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Resonance Raman Spectra of Molecular Oxygen Adducts of Co(II) Chelates in Solution Equilibria

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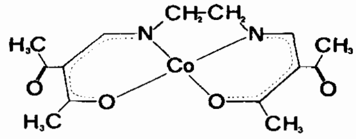
When a cobalt(II) chelate in a non-aqueous solvent absorbs oxygen in the presence of a base (B), the following equilibria are established:

$$[\mathrm{Co(chelate)B}] + \mathrm{O_2} \rightleftharpoons [\mathrm{Co(chelate)B}]\mathrm{O_2} \qquad (1)$$

$$[\mathrm{Co(chelate)B}]\mathrm{O_2} + [\mathrm{Co(chelate)B}] \rightleftharpoons (\mathrm{Co(chelate)B}]_2\mathrm{O_2} \qquad (2)$$

Thus far, uv–visible spectroscopy has been used to determine the equilibrium constants for solutions dominated by the 1:1 complexes [1]. However, this method may not be applicable to a solution containing both 1:1 and 1:2 complexes since their electronic spectra are similar. It is well known that the O_2 stretching frequencies, $\nu(O_2)$, of 1:1 and 1:2 complexes are markedly different; the former is in the region from 1200 to 1130 cm^{-1} whereas the latter is in the range from 930 to 800 cm^{-1} [2]. Thus far, these vibrations have been observed separately for each species either by IR (solid state) [3] or resonance Raman (RR) spectroscopy (solution) [4]. We now report the first simultaneous observation of $\nu(O_2)$ of 1:1 and 1:2 complexes in solution equilibria. Since their $\nu(O_2)$ are far apart, RR spectroscopy has a distinct advantage over uv–visible spectroscopy in determining the equilibrium constants and other thermodynamic data. One preliminary result is described below.

An approx. 10^{-2} mol/liter solution of Co(J-en) [5] (shown below) inCH_2Cl_2



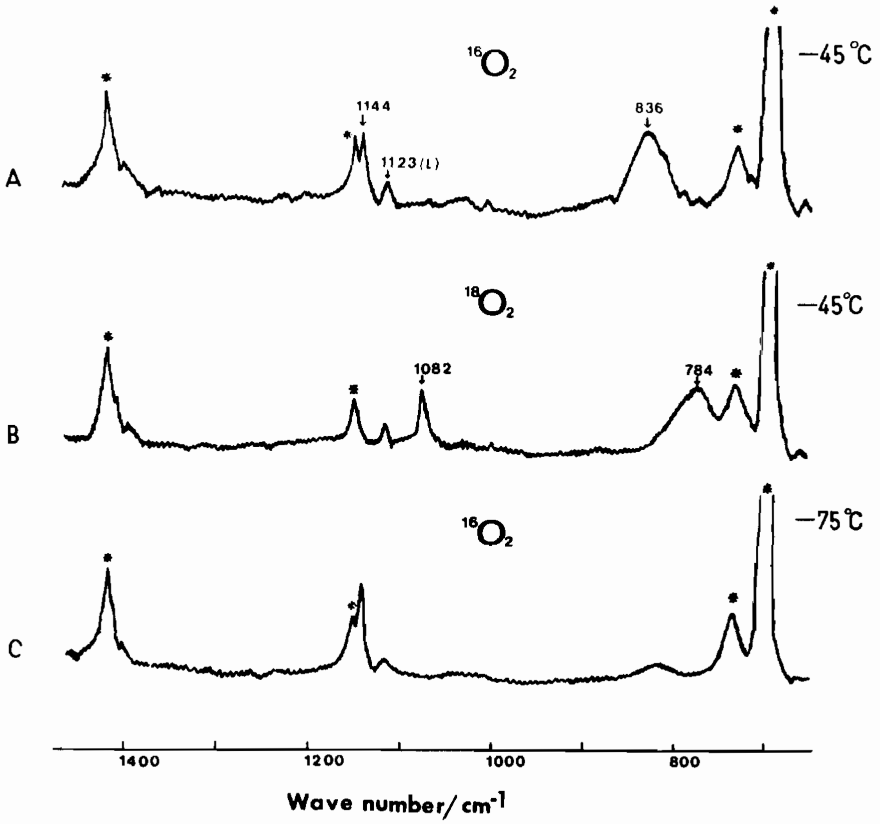


Fig. 1. Resonance Raman spectra of 1:1 and 1:2 molecular oxygen adducts of Co(J-en) in CH_2Cl_2 containing 1% pyridine (514.5 nm excitation, 60 mw).

containing 1% pyridine was saturated with O_2 at −78 °C (dry ice–acetone) using the standard vacuum line technique. The solution in a sealed tube was attached immediately to a cold tip cooled by a CTI Model 21 cryocooler. The temperature of the solution was controlled in the range from −75 °C to room temperature using a heater attached to a cold tip. The RR spectra were obtained by using a Spex Model 1401 double monochromator with a Spex digital photometer system. A Spectra-Physics Model 164 Ar-ion laser was used as the exciting source.

Figure 1 (trace A) shows the RR spectrum of the above solution at −45 °C (514.5 nm excitation, 60 mw). The bands with asterisks are due to the solvent bands at 1144 and 836 cm^{-1} can be assigned to the $\nu(O_2)$ of the 1:1 and 1:2 complexes, respectively, due to the following reasons: (1) Only these two bands were shifted to 1082 and 784 cm^{-1}, respectively, by the $^{16}O_2$–$^{18}O_2$ substitution (trace B). (2) These frequencies are in the ranges expected for the 1:1 superoxo and 1:2 peroxo complexes, respectively [2]. (3) The intensities of these two bands are sensitive to the exciting laser frequency in the visible region where the Co–O_2 CT bands are expected. Trace C was obtained by cooling the above solution to −75 °C; the 1144 cm^{-1} band is stronger than the solvent band at 1154 cm^{-1} and the 836 cm^{-1} band is almost non-existent. This result shows that only the 1:1 complex is present at this temperature. When the temperature was raised from −75 to −45 °C, the solution gave exactly the same spectrum as that shown by trace A(−45 °C). Thus, the 1:1 $\rightleftharpoons$ 1:2 equilibrium is completely reversible in this temperature range.

At present, we are studying the effects of the solvent, axial base and equatorial ligand on the equilibria by using the above method. These studies are also providing excitation profiles of $\nu(O_2)$ of both 1:1 and 1:2 complexes which are vital to the M.O. interpretation of their electronic spectra.

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References

1 M. J. Carter, D. P. Rillema and F. Basolo, *J. Am. Chem. Soc., 96,* 392 (1974).

2 R. D. Jones, D. A. Summerville and F. Basolo, *Chem. Rev., 79,* 139 (1979).

3 A. L. Crumbliss and F. Basolo, *J. Am. Chem. Soc., 92,* 55 (1970).

4 T. Szymanski, T. W. Cape, R. P. Van Duyne and F. Basolo, *Chem. Comm.,* 5 (1979).

5 K. Kubokura, H. Okawa and S. Kida, *Bull. Chem. Soc. Japan, 51,* 2036 (1978).