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Raman and Infrared Spectra of μ-O_2 Dicobalt(III) Complexes*

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Raman and infrared spectra of μ-hyperoxo and μ-peroxo ammine and cyano dicobalt(III) complexes have been studied and isotopic shifts of ν(OO) and ν(CoO) examined using ^{18}O. A μ-hyperoxo complex, $[(NH_3)_5Co(O_2)Co(NH_3)_5]X_5$ shows peaks around 1110, 620, and 440 cm^{-1} assignable to ν(OO), sν(CoO), and asν(CoO), respectively, whereas a μ-peroxo complex, $[(NH_3)_5Co(O_2)Co(NH_3)_5]X_4$ shows peaks around 805, 645, and 545 cm^{-1} assignable to ν(OO), sν(CoO), asν(CoO), respectively. These observed values are best reproduced, when the following force constants are assumed in the UBFF calculation: $K(OO)=5.6$, $K(CoO)=1.40$ mdyn/Å for μ-hyperoxo complexes and $K(OO)=2.7$, $K(CoO)=2.15$ mdyn/Å for μ-peroxo complexes. The calculated isotopic shifts are in good agreement with the observed ones. Raman and infrared spectra of dibridged μ-amido-μ-O_2 (both peroxo and hyperoxo) dicobalt(III) complex have also been characterized. A linear relationship has been found between ν(OO) and the bond order of the O_2 moiety in O_2-complexes in different oxidation states including alkali hyperoxide, alkali peroxide, hydrogen peroxide, oxygen, and O_2^+ species.

Although much work has been done on the preparation, reaction mechanisms and X-ray crystallography of O_2-bridged binuclear cobalt(III) complexes,1) the information about the vibration of oxygen–oxygen and cobalt–oxygen bonding in the complexes has been relatively poor.2–7)

The variation of O–O and Co–O stretching frequencies with the change in the oxidation state (*i.e.* peroxo to hyperoxo species) will give important information on the nature of the O–O and Co–O bonding.

As has been pointed out in the earlier communication,7) the use of Raman spectroscopy is indispensable to obtaining the O–O stretching frequencies of substances having center of symmetry, since infrared spectroscopy does not give information in these cases. The recent development of the laser light source is beginning to afford Raman spectroscopy of colored substances such as many metal complexes, and is becoming to be a useful weapon in attacking these problems.

This paper will describe the O–O and Co–O stretching vibrations of μ-hyperoxo and μ-peroxo binuclear cobalt(III) complexes with and without additional NH_2-bridge as examined by using laser-Raman and infrared spectroscopy.

Experimental

Preparation. $[(NH_3)_5Co(O_2)Co(NH_3)_5]Cl_5\cdot 3H_2O$,8) $[(NH_3)_5Co(O_2)Co(NH_3)_5](NO_3)_5$,9) $[(NH_3)_5Co(O_2)Co(NH_3)_5](SO_4)_2HSO_4\cdot 3H_2O$,10) $K_5[(CN)_5Co(O_2)Co(CN)_5]\cdot H_2O$,11) $[(NH_3)_5Co(O_2)Co(NH_3)_5]Cl_4\cdot H_2O$,12) $[(NH_3)_5Co(O_2)Co(NH_3)_5](NO_3)_4\cdot 2H_2O$,12) $[(NH_3)_5Co(O_2)Co(NH_3)_5](SO_4)_2\cdot 3H_2O$,12) $K_6[(CN)_5Co(O_2)Co(CN)_5]\cdot H_2O$,13) $[(NH_3)_4Co(NH_2)(O_2)Co(NH_3)_4]Na(ClO_4)_4$,3) and $[(NH_3)_4Co(NH_2)(O_2)Co(NH_3)_4]Cl_4\cdot 2H_2O$3) were prepared as described in the references. In addition to the dihydrate of $[(NH_3)_4Co(NH_2)(O_2)Co(NH_3)_4]Cl_4$ cited above, the trihydrate $[(NH_3)_4Co(NH_2)(O_2)Co(NH_3)_4]Cl_4\cdot 3H_2O$ was also prepared. Although the factors which decide the number of water of crystallization have not yet been clarified, these two types are easily distinguished by infrared spectra, which will be discussed later.

Found: Co, 24.57; H, 6.17; N, 26.02%. Calcd for $[(NH_3)_4Co(NH_2)(O_2)Co(NH_3)_4]Cl_4\cdot 2H_2O$: Co, 24.56; H, 6.30; N, 26.26%.

Found: Co, 23.98; H, 6.32; N, 25.40%. Calcd for $[(NH_3)_4Co(NH_2)(O_2)Co(NH_3)_4]Cl_4\cdot 3H_2O$: Co, 23.67; H, 6.48; N, 25.31%.

$[(NH_3)_4Co(NH_2)(O_2)Co(NH_3)_4](NO_3)_4$ was prepared as described in Ref. 3. Two types (which we shall name α and β) of crystals were obtained by different ways of cooling. Rapid cooling with ice at the final stage of preparation tended to give crystals of the α-type, whereas slow cooling at room temperature gave crystals of the β-type. These two types are easily distinguished by infrared spectra (see below). From the X-ray powder pattern, it was made clear that the structure previously determined by X-ray single crystal analysis14) was that of our β-type.

