

## Formation of a Mononuclear Superoxo Co<sup>III</sup> Complex with a Macrocyclic Ligand in Oxygenated Aqueous Solutions

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A mononuclear superoxo cobalt(III) complex generated by the oxygenation of a Co<sup>II</sup>-([14]aneN<sub>4</sub>) complex ([14]aneN<sub>4</sub> = 1,4,8,11-tetra-azacyclotetradecane) in an aqueous solution containing a large excess of dioxygen was found to be able to exist in equilibrium with the  $\{\{\text{Co}([\text{14]aneN}_4)(\text{OH}_2)\}_2\text{O}_2\}^{4+}$  ion, which was stable at room temperature.

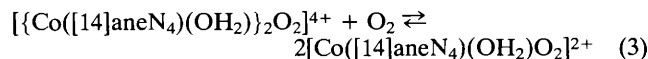
Cobalt(II) complexes with amino acids, polyamines, and macrocyclics normally form  $\mu$ -peroxo complexes *via* an intermediate mononuclear superoxo complex as in equations (1) and (2).<sup>1</sup> Except in a few cases with bulky amines, in low



dielectric solvents or at low temperatures, mononuclear superoxo complexes have not been reported. There have been very few studies<sup>2</sup> that directly investigate the chemical behaviour of mononuclear superoxo complexes  $[\text{Co}([\text{14]aneN}_4)(\text{OH}_2)\text{O}_2]^{2+}$  for a high tendency to form the dimer, in spite of extensive studies<sup>2-4</sup> on the oxygenation of the Co<sup>II</sup>-([14]aneN<sub>4</sub>) complex. We have found that a considerable amount of the 1:1 dioxygen cobalt adduct can exist stably at room temperature in equilibrium with  $\{\{\text{Co}([\text{14]aneN}_4)\}_2\text{O}_2\}^{4+}$  in dioxygen-saturated aqueous solutions where Co<sup>II</sup> complexes do not essentially exist.

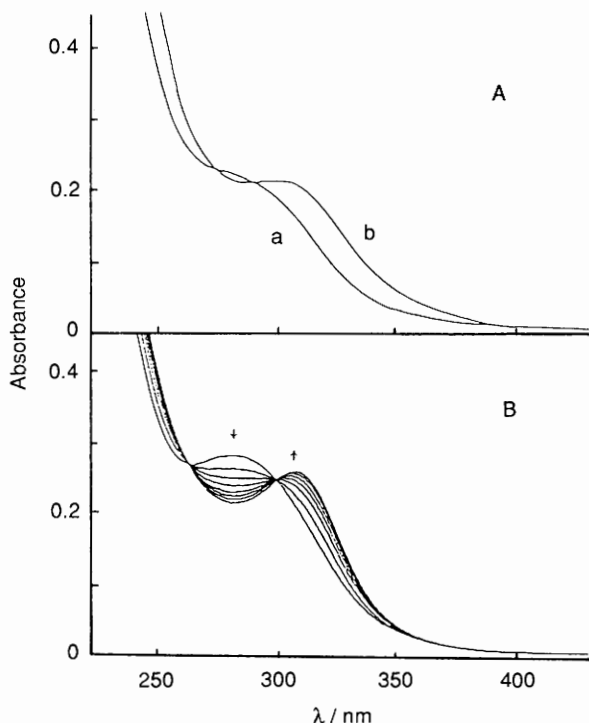
*Trans*- $\{\{\text{Co}([\text{14]aneN}_4)(\text{OH}_2)\}_2\text{O}_2\}^{4+}$  prepared by the method described in the literature<sup>5</sup> has an absorption maximum at 305 nm in O<sub>2</sub>-saturated aqueous solution, which was shifted to 280 nm (shoulder) by bubbling nitrogen through the solution (Figure 1A). The absorption spectrum was very similar to that of  $\{\{\text{Co}([\text{14]aneN}_4)(\text{OH}_2)\}_2\text{O}_2\}^{4+}$  obtained in

