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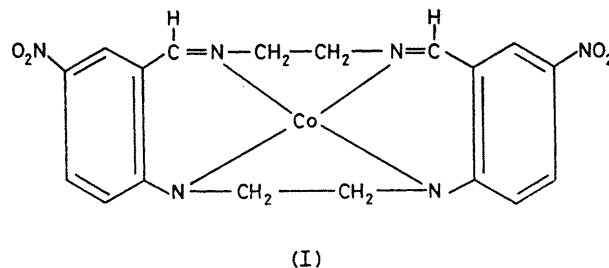
Determination of the Solution O–O Stretching Frequency of a Monomeric Dioxygen Cobalt Complex by Resonance Raman Spectroscopy

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Summary The observation of the first O–O stretching frequency in a mononuclear cobalt dioxygen complex in pyridine–*NN*-dimethylformamide solution by resonance Raman spectroscopy is reported.

THE reversible reaction of dioxygen with solutions of neutral cobalt complexes of the type Co(tetradentate ligand)(B) (B = Lewis base such as pyridine) to produce the monomeric dioxygen complexes, Co(tetradentate ligand)(B)(O₂), which serve as model systems for haemoglobin has been known for many years.^{1,2} The O–O stretching frequency (ν_{O-O}) in these compounds as well as other physical evidence has been generally accepted³ as indicating charge-transfer from the cobalt to the dioxygen to produce a species of the type Co^{III}-O₂⁻. In the majority of cases the ν_{O-O} has been determined by i.r. spectroscopy in the solid state³ although a report has recently appeared of a determination of ν_{O-O} in solution by Fourier transform i.r. spectroscopy.⁴ We note that Raman spectroscopy has been used to probe some solid binuclear μ -superoxo complexes, Co^{III}-O₂⁻-Co^{III}.⁵ Others have also examined aqueous solutions and solids of the analogous μ -peroxo derivatives, Co^{III}-O₂²⁻-Co^{III}, and have noted resonance enhancement in some instances.⁶ Although previous attempts to determine ν_{O-O} by Raman spectroscopy in mononuclear systems have proved unsuccessful, Brunner⁷ was able to determine ν_{Fe-O} (567 cm⁻¹) in oxyhaemoglobin and Spiro *et al.*⁸ recently reported ν_{Fe-O} (568 cm⁻¹) for the 'picket fence' porphyrin FeO₂ adduct. We now report what appears to be the first successful application of

resonance Raman (R.R.) spectroscopy to determine the solution O–O stretching frequency of a monomeric dioxygen cobalt complex, 7,8,15,16,17,18-hexahydro-3,12-dinitrobenzo[*e,m*][1,4,8,11]tetra-azocyclotetradecinatocobalt(III) (I), in pyridine (py)–dimethylformamide (DMF) solution (10%, v/v).



Compound (I) was prepared by the method of Carter,⁹ following the procedure outlined by Black and Lane.¹⁰ It was chosen for this study because the addition of O₂ to a py-DMF solution of (I) produces a marked change in its electronic spectrum. The monomeric dioxygen complex has an absorption maximum at 4900 Å which makes it an ideal system for R.R. spectroscopy,¹¹ when irradiated with the 4880 Å Ar⁺ laser line.

Samples of (I) were prepared in 5 mm n.m.r. tubes under rigorously anaerobic conditions by standard Schlenkware techniques.¹² The absence of O₂ was verified by e.s.r. spectroscopy^{6†} using the method described previously.¹³

† Deoxygenated solutions of (I) have the following e.s.r. parameters: $g_x = 2.303$, $g_y = 2.219$, $g_a = 2.007$, $a_z^{CO} = 112.06$, $a_z^N = 15.0$. The oxygenated compounds have the following e.s.r. parameters: $g_{||} = 1.996$, $g_{\perp} = 2.082$, $A_{||}^{CO} = 18.3$.

The R.R. spectra were obtained using saturated solutions of (I) at $-80 \pm 0.1^\circ\text{C}$. This was accomplished by spinning the samples in a low temperature apparatus and using backscattering geometry,¹⁴ on an instrument that has been previously described.¹⁵