Found: α-type, Co, 21.37; N, 32.40%, β-type, Co, 21.26; N, 32.68%. Calcd for $[(NH_3)_4Co(NH_2)(O_2)Co(NH_3)_4](NO_3)_4$: Co, 21.42; N, 33.10%.

The following ^{18}O-labeled substances were prepared using $^{18}O_2$ gas (90%) obtained from International Chemical Nuclear Nuclear Corp.: $[(NH_3)_5Co(^{18}O_2)Co(NH_3)_5](NO_3)_5$, $[(NH_3)_5Co(^{18}O_2)Co(NH_3)_5]Cl_5\cdot 3H_2O$, $[(NH_3)_4Co(NH_2)(^{18}O_2)Co(NH_3)_4](NO_3)_4$, $[(NH_3)_4Co(NH_2)(^{18}O_2)Co(NH_3)_4]Cl_4\cdot 2H_2O$.

Spectroscopic Measurements. Raman spectra of the complexes in the solid state and in aqueous solutions were recorded on a JEOL JRS-Sl laser Raman spectrophotometer equipped with a rotating cell to avoid decomposition of samples. Krypton ion laser (5682 Å) was used as a light source. Infrared spectra were recorded as KBr disks and in Nujol mulls on a JASCO IR-S spectrophotometer (4000—400 cm^{-1}) and a DS-402G spectrophotometer (700—400 cm^{-1}). Samples dispersed homogeneously in polyethylene or Nujol mulls were used for the measurements in the far infrared region (400—30 cm^{-1}) with a Hitachi FIS-3 spectrophotometer.

Results and Discussion

Single-bridged μ-Hyperoxo Dicobalt(III) Complexes. Raman (solid samples) and infrared spectra of several single-bridged μ-hyperoxo dicobalt(III) complexes ((**1**), $[(NH_3)_5Co(O_2)Co(NH_3)_5]Cl_5\cdot 3H_2O$; (**2**), $[(NH_3)_5Co(O_2)Co(NH_3)_5](NO_3)_5$; (**3**), $[(NH_3)_5Co(O_2)Co(NH_3)_5](SO_4)_2\ HSO_4\cdot 3H_2O$; (**4**), $K_5[(CN)_5Co(O_2)Co(CN)_5]\cdot H_2O$) are shown in Fig. 1. Raman spectra of **1**, **2**, **3**, and **4** show strong peaks at about 1100 cm^{-1}, whereas no peak appears in the 900—1300 cm^{-1} region of the infrared spectra except in the case of **3**, which exhibits absorptions due to sulfate and hydrogensulfate

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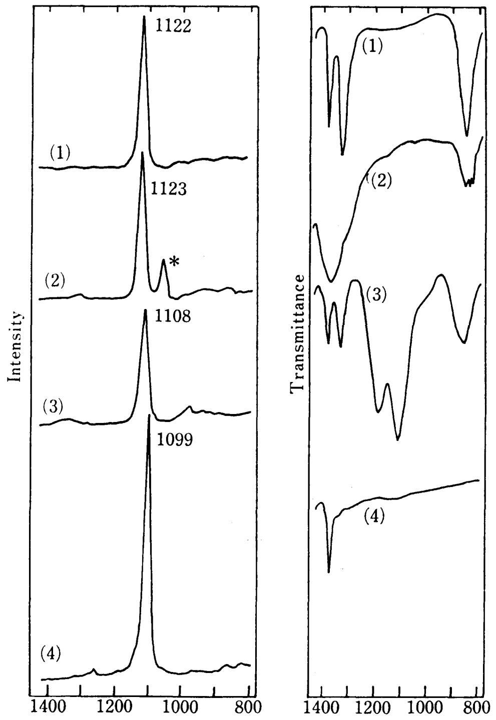
* Some parts of this paper have already been reported at XVIth International Conference on Coordination Chemistry, Dublin, 1974.



Raman spectra Infrared spectra

Fig. 1. Raman and infrared spectra of single-bridged μ-hyperoxo dicobalt(III) complexes in the rigion 1400—800 cm^{-1}.
(1): $[(NH_3)_5Co(O_2)Co(NH_3)_5]Cl_5 \cdot 3H_2O$,
(2): $[(NH_3)_5Co(O_2)Co(NH_3)_5](NO_3)_5$,
(3): $[(NH_3)_5Co(O_2)Co(NH_3)_5](SO_4)_2HSO_4 \cdot 3H_2O$,
(4): $K_5[CN)_5Co(O_2)Co(CN)_5] \cdot H_2O$.
*: $\nu_1(A_1')$ of NO_3^-.

ions. X-Ray analyses by several authors[15–17] all revealed the Co–O–O–Co moieties of these complexes to be trans-planar (C_{2h} symmetry) or close to so. The in-plane vibrational modes can therefore be classified to A_g (Raman active and infrared inactive) and B_u (Raman inactive and infrared active) species. The Raman active band (A_g) at *ca.* 1100 cm^{-1} can be assigned to ν(OO); other vibrations belonging to A_g species (sν(CoO) and sδ(CoOO)) have too high frequencies to be assigned to these bands. As shown in Fig. 2, the degree of depolarization of Raman band at *ca.* 1100 cm^{-1} of a solution sample of the chloride is about one-half indicating that this vibration is totally symmetric. The Raman spectrum of $[CoCl(NH_3)_5]Cl_2$, having the same local symmetry (C_{4v}) as that around each cobalt atom in the μ-hyperoxo-bis[pentaamminecobalt(III)] complex has no peak in the 900—1250 cm^{-1} region. These facts also support the above assignment.

