Resonance-Raman Spectra and Excited-state Geometry of the Bis(μ-acetato)(μ-oxo) Ruthenium(III) Dimeric Ion $[Ru_2(\mu\text{-}O_2CMe)_2(\mu\text{-}O)(py)_6]^{2+}$ (py = pyridine)

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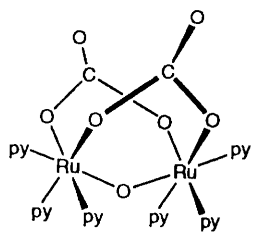
The Raman spectra of $[Ru_2(\mu\text{-}O_2CMe)_2(\mu\text{-}O)(py)_6][PF_6]_2$ (py = pyridine) at resonance with the π–π^* transition at 588 nm of the Ru–O–Ru bridge display a progression in ν_1, ν_{sym}(RuORu), 597 cm^{-1}, reaching $5\nu_1$ and five subsidiary progressions in ν_1. The spectra and associated excitation profiles have been used in conjunction with a transform method to establish that the Ru–O bond length increases by $\approx$1.2 pm on excitation to this excited state.

Diruthenium(III) complexes containing the bis(μ-acetato)(μ-oxo) moiety have been known since 1973 when Wilkinson and co-workers[1] synthesised $[Ru_2(\mu\text{-}O_2CMe)_2(\mu\text{-}O)(O_2CMe)_2(PPh_3)_2]$ as well as analogous compounds containing different carboxylate ligands, *viz.* $[Ru_2(\mu\text{-}O_2CR)_2(\mu\text{-}O)(O_2CR)_2(PPh_3)_2]$ (R = Et, Pr or Ph). Further diruthenium(III) bis(μ-carboxylato)(μ-oxo) complexes have recently been reported, namely $[Ru_2(\mu\text{-}O_2CR)_2(\mu\text{-}O)(L)_2]^{2+}$ (R = Me, CF_3, H, Ph, CCl_3 or CH_2Cl; L = 1,4,7-trimethyl-1,4,7-triazacyclononane),[2] $[Ru_2(\mu\text{-}O_2CMe)_2(\mu\text{-}O)(tpm)_2]$ [tpm = tris(pyrazolyl)methane][3] and $[Ru_2(\mu\text{-}O_2CC_6H_4OMe\text{-}p)_2(\mu\text{-}O)(O_2CC_6H_4OMe\text{-}p)_2(PPh_3)_2]$.[4] These compounds are of interest because they are analogues of the biologically important diiron core $[Fe_2(\mu\text{-}O_2CR)_2(\mu\text{-}O)]$ which occurs in haemerythrin, an iron-containing protein which has a much stronger affinity for oxygen than has haemoglobin.

The synthesis and crystal structure of $[Ru^{III}_2(\mu\text{-}O_2CMe)_2(\mu\text{-}O)(py)_6][PF_6]_2$ (py = pyridine), the compound under study in this paper, was reported in a preliminary account in 1988 by Sasaki *et al.*[5] and in a full report more recently.[6] Its crystal structure (see below) indicates that the Ru–O–Ru skeletal bond angle is 122.2°, which is similar to that of other complexes with the $Ru_2(\mu\text{-}O_2CMe)_2(\mu\text{-}O)$ core, but differs from that of complex ions with a $Ru_2(\mu\text{-}O)$ core and no bridging carboxylate ligands, *viz.* $[Ru_2OCl_{10}]^{4-}$,[7-9] and ruthenium red, $[Ru_3O_2(NH_3)_{14}]^{6+}$,[10,11] which have a linear Ru–O–Ru skeleton. The vibrational spectra, resonance-Raman spectra and excitation profiles of the ν_1, the symmetric Ru–O–Ru stretching mode ν_{sym}(RuORu), and of the $2\nu_1$ and $3\nu_1$ bands of $[Ru_2(\mu\text{-}O_2CMe)_2(\mu\text{-}O)(py)_6]^{2+}$ are now reported in order to obtain information about the bonding and structure in the ground and excited electronic states of this ion. The information has been obtained *via* an extension[12] of the transform method to the most general form which makes possible the determination of both the wavenumber of the resonance-enhanced Raman band in the resonant excited state and non-Condon factors simultaneously. The transform approach allows for the extraction of excited-state parameters on a mode-by-mode basis since the link between the observable absorption spectrum in the region of the resonant electronic state and the excitation profile of the enhanced Raman band involves parameters related to that vibrational mode only.



