Characterization of a μ-η^2:η^2-Peroxo Dinuclear Cobalt(II) Complex

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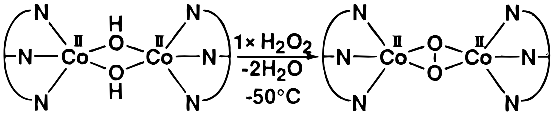
Transition metal−dioxygen complexes have been attracting interest from the standpoints of synthetic chemistry and biological chemistry because dioxygen complexes play key roles not only in a variety of catalytic oxidations but also in the physiological metabolism of dioxygen.[1] We previously succeeded in the preparation and characterization of a dinuclear Cu(II) peroxo complex, $[Cu(HB(3,5\text{-}iPr_2pz)_3)]_2(O_2)$ (**1**) ($HB(3,5\text{-}iPr_2pz)_3$ denotes hydrotris(3,5-diisopropyl-1-pyrazolyl)borate), which is the first structurally determined d-block transition metal μ-η^2:η^2-peroxo complex.[2] This dicopper peroxo complex **1** shows both very unusual and characteristic physicochemical properties associated with the μ-η^2:η^2 coordination mode of the peroxide ion: (1) two intense absorptions both attributable to a O_2^{2-} to Cu(II) ligand-to-metal charge transfer (LMCT) band; (2) a low-frequency O−O bond stretch in the resonance Raman spectrum; (3) strong antiferromagnetic coupling between the two metal ions.[2,3] In this communication, we present evidence of the formation of a dinuclear Co(II) μ-η^2:η^2-peroxo complex.

Treatment of a dinuclear Co(II) bis(μ-hydroxo) complex, $[Co(HB(3,5\text{-}iPr_2pz)_3)]_2(OH)_2$ (**2**),[4] with H_2O_2 −50 °C gave a thermally unstable dark brown compound, **3**.[5] The absorption spectrum of a solution of **3** in diethyl ether at −78 °C shows two intense bands at 350 and 493 nm. This feature of the spectrum is similar to that of the dicopper μ-η^2:η^2-peroxo complex **1**, rather than the typical dinuclear Co(III) μ-peroxo complexes having *cis* μ-1,2 or *trans* μ-1,2 binding modes.[3a,15] In an absorption spectral titration of an Et_2O solution of **2** with H_2O_2, the intensity of the spectrum was maximal when **2**:H_2O_2 = 1:1, and no change was observed even on the addition of excess H_2O_2. Thus, dark brown compound **3** is assigned to the dinuclear Co(II) μ-η^2:η^2-peroxo complex which resulted from the stoichiometric reaction of the dinuclear hydroxo complex with H_2O_2, as was found in the synthesis of the copper complex **1**[2] (Scheme 1). However, the intensity of the higher energy absorption of **3** (350 nm, $\epsilon = 8900\ M^{-1}\ cm^{-1}$) is half that of the copper complex **1** (349 nm, $\epsilon = 21000\ M^{-1}\ cm^{-1}$). These higher energy absorptions are assigned to the peroxo π^*_σ to metal d orbital charge transfer bands. Solomon *et al.* have shown that the high intensity of this band of **1** arises from greater σ-donation from the peroxo ion to copper.[3b] In contrast to **1**, the less electron-accepting character of the Co(II) ion results in the weaker intensity of the peroxo π^*_σ to Co(II) CT band of **3**.

Scheme 1



2 **3**

The resonance Raman spectrum of **3** excited at 514.5 nm in acetone at −80 °C revealed an enhanced vibrational feature at 651 cm^{-1}. This 651 cm^{-1} band is downshifted to 617 cm^{-1} in the spectrum of ^{18}O-labeled **3** synthesized by the reaction of **2** with $H_2{}^{18}O_2$. This isotope shift $[(\nu(^{16}O_2)/\nu(^{18}O_2))_{obsd} = 1.055]$ is in reasonable agreement with that expected for the O−O bond stretch $[(\nu(^{16}O_2)/\nu(^{18}O_2))_{calcd} = 1.061]$. Previously reported ν(O−O) bands for peroxo complexes were observed at 930−720 cm^{-1}, including those for dicopper μ-η^2:η^2 complexes and oxyhemocyanin,[1,7] whereas the ν(O−O) of **3** is *ca.* 90 cm^{-1} lower than the value for **1** (741 cm^{-1}). The low ν(O−O) for the copper compounds is ascribed to the mixing of the single-electron-occupied Cu(II) $d_{x^2-y^2}$ orbital and empty π-acidic peroxo σ^* orbital resulting in back-donation from copper to the antibonding O_2^{2-} orbital.[3b] It might be considered that the interaction between the highest single-electron-occupied Co(II) $d_{x^2-y^2}$ orbital and antibonding peroxo σ^* weakens the O−O bond in **3**, because metal centers in **3** are presumed to be square-pyramidal high-spin Co(II) (d^7, $S = {}^3/_2$) on the basis of the structural similarity between the Co(II) and Cu(II) bis(μ-hydroxo) complexes.[4] The back-donation from the metal center to the peroxo ligand arising from the stronger electron-donating property of the Co(II) ion compared to the Cu(II) ion might result in the higher electron density on the O_2^{2-} orbital σ^* of **3** than on that of **1**. In addition, the electron density on the antibonding O_2^{2-} π^*_σ orbital of **3** is higher than that of **1** as shown by the weaker LMCT intensity described above. High electron density on both of the antibonding peroxo orbitals (π^*_σ and σ^*) might weaken the O−O bond more in **3** than in **1**. The mononuclear Co(II) side-on superoxo complex $Co(O_2)[HB(3\text{-}tBu\text{-}5\text{-}Mepz)_3]$ also shows an unusually low superoxide O−O bond stretching at 961 cm^{-1},[8] which is extremely lower than that found for the analogous Cu(II) superoxo complex $Cu(O_2)[HB(3\text{-}tBu\text{-}5\text{-}iPrpz)_3]$ (ν(O−O) = 1112 cm^{-1}).[9] To provide a theoretical basis for this interpretation, MO calculations will be performed.