Infrared and Raman spectra of single-bridged μ-hyperoxo dicobalt(III) complexes in the KBr region are shown in Fig. 3, together with the infrared spectra of the chloride and nitrate of ^{18}O-substituted complexes. As shown in Fig. 3, the peaks at *ca.* 440 cm^{-1} in the infrared spectra are lowered by *ca.* 19 cm^{-1} by the substitution with ^{18}O. This confirms the conclusion by Ikawa *et al.*[4] who assigned the band to asν(CoO) from comparison of the infrared spectra of μ-hyperoxo complexes with those of μ-peroxo complexes and hexaammine cobalt(III) complex. The peaks in the range 505—470 cm^{-1} of the infrared spectra hardly shift indicating that the peaks are due to ν(CoN). Absence of any remarkable difference between ordinary and ^{18}O-substituted complexes in the far infrared region makes it difficult to assign δ(CoOO)(Fig. 4).[4] As regards to decaammine dicobalt(III) complexes, **1**, **2**, and **3**, the peaks at *ca.* 620 cm^{-1} in the Raman spectra (Fig. 3) are assigned to sν(CoO) by comparison with the infrared spectra (no peak around 620 cm^{-1}), although Strekas and Spiro[15] assigned the Raman band at 500 cm^{-1} to ν(CoO). The strong peaks at about 500 cm^{-1} in the Raman spectra can rather be assigned to ν(CoN), since $[CoCl(NH_3)_5]Cl_2$ also shows a strong peak at 494 cm^{-1} in the Raman spectrum. The Raman spectrum of the cyano complex **4** shows peaks at 610, 542, and 528 cm^{-1} and the peak at 610 cm^{-1} is assigned to sν(CoO) and the other two peaks are assigned to ν(CoC). A weak band assignable to sν(CoO) was observed at 618 cm^{-1} in the infrared spectrum, too. Appearance of this band can be attributed to the nonplanarity of the Co–O–O–Co moiety of the cyano complex; the following values were obtained from X-ray crystallography for the torsional angles: nitrate of the ammine complex,[16] 180°; sulfate tris-hydrogensulfate of the ammine complex,[17] 175°; potassium salt of the cyano complex,[18] 180 and 166° (two independent binuclear anions in the unit cell). The peaks at 551 and 543 cm^{-1} are assigned to ν(CoC) in the infrared spectrum of the cyano complex, since a peak assignable to ν(CoC) was observed at 565 cm^{-1} in the infrared spectrum of $K_3[Co(CN)_6]$.[19]

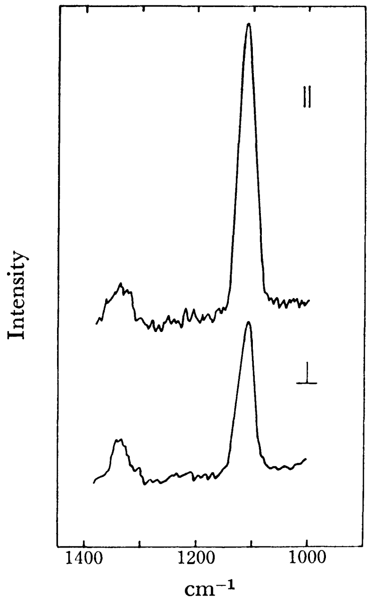
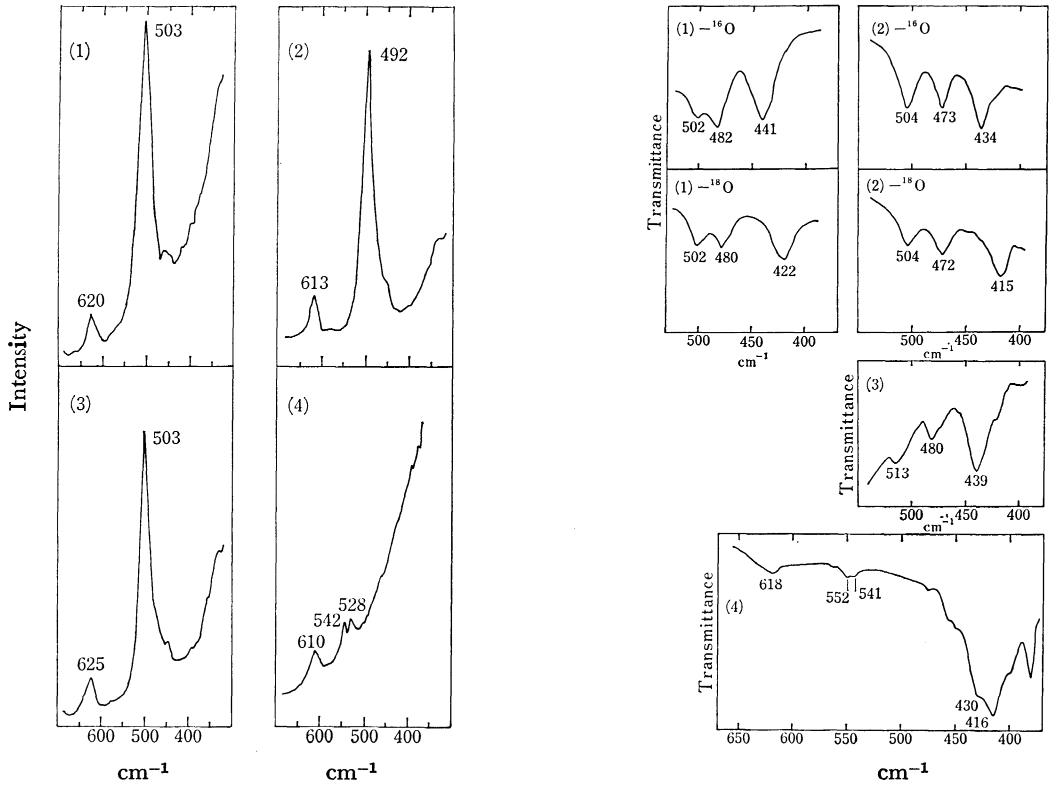


