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# Communications

## Formation and Characterization of a Mononuclear (Acylperoxo)copper(II) Complex

(Acylperoxo)copper(II) complexes as well as alkylperoxo or hydroperoxo complexes deserve attention as models for hypothetical reaction intermediates in oxidation reactions catalyzed by copper-containing monooxygenases.[1] Recently, Karlin et al.[2] reported the synthesis and X-ray crystal structure of a binuclear (acylperoxo)copper(II) complex. Herein, we report the synthesis of Cu(mCPBA)(HB(3,5-iPr$_2$pz)$_3$) (**1**) (HB(3,5-iPr$_2$pz)$_3^-$ = hydrotris(3,5-diisopropyl-1-pyrazolyl)borate[3]) by a low-temperature reaction of [Cu(HB(3,5-iPr$_2$pz)$_3$))]$_2$(OH)$_2$ (**2**) with mCPBA (*m*-chloroperbenzoic acid). To our knowledge, this is the first example of a mononuclear (acylperoxo)copper(II) complex, the properties of which may be relevant to dopamine *β*-hydroxylase[4] and the recently isolated copper-containing phenylalanine hydroxylase[5] because the active sites of both of these enzymes have been suggested to consist of a mononuclear copper ion.

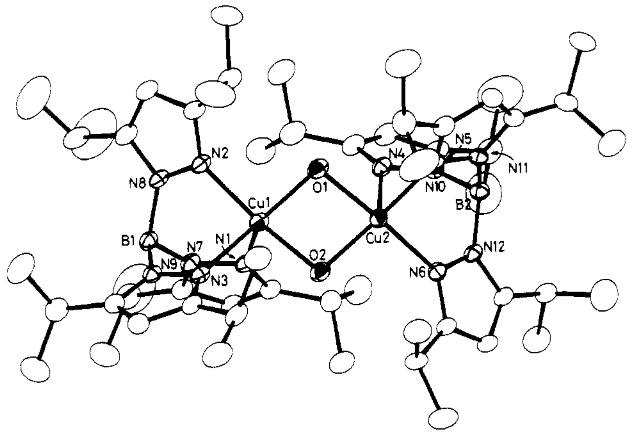

**Figure 1.** ORTEP view of **2** (CH$_2$Cl$_2$ molecules of crystallization omitted). Selected bond distances (Å) and angles (deg): Cu1–O1, 1.953 (6); Cu1–O2, 1.934 (5); Cu1–N1, 2.371 (6); Cu1–N2, 2.016 (6); Cu1–N3, 2.010 (8); Cu2–O1, 1.921 (5); Cu2–O2, 1.946 (7); Cu2–N4, 2.640 (7); Cu2–N5, 1.984 (7); Cu2–N6, 1.989 (6); Cu1···Cu2, 2.937 (2); O1–Cu1–O2, 79.2 (2); O1–Cu2–O2, 79.6 (2); Cu1–O1–Cu2, 98.6 (2); Cu1–O2–Cu2, 98.4 (2).

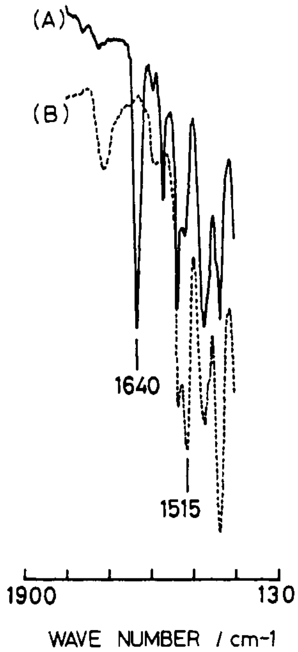

**Figure 2.** IR (KBr) spectra: (A, solid line) solids obtained from the reaction of **2** and mCPBA; (B, dashed line) solids obtained by treatment of solids from (A) with PPh$_3$.

