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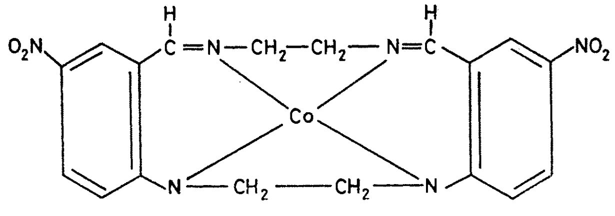
Summary The observation of the first O–O stretching frequency in a mononuclear cobalt dioxygen complex in pyridine-*NN*-dimethylformamide solution by resonance Raman spectroscopy is reported.

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)(O_2), 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 accepted[2] as indicating charge-transfer from the cobalt to the dioxygen to produce a species of the type Co^{III}–O_2^-. In the majority of cases the ν_{O-O} has been determined by i.r. spectroscopy in the solid state[3] 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}–O_2^-–Co^{III}.[5] Others have also examined aqueous solutions and solids of the analogous μ-peroxo derivatives, Co^{III}–O_2^{2-}–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, Brunner[7] 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 FeO_2 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(II) (I), in pyridine (py)–dimethylformamide (DMF) solution (10%, v/v).



(I)

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 O_2 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 O_2 was verified by e.s.r. spectroscopy[6]† using the method described previously.[13]

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† Deoxygenated solutions of (I) have the following e.s.r. parameters: $g_x = 2{\cdot}303$, $g_y = 2{\cdot}219$, $g_a = 2{\cdot}007$, $a_z^{CO} = 112{\cdot}06$, $a_z^N = 15{\cdot}0$. The oxygenated compounds have the following e.s.r. parameters: $g_\parallel = 1{\cdot}996$, $g_\perp = 2{\cdot}082$, $A_\parallel^{CO} = 18{\cdot}3$.

The R.R. spectra were obtained using saturated solutions of (I) at −80 ±0·1 °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]

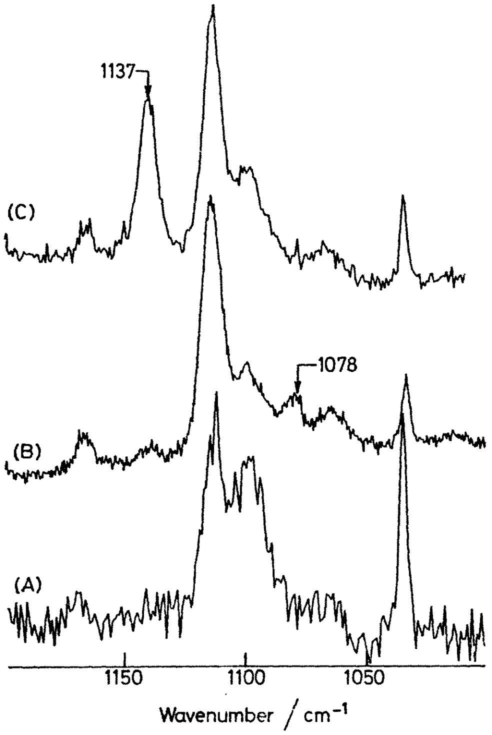

FIGURE. Raman spectra of saturated solution of (A) (I) (band pass 2·1 cm^{-1}; power 50 mW; counting interval 1·0 s; scan rate, 0·2500 Å s^{-1}), (B) (I) + $^{18}O_2$ (band pass 2·1 cm^{-1}; power 45 mW; counting interval 9·0 s; scan rate 0·0125 Å s^{-1}), and (C) (I) + $^{16}O_2$ (band pass 2·1 cm^{-1}; power 45 mW; counting interval 4·0 s; scan rate 0·0500 Å s^{-1}), in 10% py–DMF with 4880 Å excitation.