Fig. 2. Polarized Raman spectra of $[(NH_3)_5Co(O_2)$-$Co(NH_3)_5]Cl_5 \cdot 3H_2O$.

μ-Amido-μ-hyperoxo Dicobalt(III) Complexes. The Raman and infrared spectra of μ-amido-μ-hyperoxo bis[tetraamminecobalt(III)] chloride trihydrate (**5**) have peaks at 1075 and 1068 cm^{-1}, respectively, as shown in Fig. 5. These bands are assigned to ν(OO)



Raman spectra

Infrared spectra

Fig. 3. Raman and infrared spectra of single-bridged μ-hyperoxodicobalt(III) complexes in the region 700—400 cm^{-1}. Each number represents the same compound as in Fig. 1.

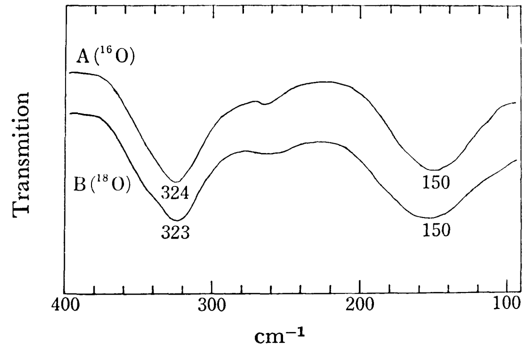
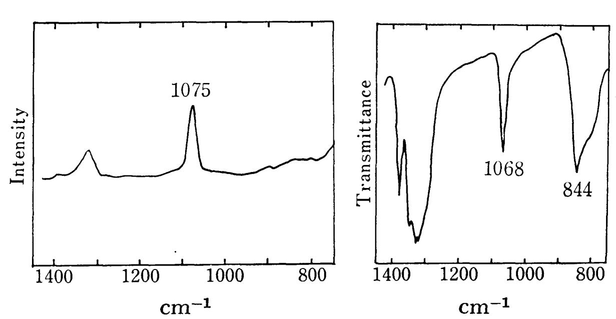


Fig. 4. Far infrared spectra of single-bridged μ-hyperoxo decaamine dicobalt(III) complexes.
(A): ^{16}O-[$(NH_3)_5Co(O_2)Co(NH_3)_5$]$Cl_5 \cdot 3H_2O$,
(B): ^{18}O-[$(NH_3)_5Co(O_2)Co(NH_3)_5$]$Cl_5 \cdot 3H_2O$.



Raman spectrum

Infrared spectrum

Fig. 5. Raman and infrared spectra of μ-amido-μ-hyperoxo bis[tetraamminecobalt(III)] chloride trihydrate, [$(NH_3)_4Co(NH_2)(O_2)Co(NH_3)_4$]$Cl_4 \cdot 3H_2O$.

by comparison with the peak positions in the Raman spectra of single-bridged μ-hyperoxo complexes and also by consideration of the degree of depolarization (*ca.* one-half) of the Raman band at *ca.* 1100 cm^{-1} of a solution samples of **5**, as shown in Fig. 6. Since the dibridged complex ion has no center of symmetry, any vibration should be both infrared and Raman active.