Experimental

The complex ion, in the form of the blue salt $[Ru_2(\mu\text{-}O_2CMe)_2(\mu\text{-}O)(py)_6][PF_6]_2$, was prepared according to the literature method,[6] and studied either in the solid state or in dichloromethane solution (Found: C, 37.3; H, 3.50; N, 7.85. Calc.: C, 37.1; H, 3.30; N, 7.65%). It is soluble in H_2O, MeCN and CH_2Cl_2, and slightly soluble in ethanol.

Raman spectra were recorded using a Spex 1401 spectrometer in conjunction with Coherent Innova argon-ion and krypton-ion lasers and a CR 590 dye laser employing rhodamine 6G. The laser powers at the sample were in the range 5–30 mW. The detection was by means of an RCA C31034 photomultiplier tube. Spectra were calibrated against the emission lines of neon. Selected spectra are shown in Fig. 1. The IR spectra were recorded as a KCl disc and bands observed at 562s, 698s (br), 760m, 838vs (br), 870w, 880s, 1015vw (br), 1045w, 1070m, 1160vw, 1224m, 1240vw, 1385vw, 1425w (br), 1450s, 1488m, 1532m (br) and 1610m cm^{-1}.

Electronic spectra of the compound in dichloromethane, recorded on a Cary 14 spectrometer, exhibited strong bands at 325 and 588 nm. The electronic spectra of the complex as a KBr disc did not exhibit any structure on being cooled from room temperature to 77 K, although the full width at half maximum of the band centred on 588 nm decreased from 3260 cm^{-1} to 3090 cm^{-1}.

Results

The strong electronic band at 588 nm is clearly due to an electric dipole allowed transition (ε = 10 000 dm^3 mol^{-1} cm^{-1}) which is considered,[6] by analogy with the assignments made for tris(pyrazolyl)methane complexes of ruthenium,[3] to be attributable to a Ru(d_π)–O(p_π) transition within the $\pi \rightarrow \pi^*$ network. Raman spectra taken at resonance with the 588 nm band display, as previously noted,[6] a strongly enhanced Raman band at 597 cm^{-1} attributable to ν_1, ν_{sym}(RuORu) (Fig. 2). The depolarization ratio (ρ) of the 597 cm^{-1} band is *ca.* 0.3 at resonance[13] and this indicates that the resonant transition is axially polarized. The spectra also show an overtone progression reaching to $5\nu_1$, and five two- to four-membered subsidiary progressions, based upon one quantum of the 1548,

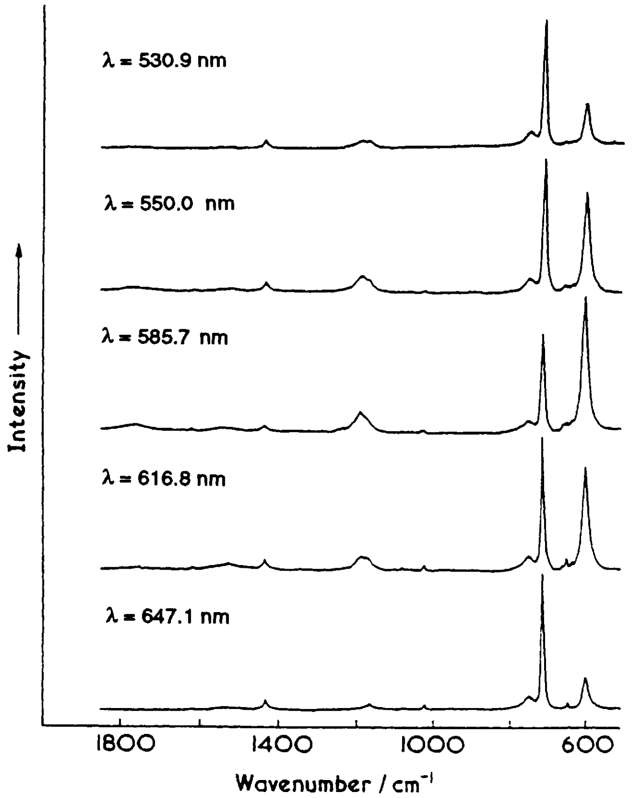


Fig. 1 Raman spectra of a solution of $[Ru_2(\mu\text{-}O_2CMe)_2(\mu\text{-}O)(py)_6][PF_6]_2$ in dichloromethane using different excitation wavelengths

