CHEMISTRY LETTERS, pp. 185-188, 1983.

MOLECULAR STRUCTURE OF A BINUCLEAR COBALT DIOXYGEN COMPLEX, $[Co_2$(2,6-BIS[BIS(2-PYRIDYLMETHYL)AMINOMETHYL]-4-METHYLPHENOLATO)(BENZOATO)DIOXYGEN]$(BF_4)_2 \cdot 2H_2O$

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The molecular structure of the title compound has been determined by the X-ray diffractometry. Two cobalt ions are linked by dioxygen, benzoate and phenolate bridges. Reversible O_2 binding was observed in the solid state. The O_2 bond distance is 1.43(3) Å which is in the range of those of the μ-peroxo cobalt complexes.

It has been demonstrated that binuclear metal complexes in sterically and electronically controlled ligand environments react with dioxygen to form 2 : 1 (metal : O_2) oxygen adducts.$^{1)}$ In the biological system, hemocyanine and hemerythrin contain two metal ions (copper for hemocyanine and iron for hemerythrin) at each oxygen binding site. For those complexes, it has been proposed that two metal ions are linked by a bridging ligand, such as phenolate, carboxylate, oxide or hydroxide ions.$^{2,3)}$

In the previous paper, we reported that the binuclear cobalt(II) complex having phenolate and acetate bridges, $[Co_2(bpmp)(CH_3COO)](ClO_4)_2$, reacts with dioxygen to form a novel μ-peroxo complex, $[Co_2(bpmp)(CH_3COO)O_2](ClO_4)_2$, where bpmp represents 2,6-bis[bis(2-pyridylmethyl)aminomethyl]-4-methylphenolate ion.$^{4)}$ The reversible O_2 binding was observed both in solution and in the solid state. To the best of our knowledge, no synthetic 2 : 1 oxygen adduct with phenolate or carboxylate bridge has been reported prior to our previous study. In this communication, we report the crystal structure of the 2 : 1 oxygen adduct having phenolate and carboxylate bridges, $[Co_2(bpmp)(benzoato)O_2](BF_4)_2 \cdot 2H_2O$ determined by the X-ray diffraction method.

The crystal was prepared as follows: To a methanol solution (50 cm^3) of

$Co(BF_4)_2 \cdot 6H_2O$ (2 mmol) and sodium benzoate (1 mmol) was added a methanol solution of Hbpmp (1 mmol). The pink color of the solution turned to brown by bubbling O_2 through the solution. The resulting brown solution was filtered and filtrate was allowed to stand overnight at room temperature. Tiny and plate-like crystals were obtained. Recrystallization from various solvents afforded only powder.

Preliminary Weissenberg photographs were taken for many crystals. All the crystals gave diffuse spots more or less, suggesting the presence of some disorder in the crystals. A crystal with dimensions 0.36 x 0.30 x 0.06 mm which showed relatively clear spots was chosen for the intensity measurement. Crystal data: monoclinic, $P2_1/a$, a=27.00(3), b=15.99(2), c=13.11(2) Å and β=127.10(6)°, V=4516(9) $Å^3$, D_c=1.51, D_m=1.48 g cm^{-3}, and Z=4. Intensities were measured on a Rigaku AFC-5 automated four-circle diffractometer with graphite-monochromated Mo Kα radiation. A total of 8904 reflections with $2\theta < 55°$ were collected. Because of poor intensity data, only 3195 unique reflections with $|Fo| > 2\sigma(|Fo|)$ were used for the structure determination. The correction for the absorption was made by the method of Busing and Levy,5) and Burnham.6) The structure was solved by the heavy atom method. The positions of cobalt atoms were determined from Patterson map. The positions of the nonhydrogen atoms of the complex cation, BF_4^- anion and oxygen atoms of water molecules were determined from successive Fourier and difference Fourier syntheses, and refined by the block diagonal least squares method. In the course of refinement, it was found that the F atoms of BF_4^- are disordered arround the B atom and two water molecules are statistically distributed to the four positions. Final refinement was proceeded with anisotropic thermal parameters for the nonhydrogen atoms of the complex cation, and isotropic thermal parameters for BF_4^- anions and the O atoms of water molecules. The final R value was 12.4%. This high figure is probably due to a disordered structure and poor quality of the data. All the calculations were carried out on the FACOM M-200 computor in the Computor Center of kyushu University by the use of the UNICS-III program system.7)