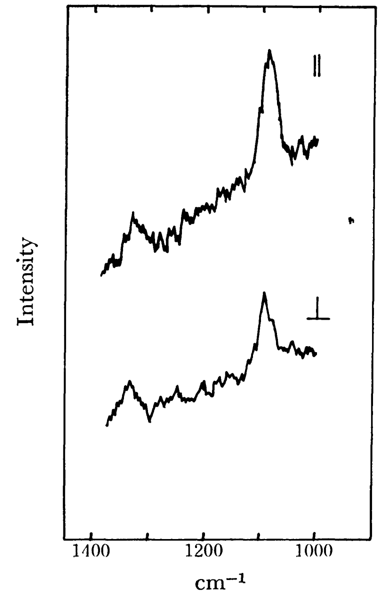


Fig. 6. Polarized Raman spectra of [$(NH_3)_4Co(NH_2)$-$(O_2)Co(NH_3)_4$]$Cl_4 \cdot 3H_2O$.

This is in accordance with the above observation. The chloride crystallizes in two forms, one with two moles of water and the other with three. They can easily be distinguished by the infrared spectra. The peak positions due to ν(OO) differ slightly (dihydrate, 1078 cm^{-1}; trihydrate, 1068 cm^{-1}) from each other and the band assigned to $\rho_r(NH_3)$ shows splitting in the dihydrate (dihydrate, 844 and 815 cm^{-1}; trihydrate, 844 cm^{-1}). The nitrate also has two crystal forms (cf. Experimental, Preparation.). Both are anhydrous and can be distinguished easily by infrared spectra. In addition to the difference in the peak position of ν(OO) (α-type, 1063 cm^{-1}; β-type, 1088 cm^{-1}), the spectrum of α-type shows a splitting of the band due to $\rho_r(NH_3)$ (α-type, 840 and 827 cm^{-1}; β-type, 830 cm^{-1}). As shown in Fig. 7, the O-O streching frequencies in the infrared spectra of ^{18}O-substituted complexes of the chloride ((A), $2H_2O$-type) and the nitrate ((B), α-type) are lower than those of the corresponding ^{16}O-complexes by 60 cm^{-1}. Since the difference in ν(OO) frequency between two crystal forms (in both chloride and

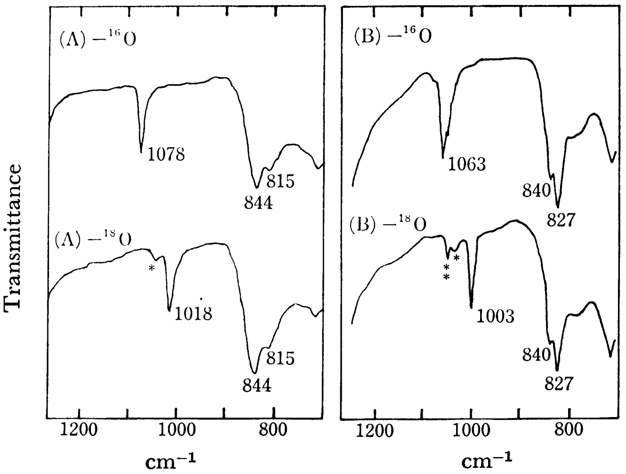


Fig. 7. Infrared spectra of chloride and nitrate of μ-amido-μ-hyperoxo bis[tetraamminecobalt(III)] in the region 1200—700 cm^{-1}.
(A): $[NH_3)_4Co(NH_2)(O_2)Co(NH_3)_4]Cl_4 \cdot 2H_2O$,
(B): $[(NH_3)_4Co(NH_2)(O_2)Co(NH_3)_4](NO_3)_4$ (α-type),
*: $\nu(^{16}O^{18}O)$, **: $\nu_1(A_1')$ of NO_3^-.

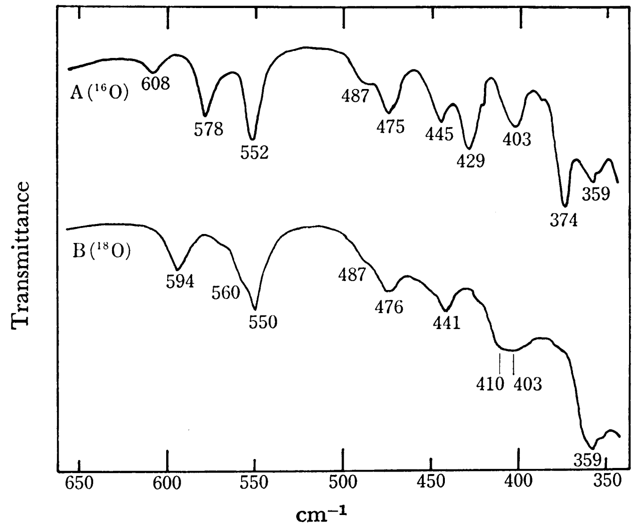


Fig. 8. Infrared spectrum of $[(NH_3)_4Co(NH_2)(O_2)Co(NH_3)_4](NO_3)_4$ (α-type) in the region 650—350 cm^{-1}.