The ^1H-NMR spectrum of **3** was also consistent with the assignment to the μ-η^2:η^2-peroxo complex. Hydroxo complex

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(5) Experimental details and characterization data for all new compounds are reported in the Supporting Information.

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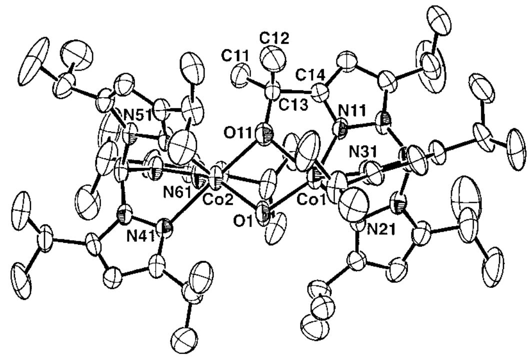


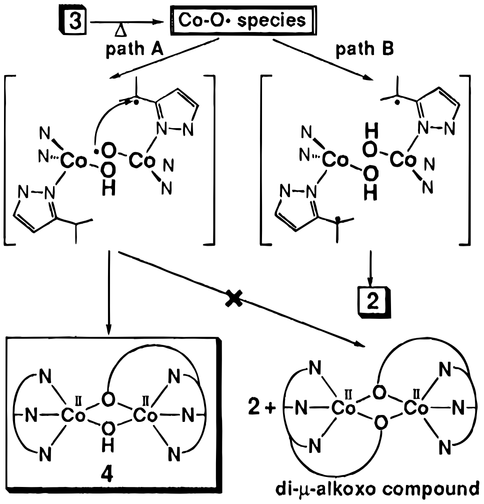
Figure 1. ORTEP diagram of μ-alkoxo$-\mu$-hydroxo complex **4** (drawn at the 50% probability level). All hydrogen atoms are omitted for clarity.

2 showed widely paramagnetic-shifted signals in the range -144 to $+82$ ppm at room temperature,[4] whereas **3** exhibits the signals in -19 to $+22$ ppm region at -80 °C and in the -26 to $+28$ ppm region at -40 °C. These observations imply antiferromagnetism for **3** owing to the magnetic coupling between both Co(II) ions through the μ-peroxo group. Theopold *et al.* reported the formation of an analogous dinuclear Co(II) μ-peroxo complex as an intermediate in the thermal decomposition of the mononuclear Co(II) superoxo complex $Co(O_2)[HB(3\text{-}iPr\text{-}5\text{-}Mepz)_3]$.[6] The ^{1}H-NMR spectrum of **3** resembles that of Theopold's complex.

Thermal decomposition of the μ-η^2:η^2 Co(II) peroxo complex **3** yielded **2** and a ligand oxygenated compound, **4**.[5] As shown in Figure 1, complex **4** adopts a low-symmetry dinuclear structure described as a μ-alkoxo$-\mu$-hydroxo dinuclear Co(II) complex, $Co_2(\mu\text{-}OH)[HB(\mu\text{-}3\text{-}OCMe_2\text{-}5\text{-}iPrpz)(3,5\text{-}iPr_2pz)_2]\text{-}[HB(3,5\text{-}iPr_2pz)_3]$. One methine C$-$H bond of the isopropyl group in two tris(pyrazolyl)borate ligands is hydroxylated (O11$-$C13 = 1.45(1) Å), resulting in the formation of an alkoxy bridge between the two cobalt(II) ions. Intramolecular methine C$-$H bond activations in the μ-η^2:η^2-peroxo complexes of Co(II) and Cu(II) were reported recently by Theopold *et al.*[6] and Tolman *et al.*[10] The hydroxylation of the methine position in a tris(pyrazolyl)borate ligand was observed in the O_2 oxidation of a bis(μ-hydroxo)manganese(II) complex.[11]

