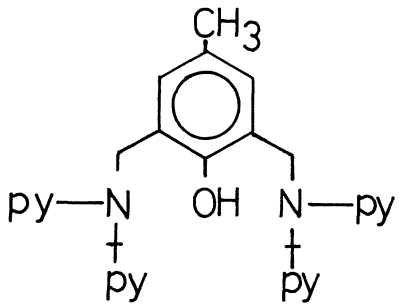
CHEMISTRY LETTERS, pp. 1745-1748, 1981.

SYNTHESIS AND PROPERTIES OF BINUCLEAR COBALT(II) OXYGEN ADDUCT WITH 2,6-BIS[BIS(2-PYRIDYLMETHYL)AMINOMETHYL]-4-METHYLPHENOL

Masatatsu SUZUKI*, Hajime KANATOMI, and Ichiro MURASE
Laboratory of Chemistry, College of General Education, Kyushu University
Ropponmatsu, Chuo-ku, Fukuoka 810

Binuclear cobalt(II) complexes, $[Co_2(bpmp)(CH_3COO)_2]ClO_4$ and $[Co_2(bpmp)(CH_3COO)](ClO_4)_2$ with 2,6-bis[bis(2-pyridylmethyl)aminomethyl]-4-methylphenol (Hbpmp), were prepared. The complexes showed the reversible oxygenation in various solvents. Two to one (Co/O_2) peroxo bridged complex, $[Co_2(bpmp)(CH_3COO)O_2](ClO_4)_2 \cdot 2H_2O$, was isolated. The oxygen adduct was fairly stable towards further reactions.

It has been demonstrated that a number of metal complexes in sterically and electronically controlled ligand enviroments reversibly combined an oxygen molecules.[1] Binuclear metal complexes in which two metal ions are in a suitable position may jointly bind an oxygen molecule to form 2 : 1 oxygen adducts. In the biological system, hemocyanin and hemerythrin contain two metal ions (copper for hemocyanin and iron for hemerythrin) at each oxygen bonding site. For oxyhemocyanin, Solomon[2] and Bosnich[3] have proposed that two copper atoms were linked by both an endogenous protein bridge and a peroxide bridge, in which a phenolate or a carboxylate ion is postulated as an endogenous bridging ligand. However, a binuclear metal chelate which forms a μ-peroxo complex has not been obtained with synthetic ligands having a phenolate or a carboxylate bridge. In this communication, we report the synthesis of a new 2 : 1 μ-peroxo cobalt complex containing phenolate and carboxylate bridges with Hbpmp.



Hbpmp

The ligand, 2,6-bis[bis(2-pyridylmethyl)-aminomethyl]-4-methylphenol (abbreviated as Hbpmp), was synthesized by the condensation of 2,6-bis(chloromethyl)-4-methylphenol with bis(2-pyridylmethyl)amine. To bis(2-pyridylmethyl)amine (10 mmol) in methanol (50 cm^3) containing triethylamine (10 mmol) was added dropwise 2,6-bis(chloromethyl)-4-methylphenol (5 mmol) with vigorous stirring at 10°C. The methanol was removed under reduced pressure and the residue was taken up in chloroform/water (1 : 1). The chloroform layer was washed several times with water and dried over Na_2SO_4. The solvent was removed under reduced pressure and the residual product (Hbpmp) was used for the preparation of the complexes without further purification.

$[Co_2(bpmp)(CH_3COO)_2]ClO_4$, **1**, was obtained as pink crystals by mixing the crude Hbpmp (1 mmol), cobalt(II) acetate tetrahydrate (1 mmol) and sodium perchlorate (1 mmol) in methanol (30 cm^3) under N_2. Found: C, 51.10; H, 4.65; N, 9.42%. Calcd. for **1**, C, 51.37; H, 4.54; N, 9.71%. The pink color of **1** in methanol turned brown by bubbling oxygen through the solution. $[Co_2(bpmp)(CH_3COO)O_2](ClO_4)_2 \cdot 2H_2O$, **2**, was isolated from the solution as brown crystals by the addition of sodium perchlorate. Found: C, 43.04; H, 3.96; N, 8.55%. Calcd. for **2**, C, 43.18; H, 4.14; N, 8.63%. Deoxygenation of the O_2-adduct, **2**, was carried out by boiling the methanol solution under N_2 for a few minutes. $[Co_2(bpmp)(CH_3COO)](ClO_4)_2$, **3**, was isolated from the resulting solution as pink crystals. Found: C, 45.14; H, 4.08; N, 8.85%. Calcd. for **3**, C, 45,52; H, 3.93; N, 9.10%.