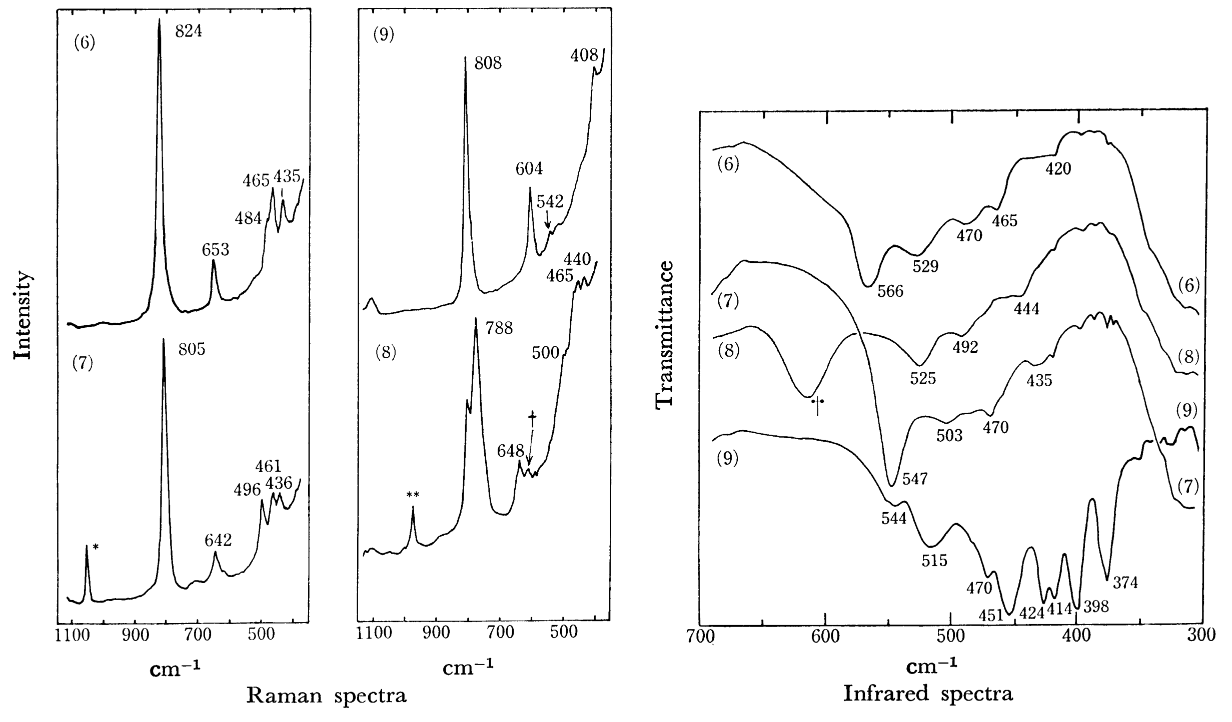


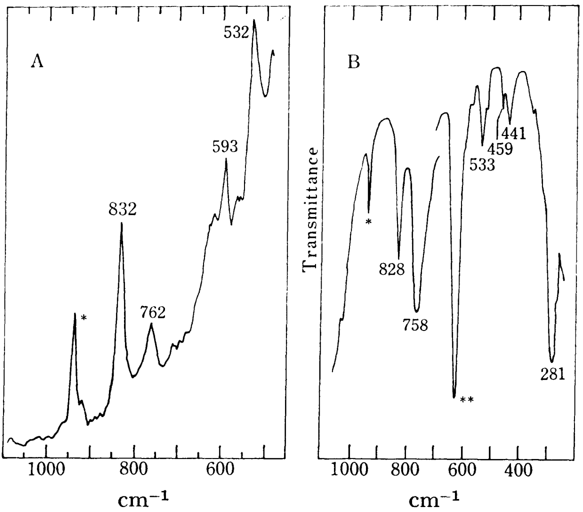
Fig. 9. Raman and infrared spectra of single-bridged μ-peroxo dicobalt(III) complexes.
(6): $[(NH_3)_5Co(O_2)Co(NH_3)_5]Cl_4 \cdot H_2O$, (7): $[(NH_3)_5Co(O_2)Co(NH_3)_5](NO_3)_4 \cdot 2H_2O$, (8): $[(NH_3)_5Co(O_2)Co(NH_3)_5](SO_4)_2 \cdot 3H_2O$, (9): $K_6[(CN)_5Co(O_2)Co(CN)_5] \cdot H_2O$,
*: $\nu_1(A_1')$ of NO_3^-, **: $\nu_1(A_1)$ of SO_4^{2-}, †: $\nu_4(F_2)$ of SO_4^{2-}.

nitrate) is not negligible, it is important to compare the ν(OO) frequency of ^{16}O- and ^{18}O-compounds of the same crystal form.

Infrared spectra of ordinary and ^{18}O-substituted samples, of the nitrate (α-type) in the 650—350 cm^{-1} region are shown in Fig. 8, A and B, respectively. The peak at 429 cm^{-1} in A shifts to 410 cm^{-1} in B, whereas that at 374 cm^{-1} in A probably to *ca.* 360 cm^{-1} in B (overlapping with a peak at 359 cm^{-1} which does not shift). The peak at a higher frequency is assigned to sν(CoO) and that at a lower frequency to asν(CoO). Shifts of some other bands can also be observed; the peaks at 608 and 578 cm^{-1} in A disappeared and a new peak appeared at 594 cm^{-1} and a shoulder at 560 cm^{-1} in B. These two peaks are tentatively assigned to the combination bands of ν(CoO), ν(CoN), and ring deformation; if they were genuine ν(CoO)'s, the magnitude of the shifts would be expected to be *ca.* 25 cm^{-1}.