Figure 1 shows the molecular structure of the complex cation. The selected bond angles and distances are given in Table 1. Two cobalt ions are linked by three bridging ligands; dioxygen, phenolate and carboxylate. Each cobalt ions is in an approximately octahedral environment and in a cis,cis-N_3O_3 structure. The coordination geometries of Co(1) and Co(2), however, are different from each other as shown in Figure 1, e.g., the O(1) is in the trans-position of the N(2)(pyridyl nitrogen atom) and the O(2) in the trans-position of the N(4)(tertiary amine nitrogen atom). The Co(1)···Co(2) distance is 3.151(7) Å. The Co-O-O-Co torsion angle is 51° which is smaller than those of μ-hydroxo-μ-peroxo and μ-amido-μ-peroxo complexes (ca.60°).[8] The Co(1)-O(1) and Co(2)-O(2) bond distances are 1.89(2) and 1.86(2) Å, respectively. The O_2 bond distance is 1.43(3) Å which is in the range of those of the μ-peroxo complexes (1.31-1.53 Å).[1,8] The complex is essentially diamagnetic (0.54 B.M.) at room temperature. This diamagnetism is consistent with that of the μ-peroxo cobalt complexes. The O_2 binding of the present complex is reversible in the solid state. Upon heating the O_2 adduct at ca.180 °C under N_2, the color changed from brown to pink and the absorption spectrum of the pink compound was the same as that of $[Co_2(bpmp)(benzoato)](BF_4)_2$.[9] In the presence of O_2, the pink compound absorbed O_2 and changed into the O_2 adduct at room temperature. This suggests that two cobalt ions in the deoxygenated molecule is held in a suitable position for the O_2 binding by phenolate and carboxylate bridges.