The R.R. spectrum of (I) in 10% py–DMF (v/v) is shown in the Figure (A). The addition of $^{16}O_2$ produces a new band at 1137 cm^{-1} which is shown in the Figure (C). The substitution of 94% $^{18}O_2$ for $^{16}O_2$ 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 $^{18}O_2$ spectrum is that the integrated intensity of the 1078 cm^{-1} band is only 21% of the 1137 cm^{-1} band in the $^{16}O_2$ spectrum. The presence of residual $^{16}O_2$ can be seen as a weak feature in the $^{18}O_2$ spectrum at 1137 cm^{-1}. An excitation profile of (**1**) in 10% py–DMF with $^{16}O_2$ and $^{18}O_2$ was performed using 4579, 4765, 4880, 4965, and 5145 Å exciting lines. The intensities of the two bands that we have assigned to ν_{O-O} varied as a function of exciting line, but in no instance did the intensity of the $^{18}O_2$ band approach that of its $^{16}O_2$ 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 peroxo region 800—960 cm^{-1}. We thus assign this 1137 cm^{-1} band to ν_{O-O} in this complex. This observation of ν_{O-O} at 1137 cm^{-1} is in accord with the formalism $Co^{III}-O_2^-$, since this frequency corresponds closely with the 1141 cm^{-1} band assigned to ν_{O-O} 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 $^{18}O_2$ adduct relative to stronger R.R. scattering at 1137 cm^{-1} for the $^{16}O_2$ 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 $^{16}O-^{16}O$ stretch by a factor of two relative to the other $Co(NO_2Cyen)$ bands was observed. There is no vibrational band in the 600—400 cm^{-1} region in either system that shows a frequency dependence upon substitution of $^{18}O_2$, and hence no band which could be assigned to the Co–O stretch. In the work[8] on the 'picket fence' porphyrin iron dioxygen adduct, the FeO band shifted 23 cm^{-1} upon substitution of $^{18}O_2$ for $^{16}O_2$.

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[1] F. Basolo, B. M. Hoffman, and J. A. Ibers, *Accounts Chem. Res.*, 1975, **8**, 384; J. P. Collman, *ibid.*, 1977, **10**, 265.
[2] L. Vaska, *Accounts Chem. Res.*, 1976, **9**, 175.
[3] C. Floriani and L. Calderazzo, *J. Chem. Soc. (A)*, 1969, 946; A. L. Crumbliss and F. Basolo, *J. Amer. Chem. Soc.*, 1970, **92**, 55.
[4] J. P, Collman, J. C. Brauman, J. R. Hulbert, and K. S. Suslick, *Proc. Nat. Acad. Sci. U.S.A.*, 1976, **73**, 333.
[5] T. Shibahara, *J.C.S. Chem. Comm.*, 1973, 864.
[6] T. B. Freedman, C. M. Yoshida, and T. M. Loehr, *J.C.S. Chem. Comm.*, 1974, 1016.
[7] H. Brunner, *Naturwiss.*, 1974, **61**, 129.
[8] J. M. Burke, J. R. Kincaid, S. Peters, R. R. Gagne, J. P. Collman, and T. G. Spiro, *J. Amer. Chem. Soc.*, 1978, **100**, 6083.
[9] M. J. Carter, Ph.D. Thesis, Northwestern University, 1973.
[10] D. St. C. Black and M. J. Lane, *Austral. J. Chem.*, 1970, **23**, 2039.
[11] T. G. Spiro, *Accounts Chem. Res.*, 1974, **7**, 339.
[12] D. F. Shriver, 'The Manipulation of Air-Sensitive Compounds,' McGraw-Hill, New York, 1969.
[13] B. M. Hoffman, D. L. Diemente, and F. Basolo, *J. Amer. Chem. Soc.*, 1970, **92**, 61.
[14] D. F. Shriver and J. B. R. Dunn, *Appl. Spectroscopy*, 1974, **28**, 319.
[15] D. L. Jeanmaire, M. R. Suchanski, and R. P. Van Duyne, *J. Amer. Chem. Soc.*, 1975, **97**, 1699.
[16] W. Holzer, W. F. Murphy, H. J. Bernstein, and J. Folfe, *J. Mol. Spectroscopy*, 1968, **26**, 543.
[17] S. Pinchas and I. Laulicht, 'Infrared Spectra of Labelled Compounds,' Academic Press, New York, 1971, pp. 297—312 and refs. therein.