Complex **2** was prepared by the reaction of Cu(Br)(HB(3,5-iPr$_2$pz)$_3$) with aqueous NaOH in toluene.[6] As shown in Figure 1, **2** has a binuclear structure bridged by two hydroxo groups.[7] Each copper ion is coordinated by three pyrazole nitrogens of the tripod ligand. Among these, the bond distance between copper and one pyrazole nitrogen is significantly elongated, suggesting that the coordination geometry around each copper can be de-

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(1) See the following reviews and papers: (a) Valentine, J. S.; Burstyn, J. N.; Margerum, L. D. *Oxygen Complexes and Oxygen Activation by Transition Metals*; Martell, A. E., Sawyer, D. T., Eds.; Plenum Press: New York, 1988; p 175. (b) Franklin, C. C.; VanAtta, R. B.; Tai, A. F.; Valentine, J. S. *J. Am. Chem. Soc.* **1984**, *106*, 814. (c) Tai, A. F.; Margerum, L. D.; Valentine, J. S. *Ibid.* **1986**, *108*, 5006. (d) Karlin, K. D.; Gultneh, Y. *Prog. Inorg. Chem.* **1987**, *35*, 219.

(2) Ghosh, P.; Tyeklar, Z.; Karlin, K. D.; Jacobson, R. R.; Zubieta, J. *J. Am. Chem. Soc.* **1987**, *109*, 6889. A hydroperoxo binuclear copper(II) complex has been also synthesized with the same ligand: Karlin, K. D.; Ghosh, P.; Cruse, R. W.; Farooq, A.; Gultneh, Y.; Jacobson, R. R.; Blackburn, N.; Strange, R. W.; Zubieta, J. *Ibid.* **1988**, *110*, 6769.

(3) Kitajima, N.; Fujisawa, K.; Fujimoto, C.; Moro-oka, Y. *Chem. Lett.* **1989**, 421.

(4) (a) Miller, S. M.; Klinman, J. P. *Biochemistry* **1985**, *24*, 2114. (b) Padgette, S. R.; Wimalasena, K.; Herman, H. H.; Sirimanne, S. R.; May, S. W. *Ibid.* **1985**, *24*, 5826. (c) Wimalasena, K.; May, S. W. *J. Am. Chem. Soc.* **1987**, *109*, 4036.

(5) Pember, S. O.; Villafranca, J. J.; Benkovic, S. J. *Biochemistry* **1986**, *25*, 6611.

(6) Satisfactory elemental analysis was obtained for **2** dried under vacuum. Anal. Calcd for $C_{54}H_{94}N_{12}O_2B_2Cu_2$: C, 59.39; H, 8.68; N, 15.39. Found: C, 59.48; H, 8.86; N, 15.27. IR: $\nu$(OH) 3645, $\nu$(BH) 2528 cm$^{-1}$. UV–vis (CH$_2$Cl$_2$): 260 ($\epsilon$ 6800), 653 nm (120).

(7) **2**·1.5CH$_2$Cl$_2$ ($C_{55.5}H_{97}N_{12}O_2B_2Cl_3Cu_2$; MW 1219.54) crystallized in the triclinic space group $P\bar{1}$ with $a$ = 16.466 (4) Å, $b$ = 16.904 (5) Å, $c$ = 14.077 (3) Å, $\alpha$ = 112.92 (2)°, $\beta$ = 99.21 (2)°, $\gamma$ = 90.76 (2)°, $V$ = 3550 (1) Å$^3$, and $Z$ = 2. Data collection ($2\theta < 50°$) was done on Rigaku AFC-5 diffractometer with graphite-monochromated Mo K$\alpha$ radiation at −75 °C to prevent the loss of CH$_2$Cl$_2$ molecules of crystallization. Block-diagonal least-squares refinement of the model based on 7226 reflections ($F_o > 3\sigma(F_o)$) converged to a final $R$ = 8.29% and $R_w$ = 10.21%. Hydrogen atoms on the boron, the pyrazole rings, and the tertiary positions of iPr groups were calculated and fixed in the refinement. The other hydrogen atoms were not included in the calculation.

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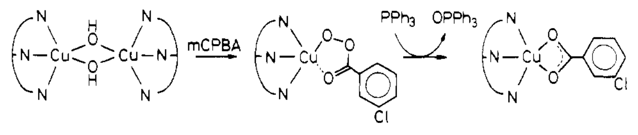
**Scheme I**



scribed as tetragonal. In accord with the binuclear structure, **2** shows strong antiferromagnetic properties; it is EPR silent in $CH_2Cl_2$ at −196 °C. $^1$H NMR ($CDCl_3$, −40 °C, ppm): −51 (s, br, 2 H, OH), 1.34 (s, br, 36 H, $Me_2$CH), 1.70 (s, br, 36 H, $Me_2$CH), 2.91 (br, 6 H, Me$_2$C$H$), 3.85 (s, br, 6 H, Me$_2$C$H$), 12.66 (s, br, 6 H, pz).

