

Resonance Raman Spectra of μ -Peroxo Binuclear Cobalt(III) Complexes

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Summary The Raman spectrum of μ -peroxo-binuclear cobalt complexes exhibits an intense peak at *ca.* 800 cm^{-1} , assigned to O_2^{2-} stretching, which is in resonance with the *ca.* 360 nm $\text{O}_2^{2-} \rightarrow \text{Co}^{\text{III}}$ charge-transfer band.

RECENT i.r. and Raman studies of several oxygen-transporting proteins¹⁻³ have suggested the presence of metal-bound superoxide or peroxide. Oxygen-bridged metal centres have been postulated in hemocyanin and hemerythrin.⁴ The Raman frequencies for model peroxo- and superoxo-bridged binuclear complexes are, therefore, of interest. While i.r. spectra of some μ -superoxo- and μ -peroxodicobalt complexes have been reported^{5,6} assignment of the

peroxide stretching frequency has not been clearly established. Recently, Raman spectra of some μ -superoxo-cobalt complexes, but no μ -peroxo-complexes, have been published.⁷

Literature methods were used to prepare the μ -peroxodicobalt(III) complexes (I)–(VII), discussed below, containing ammine (NH_3)^{8,9}, histidinato (his),¹⁰ and histamine (hm)¹¹ ligands. Laser Raman spectra of the solids or aqueous solutions of the complexes in rotating sample holders were obtained using Ar^+ excitation and a Jarrell-Ash 25-300 Raman spectrophotometer. Portions of the Raman spectra of three μ -peroxo-binuclear Co^{III} complexes and a mononuclear Co^{III} complex are presented in the Figure.

Frequencies and intensities were measured relative to $\nu_1(\text{NO}_3^-) = 1050 \text{ cm}^{-1}$ or $\nu_1(\text{SO}_4^{2-}) = 980 \text{ cm}^{-1}$.

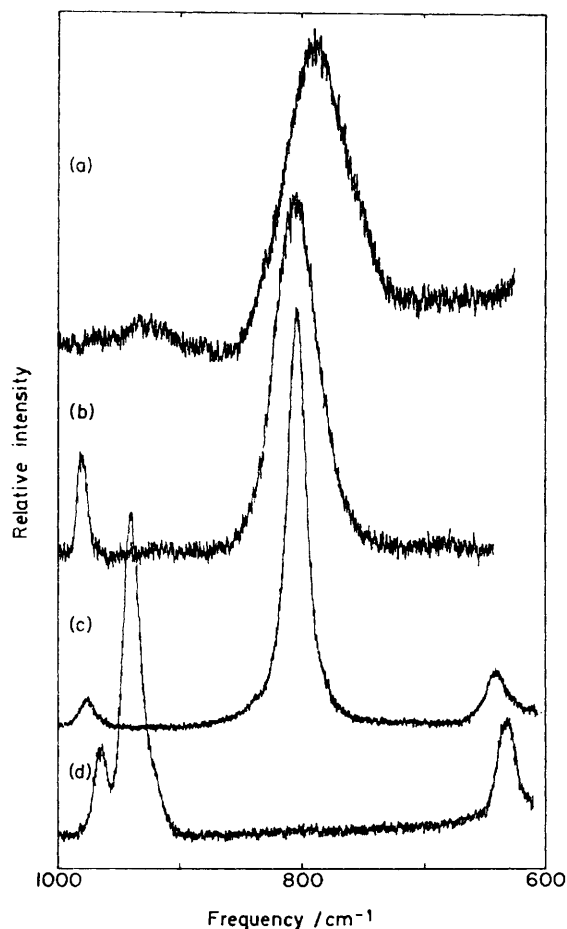


FIGURE. Raman spectra using 4765 Å laser excitation of (a) $[(\text{hm})_2\text{Co}(\text{OH}_2)\text{Co}(\text{hm})_2\text{Cl}_2]$ (solution; see text); (b) $[(\text{his})_2\text{Co}(\text{O}_2)\text{Co}(\text{his})_2] + \text{K}_2\text{SO}_4$ (solid); (c) $[(\text{NH}_3)_5\text{Co}(\text{O}_2)\text{Co}(\text{NH}_3)_5(\text{SO}_4)_2]$ (solid); (d) $[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})(\text{ClO}_4)_2]$ (solid).