Single-bridged μ-Peroxo Dicobalt(III) Complexes. The Raman (1100—450 cm^{-1}) and infrared spectra (700—300 cm^{-1}) of single-bridged μ-peroxo dicobalt(III) complexes ((**6**), $[(NH_3)_5Co(O_2)Co(NH_3)_5]Cl_4\cdot H_2O$; (**7**), $[(NH_3)_5Co(O_2)Co(NH_3)_5](NO_3)_4\cdot 2H_2O$; (**8**), $[(NH_3)_5Co(O_2)Co(NH_3)_5](SO_4)_2\cdot 3H_2O$; (**9**), $K_6[(CN)_5Co(O_2)Co(CN)_5]\cdot H_2O$) are shown in Fig. 9. Strong bands assignable to ν(OO) are found around 800 cm^{-1} in the Raman spectra.[5-7] The degree of depolarization of these bands is *ca.* 0.3 indicating that the vibration is totally symmetric. The band at 600—660 cm^{-1} ((**6**), 653; (**7**), 642; (**8**), 648; (**9**), 604 cm^{-1}) in the Raman spectra are assigned to sν(CoO). Other bands in the Raman spectra are assigned to ν(CoN) for the compounds **6**(484, 465, and 435 cm^{-1}), **7**(496, 461, and 436 cm^{-1}), and **8**(500, 465, and 440 cm^{-1}). The bands with the highest wave number and at the same time the highest intensity in the KBr region of the infrared spectra of decaammine μ-peroxo compounds (**6**, 566 cm^{-1} and possibly 529 also; **7**, 547; **8**, 525 cm^{-1}) are assigned to asν(CoO). The bands in the region from 503 to 400 cm^{-1} are assigned to ν(CoN). As for the cyano compound **9**, the band at 515 cm^{-1} in the infrared spectrum is assigned to the asν(CoO), and the band at 544 cm^{-1} and the bands from 470 to 374 cm^{-1} are assigned to ν(CoC)+δ(CoCN), by the comparison with the infrared spectra of $K_3[Co(CN)_6]$.[19] The bands at 542 and 408 cm^{-1} in the Raman spectrum of **9** are also assigned to ν(CoC)+δ(CoCN).

μ-Amido-μ-peroxo Dicobalt(III) Complexes. The Raman and infrared spectra of $[(NH_3)_4Co(NH_2)(O_2)Co(NH_3)_4]Na(ClO_4)_4$ are shown in Fig. 10A and 10B, respectively. The ν(OO) in the infrared spectrum has been reported by Mori *et al.*[3] to be at 828 cm^{-1}. The Raman spectrum of this sample shows a distinct peak at 832 cm^{-1} which confirms the previous assignment. The band at 533 cm^{-1} in the infrared spectrum and



Raman spectrum Infrared spectrum

Fig. 10. Raman and infrared spectra of μ-amido-μ-peroxobis[tetraamminecobalt(III)] complex, $[(NH_3)_5Co(NH_2)(O_2)Co(NH_3)_4]Na(ClO_4)_4$.
*: $\nu_1(A_1)$ of ClO_4^-, **: $\nu_4(F_2)$ of ClO_4^-.

