CHEMISTRY LETTERS, pp. 963-966, 1993.

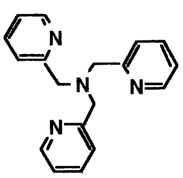
Reactivity of Copper(I) Complexes Containing Various Tetradentate Tripodal Ligands with Molecular Oxygen

Kounosuke UOZUMI, Yoshihito HAYASHI, Masatatsu SUZUKI,* and Akira UEHARA*
Department of Chemistry, Faculty of Science, Kanazawa University, Kakumamachi, Kanazawa 920-11

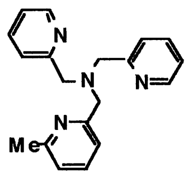
Reactivity of copper(I) complexes $[Cu(L)]^+$ containing a series of tetradentate tripodal ligands, (6-methyl-2-pyridylmethyl)$_m$(2-pyridylmethyl)$_{(3-m)}$amine (m = 1, 2, or 3) with molecular oxygen was investigated in acetone at -70 °C. It was found that the introduction of 6-methyl group(s) into pyridyl group(s) has significant influences on the stereochemistry and thermal stability of peroxo dicopper(II) complexes.

The μ-peroxo dicopper(II) complexes have been of particular interest as models for hemocyanin and tyrosinase. Several types of coordination modes of peroxo group for dicopper(II) are known. Kitajima et al. established a μ-η^2:η^2-peroxo coordination mode for dicopper(II) by using a series of tridentate hindered tripodal ligands (tris(3,5-dialkylpyrazolyl)borate).[1)] They demonstrated that their μ-η^2:η^2-peroxo dicopper(II) complexes are excellent structural and functional models for the above copper proteins. Such a μ-η^2:η^2 peroxo coordination mode has been also proposed for the peroxo complexes with various tridentate ligands.[2)] Karlin et al. established another type of peroxo coordination mode, i.e., a trans-μ-1,2-peroxo coordination mode for a complex with a tetradentate tripodal ligand (tris(2-pyridylmethyl)amine: tmpa).[3)] Some other types of peroxo coordination modes such as an unsymmetric terminal peroxo, μ-1,1-acylperoxo and -hydroperoxo coordination modes have been also proposed.[4,5)] These suggest that the stereochemistry of the peroxo dicopper(II) complexes is variable depending on the stereochemical and/or electronic effects of ligands.

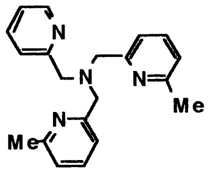
Previously, we found that a dinucleating ligand Me$_4$-tpdp which contains sterically hindered nitrogen donors stabilizes μ-peroxo diiron(III) complexes significantly: i.e., 6-methyl groups in pyridyl groups seem to weaken the electron donor ability of pyridyl nitrogens and greatly suppress an oxidative degradation of dinuclear μ-peroxo iron(III) complexes.[6)] $[Cu(tmpa)(CH_3CN)]^+$ (**1**) has been shown to form a trans-μ-1,2-peroxo complex, $[Cu_2(tmpa)_2O_2]^{2+}$ (**1a**) as mentioned above.[3a)] It was expected that the introduction of 6-methyl group(s) in tmpa stabilizes trans-μ-1,2-peroxo dicopper(II) complexes. In this study, we report the reaction of copper(I) complexes [Cu(L)]X (L = N$_4$-Mepy (**2**), N$_4$-Me$_2$py (**3**), and N$_4$-Me$_3$py (**4**), and X = ClO_4, PF_6, or BF_4) with molecular



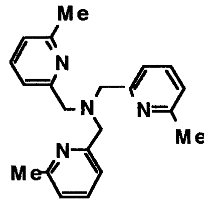
tmpa



N_4-Mepy



N_4-Me_2py



N_4-Me_3py

oxygen, where N_4-Mepy is bis(2-pyridylmethyl)(6-methyl-2-pyridylmethyl)amine, N_4-Me_2py, (2-pyridylmethyl)bis(6-methyl-2-pyridylmethyl)amine, and N_4-Me_3py, tris(6-methyl-2-pyridylmethyl)amine.

