

INFRARED AND RAMAN STUDIES OF PEROXO BIS (2, 2'-BIPYRIDYLAMINE) COBALT (III)-PERCHLORATE

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Infrared and Raman spectra of the title compound are recorded. The ν (O-O), ν_s (Co-O) and ν_{as} (Co-O) are observed in both spectra around 890, 565 cm^{-1} respectively. This confirms the unique isosceles triangular structure of the peroxocobalt (III) unit, $\text{Co}(\text{O}_2)$, with local symmetry of C_{2v} . The calculated values of force constants for the O_2^{2-} and Co-O bonds based on a valence force field are 332 257 Nm^{-1} respectively.

Key words: Cobalt (III); Peroxi; Vibration.

INTRODUCTION

The complexes formed between metal ions and nitrogen-heterocyclic ligands have been of considerable interest for the last two decades [1-4]. The 2, 2'-bipyridylamine, (HL), forms stable complexes with many transition metal ions. With Co(II), the complex ion $(\text{Co}(\text{HL})_3)^{2+}$ is formed. Johnson and Geldard reported that this complex reacts with H_2O_2 to produce the corresponding red peroxocobalt (III) species [4]. Various structures for the latter compound were proposed [4], particularly concerning the nature of the peroxo binding to Co(III). These include monomeric, $\text{Co}(\text{O}_2)$, and dimeric, $\text{Co}_2(\text{O}_2)_2$, forms. On the basis of infrared studies, the monomeric structure was preferred raising questions about the inconsistency of infrared band activities related to such a structure [4]. The monomeric structure is considered a unique one for the peroxocobalt (III) species because most of the known peroxo complexes of cobalt (III) have the dimeric structure, $\text{Co}_2(\text{O}_2)_2$, with the peroxo group acting as a bridge between two Co(III) ions [5]. However, peroxo complexes with monomeric structures are also known [6, 7, 8] but with metal ions other than Co(III) such as Pt(II), Pd(II), Ni(II) and Nb(V).

Because of our interest in the vibrational studies of the dioxygen species of transition metals [9], we report here the infrared and Raman spectra of the title compound as well as the normal coordinate analysis for the $\text{Co}(\text{O}_2)$ unit. This enables an assessment of the type of structure and bonding particularly concerning the peroxo binding in the peroxocobalt (III) unit. This is of interest since the fact that the compound under study is insoluble in most com-

mon solvents, prevent the obtaining of crystal suitable for the X-ray structural studies. The study of the dioxygen complexes of cobalt is of importance because of their relation to the biological oxygen carriers such as Co(II)-vitamin B_{12} .

EXPERIMENTAL

Preparation of compounds. Pure grade reagents $\text{Co}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$, $\text{NaClO}_4 \cdot \text{H}_2\text{O}$ and H_2O_2 (30 %) were used without further purification. The 2, 2'-bipyridylamine (HL) was crystallized from ethanol before use. The parent compound $(\text{Co}(\text{HL})_3 (\text{ClO}_4)_2)$ as well as the peroxo compound $(\text{Co}(\text{O}_2) (\text{HL})_2 \text{ClO}_4)$ were prepared according to the published method [4]. All compounds were kept in a desiccator containing P_2O_5 .

Spectroscopic measurements. Raman spectra of the solid complexes $(\text{Co}(\text{HL})_3 (\text{ClO}_4)_2)$ and $(\text{Co}(\text{O}_2) (\text{HL})_2 \text{ClO}_4)$ were measured with a Jobin Yvon HG2 spectrometer using argon excitations. Because the samples are coloured, the use of conventional rotating solid discs as well as low concentrations (20 % by weight in KBr) and laser power were necessary in order to prevent decomposition by the laser beam.

Infrared spectra were recorded from the samples either as KBr discs or in Nujol mulls using a Pye Unicam SP 2000 spectrometer.

RESULTS AND DISCUSSION

The Raman and infrared spectra of the peroxo complex $(\text{Co}(\text{O}_2) (\text{HL})_2 \text{ClO}_4)$ are shown in Fig. 1. Their assignments may be considered by first examining the bonding and geometry of the complex. It is well known