HClO<sub>4</sub> solution (0.5 M).<sup>6</sup> The shoulder at 280 nm is shifted again to a longer wavelength (305 nm) by bubbling dioxygen. Similar behaviour was also observed in acidic solutions. The above observations can be explained by the equilibrium reaction in equation (3). In basic solution, such a shift of



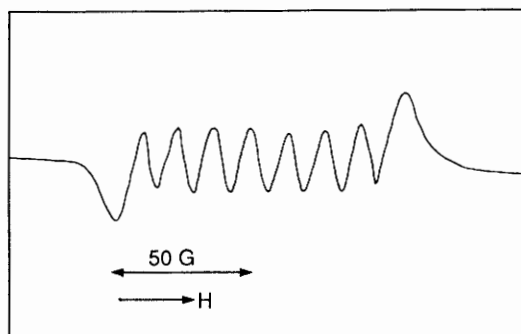
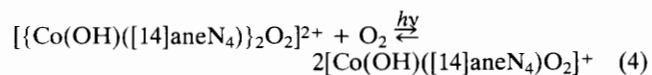
absorption maximum on bubbling oxygen was not observed. A consecutive irradiation of an O<sub>2</sub>-saturated aqueous solution of the  $\mu$ -peroxo complex with 366 nm light was accompanied by spectral changes clearly indicating the formation of a new species (Figure 1B) which seems to be a mononuclear O<sub>2</sub> adduct. In the deaerated solution none of the above spectral features were seen. A remarkable O<sub>2</sub> uptake, which depended upon oxygen concentration, was observed upon irradiation of the  $\mu$ -peroxo complex solutions by using an oxygen monitor with a Clarke-type electrode. The absorption spectrum obtained after the O<sub>2</sub> uptake was similar to the absorption spectrum due to the mononuclear O<sub>2</sub> adduct in Figure 1(A), curve b. The absorption maximum was shifted to 280 nm on bubbling nitrogen. These results can be explained reasonably by equation (4).

Equilibrium constant  $K_4$  was evaluated to be 0.13 from O<sub>2</sub> uptake upon irradiation of  $\mu$ -peroxo complex solutions



**Figure 1.** (A) Absorption spectra of  $2.5 \times 10^{-5}$  M  $[\{\text{Co}([\text{14}] \text{aneN}_4)(\text{OH}_2)_2\text{O}_2\}^{4+}]$  in neutral aqueous solution. Curve a,  $\text{N}_2$ -saturated; curve b,  $\text{O}_2$ -saturated. (B) Absorption spectra changes during the photolysis of the  $\text{O}_2$ -saturated  $2.5 \times 10^{-5}$  M  $[\{\text{Co}(\text{OH})([\text{14}] \text{aneN}_4)_2\text{O}_2\}^{2+}]$  aqueous solution at pH 11. Irradiation: 4 min intervals at 366 nm.

saturated with air and pure oxygen. The mononuclear superoxo complex can remain in the solutions for several hours under our experimental conditions. No occurrence of equation (4), without light irradiation, would be attributed to the increased bond energy on the bridge of the complex due to the hydrolysis.



**Figure 2.** ESR spectrum measured at room temperature after  $\text{O}_2$  uptake by the irradiation (366 nm) of an  $\text{O}_2$ -saturated  $[\{\text{Co}(\text{OH})([\text{14}] \text{aneN}_4)_2\text{O}_2\}^{2+}]$  aqueous solution at pH 11.

The ESR spectrum of the mononuclear complex, measured after  $\text{O}_2$  uptake by irradiation in basic solutions or after bubbling dioxygen in neutral solutions, consists of a well resolved eight-line hyperfine structure (Figure 2), which is very similar to that found for a monomeric  $\text{O}_2$  adduct of cobalt(II) Schiff bases.<sup>7</sup> This corresponds to the interaction of an unpaired electron with a single  $^{59}\text{Co}$  nucleus of spin  $7/2$  and demonstrates that the paramagnetic species contains only one cobalt atom. The signal disappeared on bubbling nitrogen through the solution. This result also strongly suggests the formation of a 1 : 1 dioxygen cobalt adduct.

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