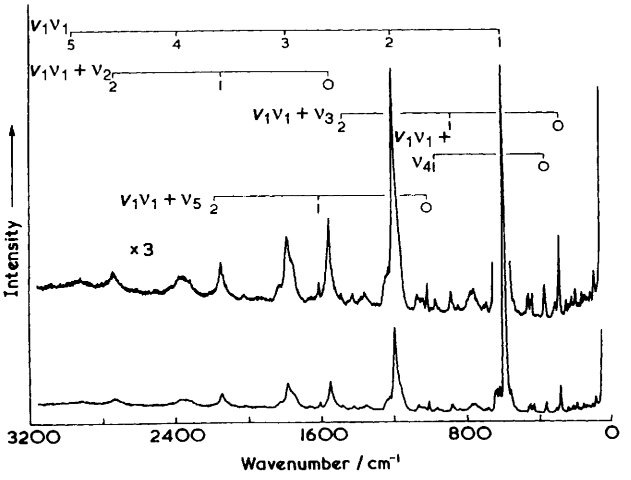


Fig. 2 Resonance-Raman spectrum of $[Ru_2(\mu\text{-}O_2CMe)_2(\mu\text{-}O)(py)_6][PF_6]_2$ as a solid with λ_0 = 568.2 nm (slits 200 μm, power 15 mW)

Table 1 Wavenumbers (cm^{-1}) of bands observed in the resonance-Raman spectrum of $Ru_2(\mu\text{-}O_2CMe)_2(\mu\text{-}O)(py)_6][PF_6]_2$

Band	Assignment
284wm	ν_3, δ(RuORu)?
366wm	ν_4
597vs (pol)*	ν_1, ν_{sym}(RuORu)
628 639 wm 648	ν_6
883w	$\nu_3 + \nu_1$
967vw	$\nu_4 + \nu_1$
1012w	ν_5
1194ms	$2\nu_1$
1224w ≈1240w	$\nu_6 + \nu_1$
1486w	$\nu_3 + 2\nu_1$
1548m	ν_2, py ring? (mode 8a, a_1, in C_{2v})
1605w	$\nu_5 + \nu_1$
1785w	$3\nu_1$
≈1830w (br)	$\nu_6 + 2\nu_1$
2075w	$\nu_3 + 3\nu_1$
2143w	$\nu_2 + \nu_1$
≈2206vw	$\nu_5 + 2\nu_1$
2364w	$4\nu_1$
≈2417vw (br)	$\nu_6 + 3\nu_1$
2731vw	$\nu_2 + 2\nu_1$
≈945vw (br)	$5\nu_1$

* Polarized, $\rho \approx 0.3$.

1012, 628, 366 and 284 cm^{-1} modes of the complex. The 1548 cm^{-1} band, designated here ν_2, is attributed to the ring mode 8a, a_1 in C_{2v} symmetry,[14] at 1580 cm^{-1} of co-ordinated pyridine, *cf.* the 1595 cm^{-1} band ν_{16}^{CC} a_{2g}, of benzene and the X-sensitive k mode of the halogenobenzenes (1603–1571 cm^{-1}).[15] The 1012 cm^{-1} band, designated ν_5, is attributed to the pyridine ring mode 12, a_1, which occurs at 1029 cm^{-1} for free pyridine.[15] The 628 cm^{-1} and associated bands, designated ν_6, are attributed to the pyridine ring mode 6a, a_2, which occurs at 605 cm^{-1} for free pyridine.[15] The 366 cm^{-1} band, designated ν_4, is attributed to the pyridine ring mode 16a, a_2, which occurs at 374 cm^{-1} for free pyridine; this is the lowest fundamental of pyridine.[15] The fifth subsidiary progression is based upon one quantum of the 284 cm^{-1} band, which is attributed to the symmetric Ru–O–Ru bend. Further weak progressions are also evident in the spectrum.