The very intense Raman peak near 800 cm^{-1} in the μ -peroxo-complexes is not present in our Raman spectra of $[\text{Co}(\text{NH}_3)_5\text{X}]$ ($\text{X} = \text{Cl}^-, \text{Br}^-, \text{OH}_2$). Upon oxidation to corresponding μ -superoxo-complexes, the 800 cm^{-1} peak disappears and an intense peak near 1100 cm^{-1} , previously assigned to $\nu(\text{O}-\text{O})$ of the μ -superoxo-bridge⁷ is observed instead. Consistent with the vibrational assignments of $\nu(\text{O}_2^{2-})$ in Na_2O_2 ,¹² oxyhemocyanin,¹ and oxyhemerythrin,³ the peaks near 800 cm^{-1} can, therefore, be assigned to the O-O stretching vibration of the bridging peroxide group.

In the monobridged peroxo-complexes, $\nu(\text{O}-\text{O})$ is assigned as follows: (I) $[(\text{NH}_3)_5\text{Co}(\text{O}_2)\text{Co}(\text{NH}_3)_5(\text{NO}_3)_4]$ (solution), 800 cm^{-1} ; (II) $[(\text{NH}_3)_5\text{Co}(\text{O}_2)\text{Co}(\text{NH}_3)_5(\text{SO}_4)_2]$ (solid), 808 cm^{-1} ; (III) $[(\text{his})_2\text{Co}(\text{O}_2)\text{Co}(\text{his})_2]$ (solid), 805 cm^{-1} . Oxidation of (III) to the superoxo-complex $[(\text{his})_2\text{Co}(\text{O}_2)\text{Co}(\text{his})_2(\text{NO}_3)_2] \cdot 2\text{H}_2\text{O}$ ¹³ shifts the peak to 1120 cm^{-1} . The peroxo-stretching frequency is slightly lower in the bridged species: (IV) $[(\text{NH}_3)_4\text{Co}(\text{O}_2, \text{NH}_2)\text{Co}(\text{NH}_3)_4(\text{NO}_3)_3] \cdot \text{H}_2\text{O}$ (solid), 793 cm^{-1} (overlapped by 820 cm^{-1} peak) and (V) $[(\text{hm})_2\text{Co}(\text{O}_2, \text{OH})\text{Co}(\text{hm})_2\text{Cl}_2]$ 790 cm^{-1} , the species presumed to be formed after oxygenation of a 1:2:5 mixture of Co^{II} , hm, 2HCl, and NaOH.¹¹ Little change or a slight increase in frequency is observed when a μ -peroxo-bridged complex is protonated in acidic solution to form the μ -hydroperoxo-complexes: (VI) $[(\text{NH}_3)_5\text{Co}(\text{O}_2\text{H})\text{Co}(\text{NH}_3)_5\text{H}_2(\text{SO}_4)_4]$ (solid), 815 cm^{-1} and (VII) $[(\text{NH}_3)_4\text{Co}(\text{O}_2\text{H}, \text{NH}_2)\text{Co}(\text{NH}_3)_4(\text{NO}_3)_4]$ (solution), 795 cm^{-1} . Compound (VI) undergoes oxidation to the superoxide during laser irradiation.

By measuring peak heights relative to $\nu_1(\text{NO}_3^-)$ or $\nu_1(\text{SO}_4^{2-})$, the peroxo-stretching mode is seen to undergo intensity enhancement as the laser excitation wavelength is decreased from 5145 to 4579 Å. For example, in compound (III) the relative intensities of the 805 cm^{-1} peak are 1.4 (4965 Å), 1.6 (4765 Å), and 1.9 (4579 Å) compared to a unit relative intensity using 5145 Å excitation. This behaviour suggests resonance with the $\text{O}_2^{2-} \rightarrow \text{Co}^{\text{III}}$ charge-transfer band assigned near 360 nm in the complexes.⁶ The Raman peaks in the 450–520 cm^{-1} region, which have been assigned to Co-N stretching vibrations in cobalt(III) ammine complexes,¹⁴ do not exhibit this resonance effect.

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