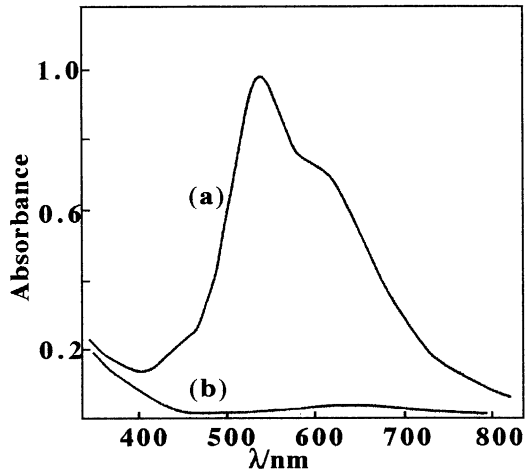


Fig. 1. Electronic spectra of **2** (a) under O_2 atmosphere and a decomposed complex (b) in acetone at -70 °C.8)

[Cu(L)]X was prepared by treating[Cu(CH_3CN)$_4$]X with L under argon atmosphere.7) Reaction of **2** with molecular oxygen gave an intense purple color in acetone at -70 °C. This purple species is very unstable even at -70 °C compared with **1a** and decays very rapidly within several minutes to give green species. The electronic spectrum of the purple species shows three bands at 440 nm (sh), 537 nm (ε (Cu_2) is at least more than 5000 mol^{-1} cm^{-1} dm^3) and 610 nm (sh) as seen in Fig. 1. The spectral pattern of the present complex closely resembles that of **1a** which has also an intense absorption band at 524 nm (ε = 11300 mol^{-1} cm^{-1} dm^3), and two shoulders at 435 nm (ε = 1700 mol^{-1} cm^{-1} dm^3) and 615 nm (ε = 5800 mol^{-1} cm^{-1} dm^3).3b) A similarity of the electronic spectra of these two complexes suggests that the purple species is a trans-μ-1,2-peroxo dicopper(II) complex. It is interesting that the introduction of 6-methyl group into tmpa decreases the thermal stability of the present peroxo dicopper(II) complex in contrast to the case of the iron complexes mentioned above.

Complex **3** reacts with molecular oxygen to give brownish orange color in acetone or dichloromethane at -70 °C. The electronic spectrum of a brownish orange species shows an intense absorption band at 378 nm (ε(Cu_2) = 22000 mol^{-1} cm^{-1} dm^3), and two weak bands at 494 nm (ε(Cu_2) = 330 mol^{-1} cm^{-1} dm^3) and 784 nm (ε(Cu_2) = 60 mol^{-1} cm^{-1} dm^3) in Fig. 2(b). The spectrum is quite different from those found for **1a** and the oxygenated complex of **2**. The O_2 uptake determined by volummetric measurement is 0.5 ± 0.1 per mole of **3**, suggesting the formation of a peroxo dicopper(II) complex (**3a**). Warming the oxygenated complex upto room temperature resulted in a color change to blue-green (Fig. 2(d)). ^{1}H NMR spectra of **3** and **3a** in acetone-d_6 at -70 °C exhibits sharp ligand resonances having chemical shifts in the range for those of diamagnetic compounds.9) After the decomposition of **3a** by warming upto room temperature, signals disappeared. These observations indicate that **3a** is diamagnetic as found for the other peroxo dicopper(II) complexes. Deoxygenation is not effected by bubbling of argon gas at -70 °C. However, the reversible binding of O_2 and CO is evidenced by the following reactions (Fig. 2): bubbling of CO gas into a brownish orange solution at -70 °C causes a rapid decolorization, and after removal of CO gas by evacuation at room temperature, reoxygenation is achieved at -70 °C to give an original spectrum of **3a** with a slight loss of intensity (spectrum (b)-2 in Fig. 2). The cycling can be repeated for several times (spectra (b)-2 - (b)-4 in Fig. 2).

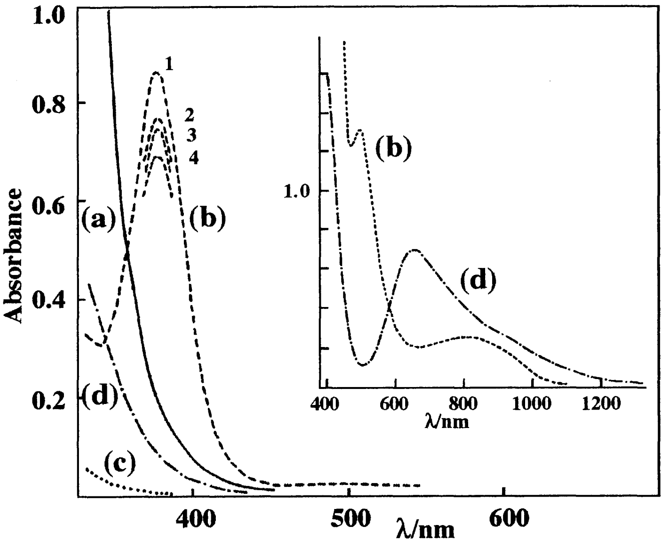


Fig. 2. Electronic spectra of **3** (a), **3a** ((b)-1 - (b)-4)), a CO adduct of **3** (c), and a decomposed complex (d) in acetone at -70 °C.[10)] The spectra of (b)-2 - (b)-4 show the repitition of reversible O_2-CO cycles. See text for details.