The wavenumbers of the overtone bands ($v_1\nu_1$) indicate that the ν_1 mode is distinctly anharmonic, the anharmonicity constant (x_{11}) being ≈ -2.3 cm^{-1}.

Discussion

The π bonding in complexes such as that studied here is usually discussed[3,6] in terms of two sets of Ru d_π–(μ-O p_π)–Ru d_π interactions, one parallel (π_1) and one perpendicular (π_2) to the Ru–O–Ru plane. Each set gives rise to one bonding (b), one essentially non-bonding (nb), and one antibonding orbital. The 10 π electrons of the bent RuORu entity are accordingly distributed as follows $(\pi_1^{b})^2(\pi_2^{b})^2(\pi_1^{nb})^2(\pi_2^{nb})^2(\pi_1^{*})^2(\pi_2^{*})^0$, the lowest transitions being to the empty π_2^* orbital.

The resonance-Raman results (Table 1) indicate that there is a substantial change to the Ru–O bond lengths on excitation to the π* state, and that there are also very slight changes to the geometry of the pyridine rings (doubtless to those which are *trans*, and therefore more effectively coupled, to the Ru–O–Ru π-bond system) and also to the Ru–O–Ru angle. The involvement of the X-sensitive k mode of the co-ordinated pyridine rings in combination band progressions with ν_1 is, perhaps, surprising. However, the angle between each pyridine ring and the Ru_2O plane[6] is only *ca.* 24°, implying the possibility of significant π-bond coupling of the rings to the Ru_2O bridge. Moreover there are precedents for the involvement of ring modes as enabling modes for progressions, *viz.* of the k mode of triphenylphosphine in the Raman spectra of the dirhodium complex $[Rh_2(O_2CMe)_4(PPh_3)_2]$,[16] and the X-sensitive p, q, r, t and y modes of triphenylarsine and triphenylstibene in the Raman spectra of the analogous complexes with $AsPh_3$ or $SbPh_3$.[17]

The excitation profiles of ν_1, $2\nu_1$ and $3\nu_1$ over the range 460–676 nm (Fig. 3) each closely match the electronic spectrum of the complex ion in the region of its π–π* band centred at 588 nm. Both from the fit between the calculated and experimental profiles of the $v_1\nu_1$ bands[18] and from the relative intensities of the first four harmonics of the ν_1 band[12] it is possible to

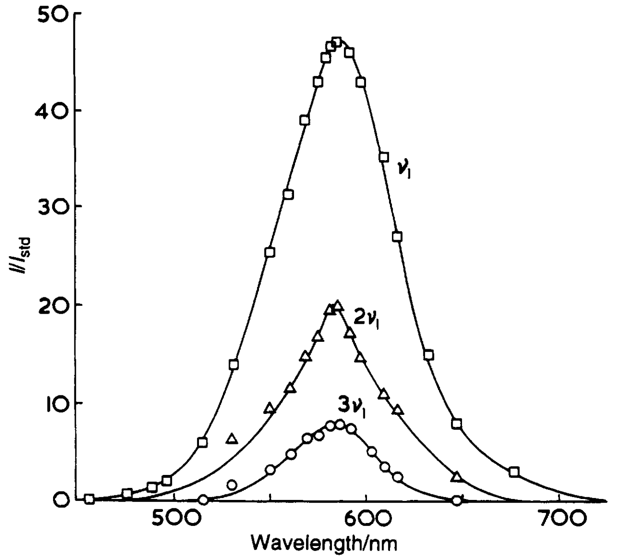


Fig. 3 Excitation profiles of ν_1, ν_{sym}(RuORu), and its first ($2\nu_1$) and second ($3\nu_1$) overtones for the complex ion $[Ru_2(\mu\text{-}O)(\mu\text{-}O_2CMe)_2(py)_6]^{2+}$ in solution in CH_2Cl_2, the intensity reference being the ν_{sym}(CCl) band of the solvent

calculate the Ru–O bond length change on excitation. The results of this analysis are outlined below.