The complex, **1**, shows an electronic spectrum with two bands at 9430 and 21100 cm^{-1} as shown in Figure 1, and has an effective magnetic moment of 4.51 B.M. at room temperature, indicating that the complex has a high-spin octahedral structure. The two acetate ions must coordinate to the cobalt(II) ions as chelating or bridging bidentate ligands in a syn-syn fashion.[4] At the present stage, however, the coordination geometry of the acetate groups is not clear. The complex is air-stable when dried. On the other hand, **3** is air-sensitive and gradually changes its color from pink to brown. Heating of the brown solid at 150°C in vacuo regenerated pink

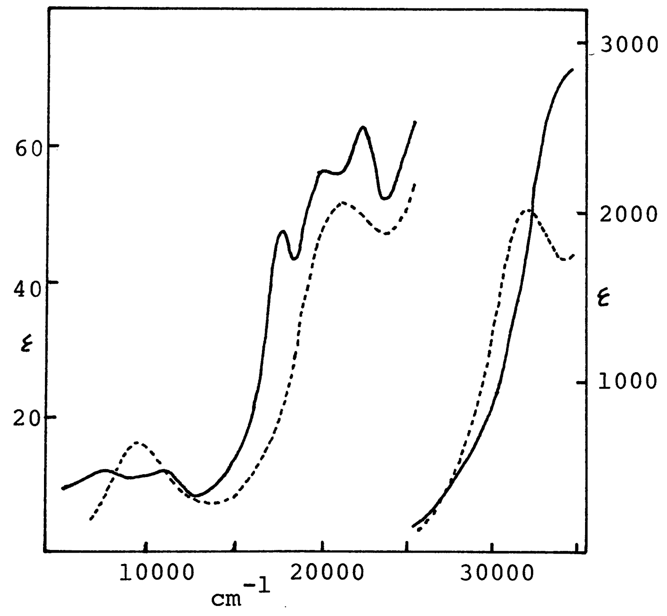


Figure 1. Electronic spectra of **1** (------) and **3** (———) in CH_3CN.

powder. Freshly prepared complex, 3, has an effective magnetic moment of 4.32 B.M. at room temperature and exhibits several bands in the visible and near infrared regions as seen in Figure 1. These observations indicate that the complex has a high-spin penta-coordinate geometry and the acetate ion appears to function as a bridging bidentate ligand.

Bubbling of oxygen through the pink methanol solution of 1 resulted in a slow color change to brown. Heating or bubbling of N_2 regenerated the pink coloration. As was mentioned before, the addition of sodium perchlorate to the brown solution afforded brown crystals, 2. Hence the oxygenation reaction may be represented as follows:

$$[Co_2(bpmp)(CH_3COO)_2]^+ + O_2 \rightleftharpoons [Co_2(bpmp)(CH_3COO)O_2]^{2+} + CH_3COO^-$$

The complex, 3, also exhibited reversible oxygenation. Figure 2(b) shows the electronic spectrum of 3 in acetonitrile in an air atmosphere. The electronic spectrum of 2 under 1 atm of oxygen was identical to Figure 2(b), suggesting that full oxygenation of 3 occurs in an air atmosphere. Although bubbling of N_2 through the acetonitrile solution of 2 resulted in deoxygenation reaction, this reaction was extremely slow at room temperature. However, heating at about 80°C caused the fast deoxygenation reaction and no decomposition was observed after ten times repeating of the oxygenation-deoxygenation process.