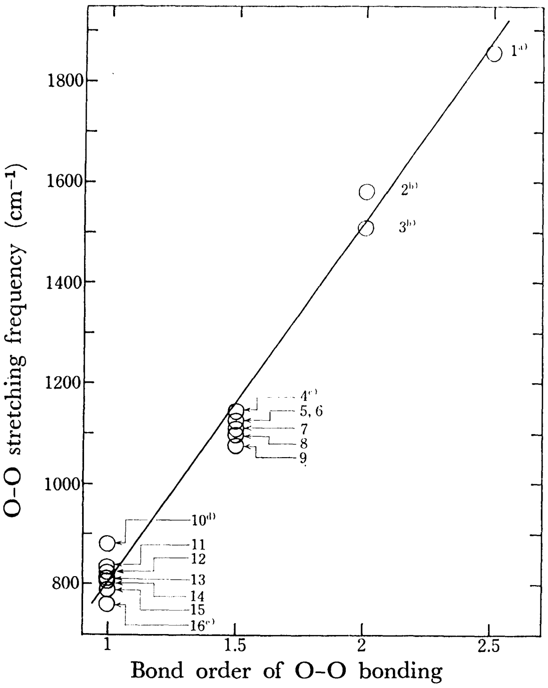


Fig. 11. Relationship between the bond order of oxygen-oxygen bonding and ν(OO) frequency.
(1): O_2AsF_6,[a] (2): $O_2(^3\Sigma_g^-)$,[b] (3): $O_2(^1\Delta_g)$, (4): KO_2,[c] (5): $[(NH_3)_5Co(O_2)Co(NH_3)_5](NO_3)_5$, (6): $[(NH_3)_5Co(O_2)Co(NH_3)_5]Cl_5\cdot 3H_2O$, (7): $[(NH_3)_5Co(O_2)Co(NH_3)_5](SO_4)_2\cdot HSO_4\cdot 3H_2O$, (8): $K_5[(CN)_5Co(O_2)Co(CN)_5]\cdot H_2O$, (9): $[(NH_3)_4Co(NH_2)(O_2)Co(NH_3)_4]Cl_4\cdot 3H_2O$, (10): H_2O_2,[d] (11): $[(NH_3)_4Co(NH_2)(O_2)Co(NH_3)_4]Na(ClO_4)_4$, (12): $[(NH_3)_5Co(O_2)Co(NH_3)_5]Cl_4\cdot H_2O$, (13): $K_6[(CN)_5Co(O_2)Co(CN)_5]\cdot H_2O$, (14): $[(NH_3)_5Co(O_2)Co(NH_3)_5](NO_3)_4\cdot 2H_2O$, (15): $[(NH_3)_5Co(O_2)Co(NH_3)_5](SO_4)_2\cdot 3H_2O$, (16): Na_2O_2.[e]
(a) J. Shamir, J. Binenboym, and H. H. Claassen, *J. Am. Chem. Soc.*, **90**, 6223 (1968). (b) G. Herzberg, "Spectra of Diatomic Molecules," van Nostrand (1950). (c) J. B. Bates, M. H. Brooker, and G. H. Boyd, *Chem. Phys. Lett.*, **16**, 391 (1972). (d) F. J. Blunt, P. J. Hendra, and J. R. Mackenzie, *Chem. Commun.*, **1969**, 278. (e) J. C. Evans, *Chem. Commun.*, **1969**, 682.

the bands at 593 and 532 cm^{-1} in the Raman spectrum are assigned tentatively to ν(CoO). Peaks at 762 cm^{-1} (Raman) and 758 cm^{-1} (infrared) are assigned to $\rho_r(NH_3)$.

Relationship between the Bond Order and the Oxygen–Oxygen Stretching Frequencies of O_2-compounds. An approximately linear relationship exists between the bond order of oxygen–oxygen bonding and ν(OO) as shown in Fig. 11. The relationship can be expressed by the following equation

$$\nu(\mathrm{OO}) = 710 \times BO + 70,$$

where ν(OO) is the wave number of the O–O stretching vibration in cm^{-1} and BO is the bond order. The large differences of ν(OO) between μ-hyperoxo and μ-peroxo complexes clearly support the idea that these two kinds of complex have different oxidation states of bridging O_2-moieties, and that the cobalt atoms in both types of complex are of oxidation state three.[20] The substitution of ammonia with cyanide ions gives little influence on ν(OO) in both μ-hyperoxo and μ-peroxo complexes.

Calculations of Force Constants. The force constants of the single-bridged μ-hyperoxo and μ-peroxo complexes were calculated using UBFF and a four-body model (μ-hyperoxo, trans planar; μ-peroxo, torsional angle of 146°). The change of the torsional angle gave only a small influence on the calculated values. Bond lengths and angles used for the calculation were those of the nitrate[16] in the case of the μ-hyperoxo complex and those of the sulfate[22] in the case of the μ-peroxo complex. The calculated and observed values are summarized in Table 1, together with the force constants employed. The calculated isotopic shift of asν(CoO) for μ-hyperoxo complex is in good agreement with the observed ones.

Table 1. Observed and calculated frequencies of μ-hyperoxo and μ-peroxo dicobalt(III) complexes in cm^{-1}

(A) $[(NH_3)_5Co(O_2)Co(NH_3)_5]X_5$

			ν(OO)	sν(CoO)	asν(CoO)
Obsd	nitrate	^{16}O	1123	613	434
		^{18}O	—	—	415
	chloride	^{16}O	1122	620	441
		^{18}O	—	—	422
	sulfate	^{16}O	1108	625	439
Calcd		^{16}O	1114	621	439
		^{18}O	1050	587	420

(K(OO)=5.6, K(CoO)=1.40, H(CoOO)=0.30, F(CoO)=0.05 mdyn/Å)

(B) $[(NH_3)_5Co(O_2)Co(NH_3)_5]X_4$

			ν(OO)	sν(CoO)	asν(CoO)
Obsd	nitrate	^{16}O	805	642	547
	chloride	^{16}O	824	653	566, 529
	sulfate	^{16}O	788	648	525
Calcd		^{16}O	799	649	543

(K(OO)=2.7, K(CoO)=2.15, H(CoOO)=0.30, F(CoO)=0.05 mdyn/Å)

The O–O stretching frequencies in the Raman as well as the infrared spectra of the ^{18}O-substituted μ-amido-μ-hyperoxo complexes are lower by 60 cm^{-1} than those for the corresponding ^{16}O-complexes. The isotopic shift calculated from a simple valence force field and a five membered ring model $\overline{\mathrm{Co–N–Co–O–O}}$ is 61 cm^{-1} with a force constant K(OO) of 5.1 mdyn/Å.

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