A significant difference between the electronic spectra of **1a** and **3a** suggests that the structure of **3a** is not of a trans-μ-1,2-peroxo type. Kitajima's complexes (μ-η^2:η^2-peroxo complexes) have two absorption bands at ca. 350 and ca. 530 - 600 nm with molar extinction coefficients of 18000 - 21000, and ca. 800 - 1200 mol^{-1} cm^{-1} dm^3, respectively.[1e)] An intense absorption band at 378 nm for **3a** is reminiscent of those of Kitajima's complexes, although the transition energy is somewhat lower than those of Kitajima's complexes. Karlin et al. reported that their peroxo dicopper(II) complexes whose structures are proposed to be of a μ-η^2:η^2-peroxo type give an additional absorption band in the 400 - 500 nm region along with a band in the 500 - 600 nm region and there are large variations in intensities and transition energies of those two bands depending on the nature of the ligands.[2c)] It is notable that although **3a** shows only one absorption band in the 400 - 600 nm region as well as Kitajima's complexes, its intensity and transition energy differ from those of Kitajima's complexes. It is difficult to presume the structure of **3a** from its electronic spectrum at the present stage.

In contrast to the case of **3**, **4** dose not react with molecular oxygen at -70 °C in various solvents, but reacts slowly at room temperature, resulted in an irreversible oxidation, implying that N_4-Me_3py stabilizes copper(I) oxidation state. This is in line with the observations found for the reactivity of dinuclear iron(II) complexes with molecular oxygen.

It should be noted that the introduction of methyl group(s) in the 6th position of pyridyl group(s) in the present type of tetradentate tripodal ligands significantly affects not only the reactivity of the copper(I) complexes with molecular oxygen, but also the stereochemistry and thermal stability of the peroxo dicopper(II) complexes. Further studies are in progress.

The present study was supported by a Grant-in-Aid for Scientific Research on Priority Areas (No. 03241105) by the Ministry of Education, Science and Culture, Japan, to which our thanks are due.

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7) $[Cu(N_4\text{-Mepy})]ClO_4 \bullet 1/2H_2O$: Anal. Found: C, 47.99; H, 4.42; N, 11.71%. Calcd for $C_{19}H_{21}N_4CuClO_{4.5}$: C, 47.90; H, 4.44; N, 11.76%. $[Cu(N_4\text{-Me}_2py)]PF_6$: Anal. Found: C, 46.03; H, 4.28; N, 10.67%. Calcd for $C_{20}H_{22}N_4CuF_6P$: C, 45.59; H, 4.21; N, 10.63%. $[Cu(N_4\text{-Me}_3py)]BF_4$: Anal. Found: C, 52.33; H, 4.93; N, 11.62%. Calcd for $C_{21}H_{24}N_4CuBF_4$: C, 52.24; H, 5.01; N, 11.60%.

8) An acetone solution of **2** (5.6×10^{-4} mol dm^{-3}/Cu_2) was reacted with O_2 and ca. 1 minute later the spectrum (a) was recorded by an optical fiber equipment with the corrected light path length of 0.39 cm. A preliminary measurement indicated that the half life time of the oxygenated species is ca. 100 s.

9) ^1H NMR of **3** (acetone-d_6, 400 MHz) : δ 2.92 (6H, s, CH_3), 4.29 (6H, s, CH_2), 7.38 (2H, d, 6-Mepy), 7.47 (2H, d, 6-Mepy), 7.55 (2H, m, py), 7.85 (2H, t, 6-Mepy), 7.94 (1H, t, py), 9.01 (1H, d, py). ^1H NMR of **3a** (acetone-d_6, 400 MHz) : d 1.82 (6H, s, CH_3), 4.50 (2H, s, CH_2), 4.62 (2H, d, CH_2), 4.95 (2H, d, CH_2), 7.15 (3H, m, py and 6-Mepy), 7.47 (3H, m, py and 6-Mepy), 7.85 (3H, m, py and 6-Mepy), 8.65 (1H, d, py).

10) The concentration of **3** was 1.0×10^{-4} mol dm^{-3}/Cu_2 and that in the insert was 1.0×10^{-2} mol dm^{-3}/Cu_2. The spectra were measured with an optical fiber equipment with the corrected light path length of 0.39 cm.

(Received March 11, 1993)