$$[Co_2(bpmp)(CH_3COO)]^{2+} + O_2 \rightleftharpoons [Co_2(bpmp)(CH_3COO)O_2]^{2+}$$

The oxygen adduct, 2, was essentially diamagnetic (0.48 B.M.) at room temperature. The Raman spectrum of the complex showed an intense band at ca. 820 cm^{-1}

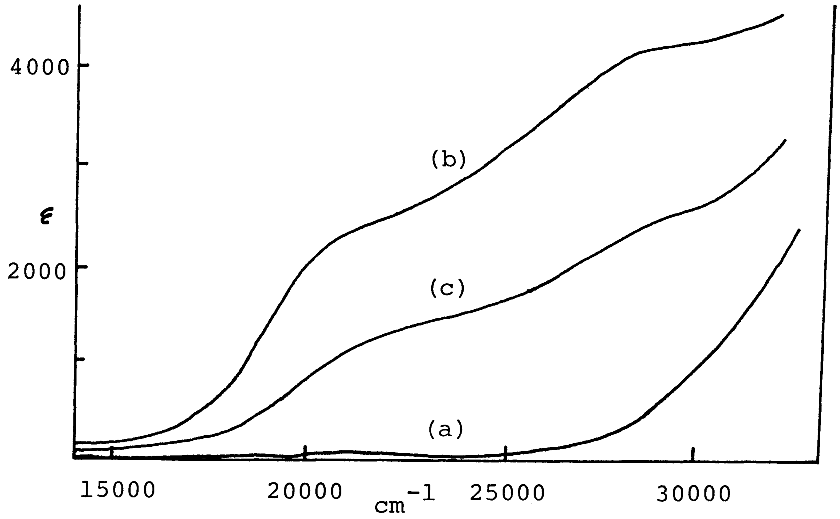


Figure 2. Spectral change of 3 in CH_3CN at room temperature. (a) under N_2, (b) in an air atmosphere, (c) N_2 bubbling through (b) for 24 h.

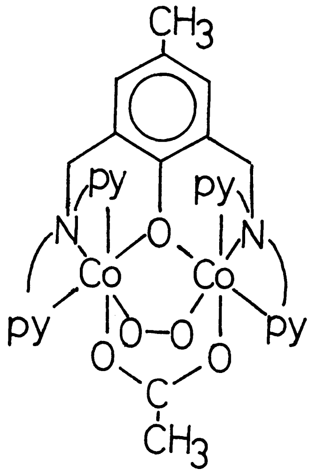


Figure 3.

A possible structure

and no other band was observed in the region of 1000 - 700 cm^{-1}.5) Therefore, we tentatively assigned this band to the stretching vibration of O_2. This suggests that the oxygen coordinates to the metal ions in μ-peroxo fashion. The IR spectrum of **2** showed ν_{asymm}, and ν_{symm}(COO$^-$) at 1530 and 1410 cm^{-1}, respectively. Judging from the small difference between ν_{asymm} and ν_{symm}(120 cm^{-1}) and general feature of octahedral coordination in cobalt(II) oxygen adducts, the acetate ion in the complex seems to function as a bridging bidentate ligand. A possible structure is given in Figure 3.

It is well known that the many cobalt complexes form μ-peroxo-μ-hydroxo or μ-peroxo-μ-amido complexes.1) The oxygenation of some complexes is reversible only within the buffer region where significant amount of the peroxo monobridged complexes exist. At high pH where the dibridged species is predominant, the oxygen moiety is "locked in" so firmly as to make the oxygenation irreversible. It is interesting that, although the present oxygen adduct is bridged by phenolate and carboxylate ions, the oxygen moiety is not "locked in" and the complex exhibits excellent reversible oxygenation. Further investigations of this type of binuclear complexes are in progress.

We thank Proffesor Y. Gondo for measurement of the Raman spectra, and Proffesor S. kida, Proffesor H. Okawa and Dr. Y. Nishida for their helpfull discussions.

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(Received October 5, 1981)