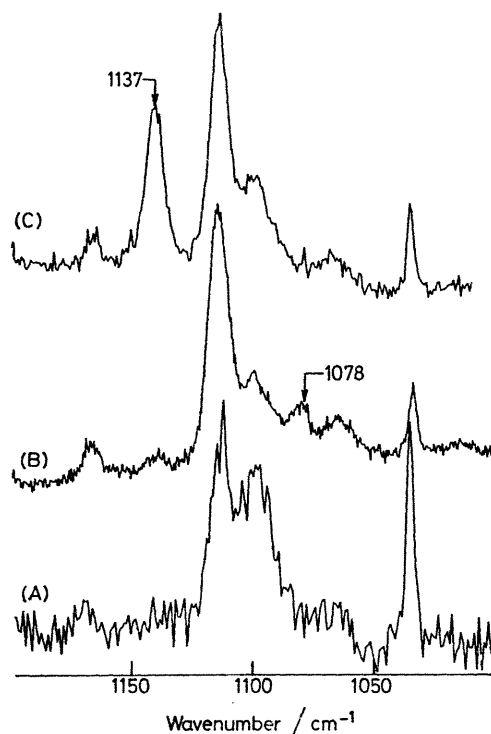


FIGURE. Raman spectra of saturated solution of (A) (I) (band pass 2.1 cm^{-1} ; power 50 mW ; counting interval 1.0 s ; scan rate, 0.2500 \AA s^{-1}), (B) (I) + $^{18}\text{O}_2$ (band pass 2.1 cm^{-1} ; power 45 mW ; counting interval 9.0 s ; scan rate 0.0125 \AA s^{-1}), and (C) (I) + $^{18}\text{O}_2$ (band pass 2.1 cm^{-1} ; power 45 mW ; counting interval 4.0 s ; scan rate 0.0500 \AA s^{-1}), in 10% py-DMF with 4880 \AA excitation.

The R.R. spectrum of (I) in 10% py-DMF (v/v) is shown in the Figure (A). The addition of $^{18}\text{O}_2$ produces a new band at 1137 cm^{-1} which is shown in the Figure (C). The substitution of 94% $^{18}\text{O}_2$ for $^{16}\text{O}_2$ causes the O-O stretch to shift to 1078 cm^{-1} , as can be seen in the Figure (B and C).

The surprising feature of the $^{18}\text{O}_2$ spectrum is that the integrated intensity of the 1078 cm^{-1} band is only 21% of the 1137 cm^{-1} band in the $^{16}\text{O}_2$ spectrum. The presence of residual $^{16}\text{O}_2$ can be seen as a weak feature in the $^{18}\text{O}_2$ spectrum at 1137 cm^{-1} . An excitation profile of (I) in 10% py-DMF with $^{16}\text{O}_2$ and $^{18}\text{O}_2$ was performed using 4579 , 4765 , 4880 , 4965 , and 5145 \AA exciting lines. The intensities of the two bands that we have assigned to ν_{0-0} varied as a function of exciting line, but in no instance did the intensity of the $^{18}\text{O}_2$ band approach that of its $^{16}\text{O}_2$ counterpart. In all cases the completeness of oxygenation was verified by e.s.r. spectroscopy.† It is noteworthy that we never observed any new vibrational features in the peroxy region $800\text{--}960\text{ cm}^{-1}$. We thus assign this 1137 cm^{-1} band to ν_{0-0} in this complex. This observation of ν_{0-0} at 1137 cm^{-1} is in accord with the formalism $\text{Co}^{\text{III}}\text{-O}_2^-$, since this frequency corresponds closely with the 1141 cm^{-1} band assigned to ν_{0-0} in KO_2 ¹⁶ and is in good agreement with previously obtained superoxo stretching frequencies.¹⁻⁴

Our repeated observation of weak R.R. scattering at 1078 cm^{-1} for the $^{18}\text{O}_2$ adduct relative to stronger R.R. scattering at 1137 cm^{-1} for the $^{16}\text{O}_2$ adduct suggests that this observation, while somewhat anomalous, is in fact real. Anomalous i.r. intensity and Raman frequency for some ^{18}O enriched compounds compared to their ^{16}O analogues has been previously reported.¹⁷ However, the i.r. intensity differences for ^{18}O substitution are always less than a factor of two, while the Raman intensity difference reported here is about a factor of five. Furthermore, anomalous Raman intensity changes for ^{18}O substitution have not been previously reported. The axial base on the cobalt dioxygen complex was changed from pyridine to *N*-methylimidazole. As a result of this substitution, a decrease in the intensity of the $^{16}\text{O}\text{-}^{16}\text{O}$ stretch by a factor of two relative to the other $\text{Co}(\text{NO}_2\text{C}_5\text{H}_4\text{N})_2$ bands was observed. There is no vibrational band in the $600\text{--}400\text{ cm}^{-1}$ region in either system that shows a frequency dependence upon substitution of $^{18}\text{O}_2$, and hence no band which could be assigned to the Co-O stretch. In the work⁸ on the 'picket fence' porphyrin iron dioxygen adduct, the FeO band shifted 23 cm^{-1} upon substitution of $^{18}\text{O}_2$ for $^{16}\text{O}_2$.

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