When a solution of **2** in pentane was treated with a ca. 2-equiv amount of mCPBA at −20 °C, a slight color change from blue to greenish blue was noted within ca. 10 min. Removal of the unreacted mCPBA by filtration followed by evaporation at −20 °C afforded **1** as a thermally unstable solid[8] that exhibited the characteristic IR band at 1640 cm$^{-1}$ assigned to the acyl carbonyl group (Figure 2). The frequency is ca. 100 cm$^{-1}$ down-shifted as compared with that of free mCPBA (1735 cm$^{-1}$). Fe(mCPBA)TTPPP[9] (TTPPP = 5,10,15,20-tetrakis(2,4,6-triphenylphenyl)porphyrinate), in which the acyl carbonyl group is not coordinated by the iron, shows a band at 1744 cm$^{-1}$. Hence, the acyl carbonyl group is suggested to coordinate to copper, and **1** is ascribed to a pentacoordinated complex with a $N_3O_2$ ligand donor set. The structure is also supported by the EPR spectrum, which is typical for a square-pyramidal mononuclear copper(II) complex ($g_\parallel = 2.27$, $g_\perp = 2.07$, and $A_\parallel = 160$ G at −196 °C in $CH_2Cl_2$).

Complex **1** is moderately stable at −20 °C (the half-life time in $CH_2Cl_2$ is ca. 0.5 h), although it decomposes at room temperature even in the solid. When $PPh_3$ was added to a solution of **1** at −20 °C, an instantaneous color change to green took place with the quantitative formation of $OPPh_3$. The solids obtained by the evaporation of the resulting solution exhibited the characteristic new band at 1515 cm$^{-1}$, as shown in Figure 2. The band is attributable to the carbonyl group of the benzoato complex Cu(mCBA)(HB(3,5-iPr$_2$pz)$_3$)[10] (**3**), of which the crystal structure is shown in Figure 3.

As described above, **1** readily oxidizes $PPh_3$. However, the oxidizing capability is apparently less than that of free mCPBA. For instance, **1** did not react with cyclohexene at −20 °C, whereas free mCPBA oxidizes cyclohexene to cyclohexene oxide under comparable reaction conditions. The addition of protons to the reaction solution of **1** did not affect the result. The low reactivity of **1** is in striking contrast to the high reactivity of Fe(mCPBA)(TTPPP). The iron complex undergoes heterolytic cleavage by $H^+$ to give an oxoiron(IV) porphyrin $\pi$-cation-radical complex,[11] which is extremely effective for the oxo-transfer reaction of cyclohexene even at a low temperature. Therefore, the occurrence of a heterolytic O–O bond cleavage to form an oxocopper(III) cation or oxocopper(IV) intermediate (which is expected to show the high oxo-transfer reactivity) seems unlikely in the present system, although such a reaction is suggested as an elemental step in the enzymatic oxidations catalyzed by dopamine $\beta$-hydroxylase.[4]

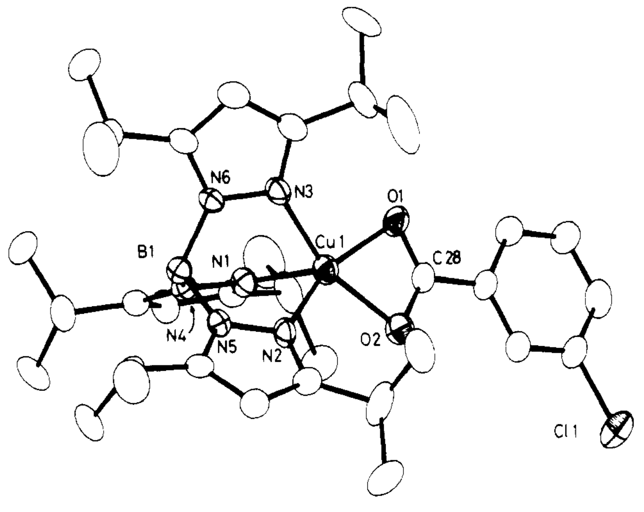


**Figure 3.** ORTEP view of **3**. Selected bond distances (Å) and bond angles (deg): Cu1–N1, 2.171 (9); Cu1–N2, 1.977 (8); Cu1–N3, 1.980 (9); Cu1–O1, 2.043 (7); Cu1–O2, 2.013 (8); O1–C28, 1.246 (15); O2–C28, 1.252 (14); O1–Cu1–O2, 64.7 (3); O1–C28–O2, 120.6 (10).