A plausible mechanism for the formation of the μ-alkoxo$-\mu$-hydroxo complex **4** is presented in Scheme 2. The O$-$O bond is weakened because of the μ-η^2:η^2 coordination mode as shown in the unusually low ν(O$-$O) vibration. Homolytic rupture of the O$-$O bond occurs easily, forming two Co$-$O$^\bullet$ species. These two Co$-$O$^\bullet$ species simultaneously attack the same methine position of a pyrazole which is located at the apex of an N_2(pyrazolyl)O_2(peroxo) basal plane. One Co$-$O$^\bullet$ abstracts the H atom, and the other Co$-$O$^\bullet$ binds the resulting methine radical to form the Co$-$O$-$R. In the present system, bis(μ-hydroxo) complex **2** was also produced but the dinuclear bis(μ-alkoxo) compound[12] that was expected to form upon rearrangement of the radical intermediate was not observed. In addition, the thermal decomposition of **3** in toluene-d_8 did not yield the corresponding deuterated product, suggesting that the hydrogen atoms of the hydroxy groups in **2** and **4** did not originate from the solvent used.[6,10] Therefore, we concluded that two decomposition pathways might exist: one methine C$-$H is attacked, resulting in **4** (path A), and two methines which are located in apical positions of basal planes at the same distances from the oxygen atoms are attacked, resulting in **2** (path B).[13] These observations also suggest that the μ-peroxo ligand in **3** coordinates in the *planar* (not *bent*) μ-η^2:η^2 binding mode, as in oxyhemocyanin complexes and the Cu(II) complex **1**.

Scheme 2



In summary, it was revealed that a dinuclear Co(II) peroxo complex has the μ-η^2:η^2 coordination mode on the basis of spectroscopic properties and reactivity. In addition, aliphatic C$-$H bond activation yielded the novel μ-alkoxo$-\mu$-hydroxo compound via the thermal decomposition of the μ-peroxo complex. Further work is being undertaken, including oxidative reactions under various conditions.

Acknowledgment. We thank Dr. K. Fujisawa and Mr. K. Fujita for help in measuring the resonance Raman spectra and Prof. K. H. Theopold of the University of Delaware for the providing of preprint of ref 6 and stimulating suggestions. We appreciate the editing of the manuscript by Dr. H. Suga of Harvard Medical School and Ms. T. Ogihara. This research was supported in part by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, Sports, and Culture of Japan. S.H. was supported by Research Fellowships from the Japan Society for the Promotion of Science for Young Scientists.

Supporting Information Available: Text giving details of synthesis and spectroscopic data for **3** and a summary of experiment and physical characterization, listings of crystal data and data collection details, isotropic and anisotropic thermal parameters, and bond distances and angles for **4**, a fully labeled ORTEP diagram of **4**, UV$-$vis and resonance Raman spectra of **3**, and a ^{1}H-NMR spectrum of **4** (17 pages). Ordering information is given on any current masthead page.

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(12) The dicobalt(II) bis(μ-alkoxo) compound, $[Co(HB(\mu\text{-}3\text{-}OCMe_2\text{-}5\text{-}iPrpz)(3,5\text{-}iPr_2pz)_2)]_2$, has been produced by the reaction of **2** with excess amount of H_2O_2 and/or with 2 equiv of alkylhydrogenperoxide.

(13) Theopold[6] and Tolman[10] suggested that O$-$O bond homolysis occurred in concert with the methine C$-$H hydrogen abstraction. Although we could not rule out such a possibility, the kinetic studies reported by them would not be able to distinguish the concerted mechanism from our proposed mechanism if O$-$O bond rupture is a very fast process and C$-$H bond cleavage is the rate-determining step. Mahapatra, S.; Halfen, J. A.; Wilkinson, E. C.; Pan, G.; Cramer, C. J.; Que, L., Jr.; Tolman, W. B. *J. Am. Chem. Soc.* **1995**, *117* , 8865.

(14) A solvent-dependent equilibrium between $[Cu_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}O_2)]^{2+}$ and $[Cu_2(\mu\text{-}O)_2]^{2+}$ has been reported very recently. We measured the UV$-$vis spectra of **3** in various solvents (pentane, CH_2Cl_2, Et_2O, acetone); however, we never observed the change of the feature of the spectra of the present cobalt compound. Halfen, J. A.; Mahapatra, S.; Wilkinson, E. C.; Kaderli, S.; Young, V. G., Jr.; Que, L., Jr.; Zuberbühler, A. D.; Tolman, W. B. *Science* **1996**, *271*, 1397.