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