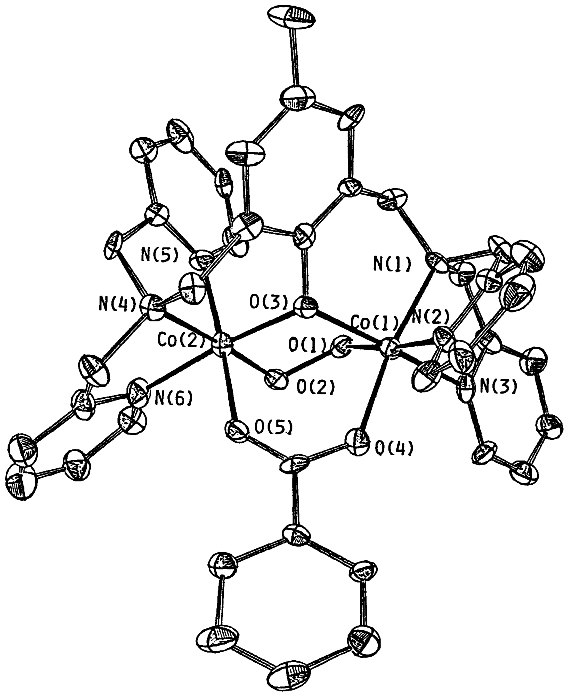

Figure 1. ORTEP Drawing of The Complex Cation

Table 1. Bond Distances(l/Å) and Bond Angles(ϕ/°)
Esd's are in parentheses

Co(1)-O(1)	1.893(15)	O(1)-Co(1)-O(3)	86.1(7)	O(2)-Co(2)-O(3)	92.1(8)
Co(1)-O(3)	1.911(18)	O(1)-Co(1)-O(4)	95.2(6)	O(2)-Co(2)-O(5)	90.3(7)
Co(1)-O(4)	1.927(13)	O(1)-Co(1)-N(1)	91.4(7)	O(2)-Co(2)-N(4)	176.1(8)
Co(1)-N(1)	1.939(15)	O(1)-Co(1)-N(2)	174.1(6)	O(2)-Co(2)-N(5)	94.9(8)
Co(1)-N(2)	2.031(18)	O(1)-Co(1)-N(3)	86.3(8)	O(2)-Co(2)-N(6)	91.6(9)
Co(1)-N(3)	1.940(25)	O(3)-Co(1)-N(1)	96.8(8)	O(3)-Co(2)-N(4)	91.7(8)
		O(3)-Co(1)-N(2)	90.0(8)	O(3)-Co(2)-N(5)	93.9(7)
Co(2)-O(2)	1.863(17)	O(3)-Co(1)-N(3)	172.4(7)	O(3)-Co(2)-N(6)	170.3(6)
Co(2)-O(3)	1.902(17)	O(3)-Co(1)-O(4)	90.5(7)	O(3)-Co(2)-O(5)	86.4(6)
Co(2)-O(5)	1.913(13)	O(4)-Co(1)-N(1)	170.5(9)	O(5)-Co(2)-N(4)	89.9(7)
Co(2)-N(4)	2.003(21)	O(4)-Co(1)-N(2)	89.3(6)	O(5)-Co(2)-N(5)	174.8(9)
Co(2)-N(5)	1.906(16)	O(4)-Co(1)-N(3)	90.5(8)	O(5)-Co(2)-N(6)	84.6(7)
Co(2)-N(6)	1.919(24)	N(1)-Co(1)-N(2)	84.6(7)	N(4)-Co(2)-N(5)	84.9(8)
		N(1)-Co(1)-N(3)	83.1(8)	N(4)-Co(2)-N(6)	84.6(9)
O(1) -O(2)	1.430(26)	N(2)-Co(1)-N(3)	97.6(9)	N(5)-Co(2)-N(6)	94.8(9)
Co(1)-Co(2)	3.151(7)	Co(1)-O(1)-O(2)	109.3(9)	Co(2)-O(2)-O(1)	112.0(9)
		Co(1)-O(3)-Co(2)	111.5(6)		

Thus far, the Co-O bond distances of the reversible μ-peroxo complexes are longer than 1.91 Å and the O_2 bond distances of those complexes are in the range of 1.31-1.38 Å.$^{10)}$ On the other hand, the Co-O bond distances of the irreversible μ-peroxo complexes are shorter than 1.90 Å and the O_2 bond distances are longer than 1.45 Å. These facts suggest that the reversibility of the O_2 binding is related to the Co-O and O_2 bond distances. Schaefer and Avdeef reported that $[Co(salen)pip]_2O_2$ releases O_2 at ca.95 °C.$^{10)}$ The Co-O bond distance of the complex is 1.91 Å and the O_2 bond distance is 1.38 Å which is the longest in the literature values.$^{10)}$ The present complex released O_2 at ca.180 °C. Thus the complex is thermally much more stable than $[Co(salen)pip]_2O_2$. Although a detailed comparison of the Co-O and O_2 bond distances of the present complex with those of $[Co(salen)pip]_2O_2$ can not be made because of our poor result in the bond distances, the difference in the thermal stability probably indicates that the Co-O bond distance of the present complex is shorter and the O_2 bond distance is longer than those of $[Co(salen)pip]_2O_2$, respectively.

We thank Proffesor S. Kida, Proffesor H. Okawa, Dr. Y. Nishida and Dr. M. Mikuriya for allowing us to use automated diffractometer and helpful discussions. We also thank Proffesor S. Kawano and Dr. Uechi for helpful discussions.

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(Received November 8, 1982)