Laser-Raman and Infrared Spectra of μ-Superoxo-dicobalt(III) Complexes

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Summary Laser-Raman spectra of the chloride, nitrate, and acid sulphate of the μ-superoxo-bis[penta-amminecobalt(III)] cation and the chloride of the μ-amido-μ-superoxo-bis[tetra-amminecobalt(III)] cation have intense peaks at *ca.* 1100 cm^{-1} attributed to O–O stretching.

A FEW i.r. spectra of μ-superoxo-dicobalt(III) complexes have been reported,[1] but even in these reports there has been no description of any absorption due to the superoxo-bridge. No Raman spectra have been published, mainly on account of the deep colour and easy decomposition of the complexes.

Laser-Raman spectra of solid $[(NH_3)_5CoO_2Co(NH_3)_5]Cl_5,4H_2O$, $[(NH_3)_5CoO_2Co(NH_3)_5](NO_3)_5$, and $[(NH_3)_5CoO_2Co(NH_3)_5](SO_4)_2,HSO_4,3H_2O$ were obtained, using 5682 Å excitation radiation from a krypton ion laser and rotating cell [Figures (a), (b), and (c)]. The spectra have intense peaks at 1122, 1122, and 1110 cm^{-1}, respectively, which can be attributed to the O–O stretching for the reasons given below. The i.r. spectra of the chloride and nitrate have no appreciable peak in the 900—1300 cm^{-1} region.

X-Ray studies show that the Co–O–O–Co unit has a *trans*-coplanar structure (C_{2h} symmetry) in the nitrate and trihydrogen tetrasulphate of the μ-superoxo-bis[penta-amminecobalt(III)] cation,[2] with O–O distances of 1·31 and 1·32Å, respectively. The complex cation $[(NH_3)_5CoO_2Co(NH_3)_5]^{5+}$ may be described approximately in terms of a *trans*-coplanar four-body model, *i.e.* $\{(NH_3)_5Co\}$–O–O–$\{Co(NH_3)_5\}$. In the point group C_{2h}, the vibrational modes can be divided into A_g (Raman active, i.r. inactive) and B_u (Raman inactive, i.r. active) species.

The fact that the mutual exclusion rule applies in the chloride and nitrate supports assignment of the band at *ca.* 1100 cm^{-1} to O–O stretching. This also suggests a *trans*-coplanar structure for the chloride, although this has not yet been determined by *X*-ray analysis.

The Raman and i.r. spectra of μ-amido-μ-superoxo-bis-[tetra-amminecobalt(III)] chloride have peaks at 1075 [Figure (d)] and 1068 cm^{-1}, respectively. The five-membered ring $\overline{\mathrm{Co{-}N{-}Co{-}O{-}O}}$ in $[(NH_3)_4CoO_2(NH_2)Co(NH_3)_4](NO_3)_4$ is very nearly planar[3] and may be regarded as having C_{2v} symmetry. In the point group C_{2v}, the vibrational modes are classified into A_1 and B_1 species, and both are Raman and i.r. active. This also is in accordance with the above observation.†

The O–O stretching frequencies in the Raman as well as the i.r. spectra of the ^{18}O-substituted μ-amido-μ-superoxo-complexes are 60 cm^{-1} lower than those for the corresponding ^{16}O-complex. The isotopic shift of the O–O stretching frequency calculated from a simple valence force field and five-membered ring model, is 61 cm^{-1}, with a force constant K_{O-O} of 5·1 mdyn/Å. The force constant K_{O-O} for the μ-superoxo-bis[penta-amminecobalt(III)] complex, on the assumption of a four-body model, was calculated to be 5·6 mdyn/Å.

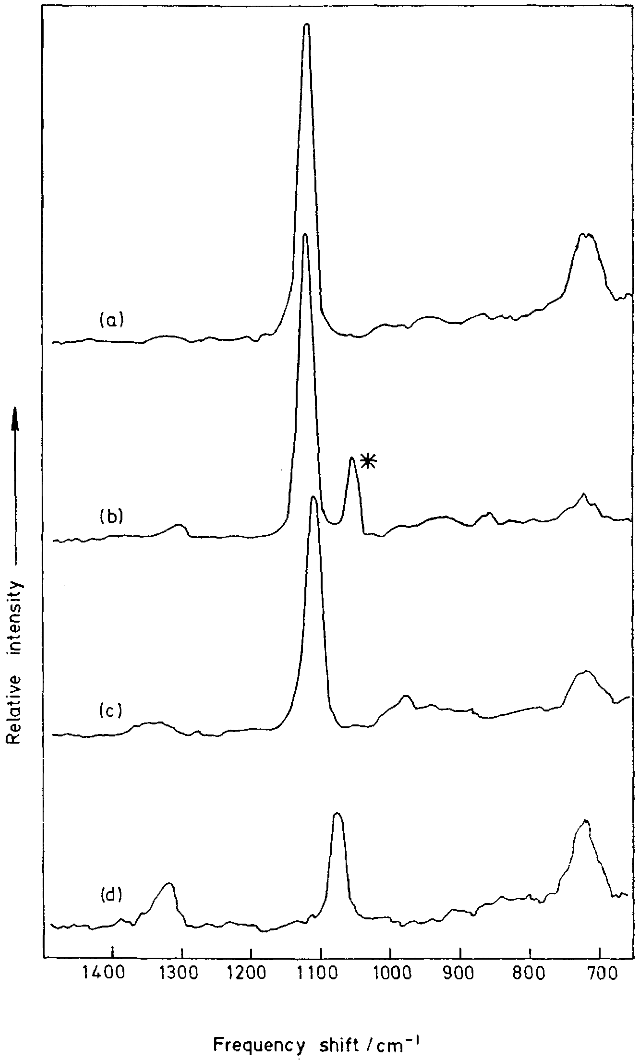

FIGURE. Raman spectra of μ-superoxo-complexes: (a) $[(NH_3)_5CoO_2Co(NH_3)_5]Cl_5,4H_2O$; (b) $[(NH_3)_5CoO_2Co(NH_3)_5](NO_3)_5$; (c) $[(NH_3)_5CoO_2Co(NH_3)_5](SO_4)_2,HSO_4,3H_2O$; (d) $[(NH_3)_4CoO_2(NH_2)Co(NH_3)_4]Cl_4,3H_2O$.
* = $\nu_1(A_1')$ of NO_3^-.

The Raman spectrum of $[CoCl(NH_3)_5]Cl_2$, having the same symmetry (C_{4v}) as the local symmetry around each cobalt atom in the μ-superoxo-bis[penta-amminecobalt(III)]

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† The degrees of depolarization of the Raman line at *ca.* 1100 cm^{-1} of solution samples of μ-superoxo- and μ-amido-μ-superoxo-complexes are both about one-half, showing that the vibrations are totally symmetric.

complex, has no peak in the 900—1250 cm^{-1} region. This fact also supports the assignment of the peak at *ca.* 1100 cm^{-1} to the O–O stretching mode.

The author is grateful to Professor M. Mori and Professor T. Miyazawa for valuable suggestions and to Drs. S. Hirai and T. Hinomoto of JEOL Ltd. for Raman spectra.

(*Received*, 13*th August* 1973; *Com.* 1152.)

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