**Acknowledgment**. We thank Dr. K. Toriumi for his kind help in the final refinements of the X-ray analysis of **2**. Financial support for this study by the Ministry of Education, Science and Culture of Japan (Grants 62430018 and 1607003) is gratefully acknowledged. N.K. is also grateful to the Kawakami Memorial Foundation for financial support.

**Supplementary Material Available:** For **2** and **3**, text covering crystallographic details, figures showing fully labeled ORTEP structures, and tables of atomic coordinates, thermal parameters, bond distances, and bond angles (32 pages); tables of observed and calculated structure factors (25 pages). Ordering information is given on any current masthead page.

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(8) Isolation of **1** as a pure crystalline solid has been unsuccessful so far, owing to the instability of **1** and the contamination of **3**.

(9) Groves, J. T.; Watanabe, Y. *Inorg. Chem.* **1987**, *26*, 785.

(10) An authentic sample of **3** was obtained by the reaction of Cu(HB(3,5-iPr$_2$pz)$_3$)$^3$ with mCPBA. Anal. Calcd for $C_{34}H_{50}N_6BO_2CuCl$: C, 59.65; H, 7.36; 12.28. Found: C, 59.60; H, 7.40; N, 12.25. EPR ($CH_2Cl_2$, −196 °C): $g_\parallel = 2.29$, $g_\perp = 2.06$, $A_\parallel = 141$ G. UV–vis ($CH_2Cl_2$): 757 nm ($\epsilon$ 130). **3** (MW 684.62) crystallized in the monoclinic space group $P2_1/n$ with $a = 15.887$ (2) Å, $b = 18.783$ (2) Å, $c = 12.531$ (2) Å, $\beta = 96.06$ (2)°, $V = 3718$ (1) Å$^3$, and $Z = 4$ for 2759 observed reflections ($2\theta < 45°$; $F_o > 3\sigma(F_o)$) taken on a Rigaku AFC-5 diffractometer at 25 °C. The structure was refined by a full-matrix least-squares method to final residuals $R = 6.29\%$ and $R_w = 6.05\%$. Hydrogen atoms on the boron, the pyrazole rings, and the tertiary positions of the iPr groups were calculated. The other hydrogen atoms were not included in the calculation.

(11) Groves, J. T.; Watanabe, Y. *J. Am. Chem. Soc.* **1986**, *108*, 7834. An acylperoxoplatinum complex was also reported to be effective for an oxo-transfer reaction of cyclohexene: Chen, M. J. K.; Kochi, J. K. *J. Chem. Soc., Chem. Commun.* **1977**, 204.

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## Soluble and Volatile Alkoxides of Bismuth. The First Structurally Characterized Bismuth Trialkoxide: $[Bi(\mu\text{-}\eta^1\text{-}OCH_2CH_2OMe)_2(\eta^1\text{-}OCH_2CH_2OMe)]_\infty$

We and others[1] are interested in bismuth alkoxides as potential precursors for solution-phase and vapor-phase syntheses of bismuth-containing oxide superconductors. Mehrotra and Rai previously described the synthesis of simple alkoxides of bismuth(III) according to eq 1.[2] The compounds were reported to

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(1) (a) Sauer, N. N.; Garcia, E.; Salazar, K. V.; Ryan, R. R. *Abstracts of Papers*, 197th National Meeting of the American Chemical Society, Dallas, TX; American Chemical Society: Washington, DC, 1989; INOR-251. (b) Sauer, N. N.; Garcia, E.; Ryan, R. R. *Abstracts of Papers*, 198th National Meeting of the American Chemical Society, Miami Beach, FL; American Chemical Society: Washington, DC, 1989; INOR-256. (c) For related bismuth–amide chemistry see: Clegg, W.; Compton, N. A.; Errington, R. J.; Norman, N. C.; Wishart, N. *Polyhedron* **1989**, *8*, 1579.

(2) Mehrotra, R. C.; Rai, A. K. *Indian J. Chem.* **1966**, *4*, 537.

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