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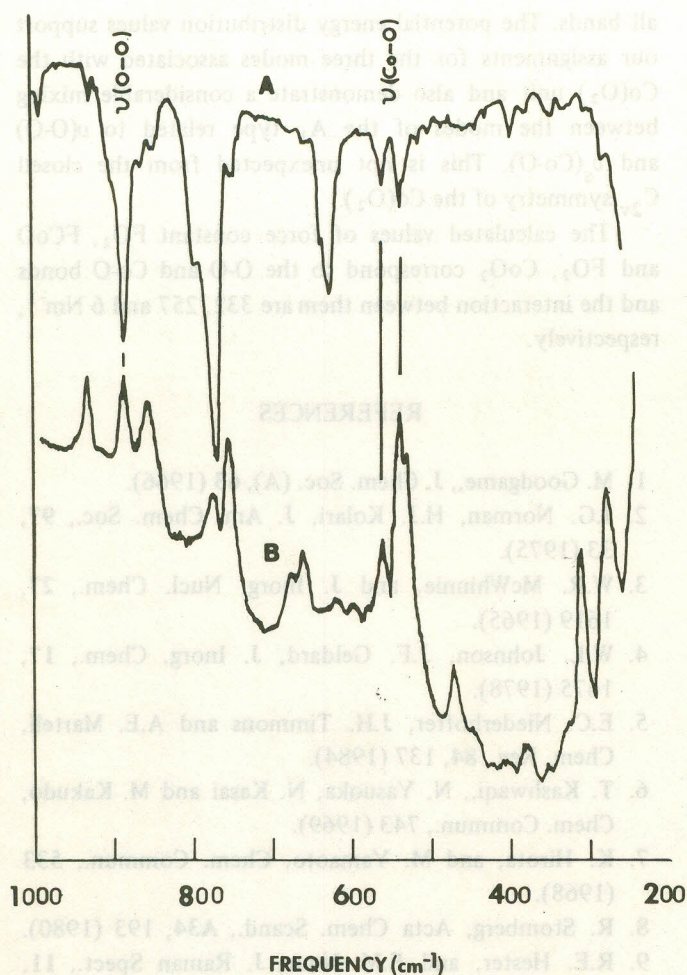
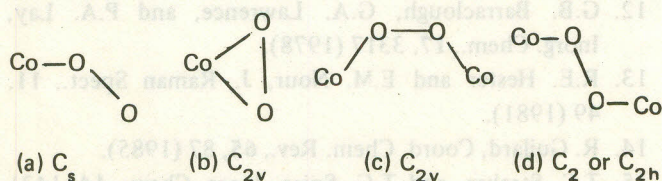


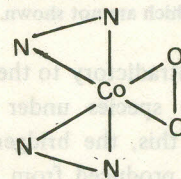
Fig. 1. Infrared (A) and Raman (B) Spectra of $(\text{Co}(\text{O}_2)(\text{HL})_2)\text{ClO}_4$ in KBr.

that the dioxygen-cobalt (III) complexes are classified into four main types [10].



where the dioxygen acts as a monodentate or a bidentate ligand. The nature of the peroxide binding to Co(III) in the complex under study may be examined from this point of view. Fig. 1 demonstrates that three vibrational modes are associated with the peroxocobalt unit and they are all active in both infrared and Raman spectra. Taking this into consideration and the fact that the Co(III): O_2^{2-} ratio is 1 : 1 and applying the symmetry selection rules (Table 1) lead to the conclusion that the peroxocobalt unit may possess either structure (a) or (b). In structure (a) the peroxy group acts as a monodentate; the unit has

the C_s symmetry and is expected to display 3 modes of vibrations of the type $3A'$ which are i.r. and Raman active. These are $\nu(\text{O-O})$, $\nu(\text{Co-O})$ and $\delta(\text{CoO}_2)$. In structure (b), the peroxy acts as a bidentate and the unit belongs to the C_{2v} symmetry. It is expected to display 3 vibrations of the type $2A_1 + B_2$. All are also i.r. and Raman active. These are classified as $\nu(\text{O-O})$; (A_1), $\nu_s(\text{Co-O})$; (A_1) and $\nu_{as}(\text{Co-O})$; (B_2) and are assigned as shown in Table 2. So both C_{2v} and C_s structures have the same vibrational activities and agree in the observation of both $\nu(\text{O-O})$ and $\nu(\text{Co-O})$ but differ in the nature of the third motion $\nu_{as}(\text{Co-O})$ of C_{2v} and $\delta(\text{CoO}_2)$ of C_s . The C_s symmetry structure (a) was ruled out on the basis that the $\delta(\text{CoO}_2)$ mode should occur at a much lower frequency [11] than observed (see Fig. 1). In addition the two low frequency bands around 565 and 542 cm^{-1} are characteristic of the Co-O vibrations [11, 12, 13] and should be assigned to $\nu_s(\text{Co-O})$ and $\nu_{as}(\text{Co-O})$, respectively. Normal coordinate analysis agrees with these assignments as will be discussed later in the text. All of these features support the C_{2v} symmetry structure (b) for the peroxocobalt unit in the $(\text{Co}(\text{O}_2)(\text{HL})_2)\text{ClO}_4$ within the configuration:



where $\text{N}-\text{N} = \text{HL}$. The C_{2v} structure of the $\text{Co}(\text{O}_2)$ unit was also observed in many other peroxometal species such as $\text{Pt}(\text{O}_2)(\text{PPh}_3)_2$, $\text{Pd}(\text{O}_2)(\text{tert-BuNC})_2$, $\text{Ni}(\text{O}_2)(\text{tert-BuNC})_2$, $\text{Ti}(\text{O}_2)\text{F}_5^{3-}$ and $\text{Nb}(\text{O}_2)\text{F}_5^{2-}$ [6, 7, 8, 14]. However, it should be mentioned that most of the known peroxocobalt (III) species are dimers having bridged structures with *cis* or *trans* configurations [5]: structures (c) and