The complex polarisability, α, depends, in a quadratic electron–phonon coupling, linear non-Condon (NC) model, on three parameters: the nuclear displacement upon excitation, Δ, the vibrational wavenumber of the mode of interest in the excited electronic state, ν_e, and the linear non-Condon parameter m.[13] The resonance-Raman band intensity, I, of each harmonic, j, depends linearly on the square modulus of the complex polarisability. Thus the following system of simultaneous equations can be written,

$$C|\alpha_j^{NC}(\nu_0, \Delta, \nu_e, m)|^2 = I_j, j = 1, 2, 3 \text{ or } 4 \qquad (1)$$

where C is a proportionality constant and ν_0 is the wavenumber of the excitation line. The solution of the above system $\{\Delta, \nu_e, m, C\}$, contains the parameters of interest as a subset $\{\Delta, \nu_e, m\}$ solution of equation (2).

$$\sum_{i=2}^{4}\left(\left|\frac{\alpha_i}{\alpha_1}\right|^2 - \frac{I_i}{I_1}\right)^2 = 0 \qquad (2)$$

Equation (2) is difficult to solve by classical methods (*e.g.* steepest descent or Newton) because it is implicit in one unknown (ν_e) and non-linear in another (Δ). However, the minimum in the function $X(\Delta, \nu_e, m)$, equation (3), can be found

$$X(\Delta, \nu_e, m) = \sum_{i=2}^{4}\left(\left|\frac{\alpha_i}{\alpha_1}\right|^2 - \frac{I_i}{I_1}\right)^2 \qquad (3)$$

across a multidimensional grid spanning the range of interest in (Δ, ν_e, m) space. The minimum found for X (0.0012) corresponds to the values $\nu_e = 517\ \text{cm}^{-1}$, $\Delta = 2.5$ pm, and $m = -0.025$. Applying to these results the precision estimated for the experiment ($\pm 5\%$ on the band intensities I_1–I_4), the parameters are estimated to have the values $\nu_e = 517 \pm 5\ \text{cm}^{-1}$, $\Delta = 2.5 \pm 0.5$ pm, and $m = -0.025 \pm 0.01$.

The calculated excitation profile of the fundamental (ν_1) is consistently higher than the experimental one on the high-wavenumber side (see Fig. 4). However it was found that a closer fit between the calculated and experimental excitation profiles of the fundamental (ν_1) resulted in a reduction in the intensity of the calculated excitation profile of the first overtone ($2\nu_1$), and this then gave a worse fit between the calculated and experimental profiles of $2\nu_1$. This highlights the importance of calculating the best fit to the excitation profile of the overtone in addition to that of the fundamental.

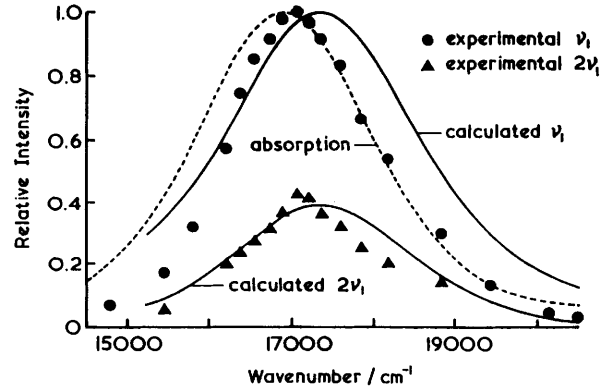


Fig. 4 Calculated (full lines) and experimental excitation profiles of the ν_1 (●) and $2\nu_1$ (▲) bands of the ion, together with the absorption spectrum (– – – –)

The nuclear displacement, Δ, corresponds to the vector component of the nuclear motion along the bisector of the Ru–O–Ru angle, since the calculated fits are for the symmetric Ru–O stretching mode (ν_1) and its overtone ($2\nu_1$). Thus the Ru–O bond (equilibrium bond length 186 pm)[6] is estimated to lengthen by 1.2 ± 0.3 pm in the resonant excited state.

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