Table 1. Infrared and Raman activities of peroxocobalt unit in each probable structure

Structure	Vibrations	Activity
Monomers (CoO_2):		
C_s	$3A'$	i.r., Raman
C_{2v}	$2A_1 + B_2$	i.r., Raman
Dimers (Co_2O_2):		
Planar: C_{2v}	$3A_1 + 2B_2$	i.r., Raman
	A_2	Raman
C_{2h}	$3A_g$	Raman
	$A_u + 2B_u$	i.r.
Non-planar: C_2	$4A + 2B$	i.r., Raman

Table 2. Stretching frequencies (cm^{-1}) for metal-peroxo species with triangular C_{2v} symmetry.

Compound	$\nu(\text{O-O})$	$\nu_s(\text{M-O})$	$\nu_{as}(\text{M-O})$	Ref.
$(\text{Co}(\text{O}_2)(\text{HL})_2)\text{ClO}_4$	890	565	542	present work
$\text{Pt}(\text{O}_2)(\text{Pph}_3)_2$	828	472		17
$\text{Pd}(\text{O}_2)(\text{tert-BuNC})_2$	893	484		17
$\text{Ni}(\text{O}_2)(\text{tert-BuNc})_2$	898	552	523	17
$\text{K}(\text{Ti}(\text{O}_2)\text{F}_3) \cdot 3\text{H}_2\text{O}$	860,900	610	530	18

Table 3. Observed and calculated frequencies (cm^{-1}), potential energy distributions and assignments for $(\text{Co}(\text{O}_2))$ in $(\text{Co}(\text{O}_2)(\text{HL})_2)\text{ClO}_4$.

Observed	Calculated	P.E.D.*		Assignments
		FO_2	FCoO	
890	891	83	17	83% $\nu(\text{O-O}) + 17\% \nu(\text{Co-O})$
565	566	16	84	84% $\nu(\text{Co-O}) + 16\% \nu(\text{O-O})$
542	542	-	100	$\nu_{as}(\text{Co-O})$

*Potential energy distributions totals 100 including contributions from interaction constants, which are not shown.

(d). This seems to be contradictory to the proposed monomeric structure for the species under study, $(\text{Co}(\text{O}_2)(\text{HL})_2)\text{ClO}_4$. To clarify this, the bridged peroxodicobalt (III) complexes were all produced from the oxidation of two $\text{Co}(\text{II})$ ions with molecular oxygen. This reaction depends in certain cases on the nature of the ligand coordinated to $\text{Co}(\text{II})$ and may also produce the monomer superoxocobalt (III) with structure a. Here, the dioxygen exists as superoxide, O_2^- , and is able to act only as a monodentate. The $\nu(\text{O-O})$ in this case occurs at a much higher value $\sim 1100 \text{ cm}^{-1}$ than that of the peroxide $800\text{-}900 \text{ cm}^{-1}$ [11, 15]. This is well understood on the basis of the increase of the electron density in the $\pi^*(\text{O}_2)$ in the case of O_2^{2-} compared with that of O_2^- . The monomeric complex under study was produced in a different way than that of the dimer. It was formed by the direct reaction of the peroxide (H_2O_2) with the cobalt complex.

Normal coordinate analysis. The analysis has been carried out for the $\text{Co}(\text{O}_2)$ unit under C_{2v} symmetry structure (b), using Wilson's GF matrix method [19] and based on a valence force field. The details of the calculations are similar to that described in previous communication [20]. The bond lengths of both O-O and Co-O were taken from related species [16]. Table 3 includes the observed and calculated frequencies, their potential energy distribution values as well as quantitative assignments for

all bands. The potential energy distribution values support our assignments for the three modes associated with the $\text{Co}(\text{O}_2)$ unit and also demonstrate a considerable mixing between the modes of the A_1 type related to $\nu(\text{O-O})$ and $\nu_s(\text{Co-O})$. This is not unexpected from the closed C_{2v} symmetry of the $\text{Co}(\text{O}_2)$.

The calculated values of force constant FO_2 , FCoO and FO_2 , CoO_2 correspond to the O-O and Co-O bonds and the interaction between them are 332, 257 and 6 Nm^{-1} , respectively.

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