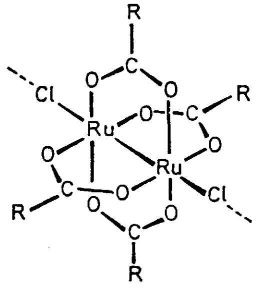
Resonance Raman Spectra of Chlorotetra-acetato- and Chlorotetra-butyrato-diruthenium

By **Robin J. H. Clark** * and **Malcolm L. Franks**, Christopher Ingold Laboratories, University College, London WC1H 0AJ

The metal–metal bonded species $[Ru_2Cl(O_2CMe)_4]$ and $[Ru_2Cl(O_2CPr)_4]$ both display a resonance Raman spectrum when irradiated with exciting lines which approach the wavenumber of the first electronic band maximum of each compound. The spectra are characterised in both cases by an overtone progression in the metal–metal stretching frequency, ν_1(Ru–Ru) a_{1g}, reaching $5\nu_1$ for $[Ru_2Cl(O_2CMe)_4]$ and $4\nu_1$ for $[Ru_2Cl(O_2CPr)_4]$. Additionally, in the case of $[Ru_2Cl(O_2CMe)_4]$ a second progression has been observed, extending as far as $\nu_2 + 3\nu_1$, where ν_2 is the ν_2(Ru–O) a_{1g} fundamental. The observation of such overtone progressions permits the determination of the spectroscopic constants ω_1 and x_{11} for each molecule. The results form the basis for reassigning the electronic band in the visible region (the resonant electronic transition) of these compounds to the $b_{1u} \leftarrow b_{2g}$ ($\delta^* \leftarrow \delta$) transition of the ruthenium–ruthenium moiety.

RESONANCE Raman (r.r.) spectra are observed when a molecule in the gaseous state under high pressure or in a condensed state is excited with a laser line whose frequency corresponds or closely corresponds with the band maximum of an allowed electronic transition of the molecule. Normally such spectra are characterised by an enormous enhancement in the intensity of a totally symmetric fundamental of the molecule together with the appearance of high-intensity overtone progressions in this same fundamental.[1-5]

Several metal–metal bonded systems have been shown to display the r.r. effect because their allowed electronic transitions are readily accessible with the excitation frequencies available and because multiple metal–metal bonds are highly polarisable. So far the only detailed r.r. studies on such systems have been on ions of the type $[M_2X_8]^{n-}$, namely the $[Mo_2Cl_8]^{4-}$ ion [6,7] and the $[Re_2Cl_8]^{2-}$ and $[Re_2Br_8]^{2-}$ ions.[8] In these cases, long overtone progressions in the ν_1(M–M) a_{1g} fundamental are observed by exciting a Raman spectrum of each ion with a laser line whose wavenumber closely corresponds with that of the intense 'metal–metal' transition $b_{1u} \leftarrow b_{2g}$ ($\delta^* \leftarrow \delta$) [7-10] of the ion ($D_{4h}$ nomenclature). The carboxylate-bridged, chlorine-bridged species $[Ru_2Cl(O_2CMe)_4]$ and $[Ru_2Cl(O_2CPr)_4]$ (I) both show a single broad band in their diffuse-reflectance spectra (at *ca.* 21 000 cm^{-1}) [11,12] assigned as $a_{1g} \leftarrow b_{2g}$ ($\sigma_n \leftarrow \delta$) and/or $a_{2u} \leftarrow b_{2g}$ ($\sigma_n' \leftarrow \delta$) [12] and hence electric-dipole forbidden. In the light of recent studies on metal–metal bonded systems,[7,8,10] for which the original molecular-orbital (m.o.) diagram [12,13] has been shown to be incorrect, this assignment becomes questionable. As r.r. spectra have thus far only been observed,[5] and are only expected to be observed,[14] for systems in which the resonant electronic transition is electric-dipole allowed, r.r. spectroscopy can be used as a tool in the assignment of the electronic structure of the compounds $[Ru_2Cl(O_2CMe)_4]$ and $[Ru_2Cl(O_2CPr)_4]$. The Raman spectra of these compounds have thus been investigated with a variety of exciting lines. In both cases r.r. spectra have been observed, in particular overtone progressions in the ν_1(Ru–Ru) a_{1g} fundamental. The observation of these overtone progressions implies that the 21 000 cm^{-1} electronic transition is electric-dipole allowed, it allows the determination of the spectroscopic constants ω_1 and x_{11} for these carboxylate-bridged, approximately D_{4h}, systems, and it hence affords a comparison with the $[M_2X_8]^{n-}$ D_{4h} system.



(I)

EXPERIMENTAL

Preparation of Samples.—The compounds $[Ru_2Cl(O_2CMe)_4]$ and $[Ru_2Cl(O_2Pr)_4]$ were prepared by the method of Stephenson and Wilkinson.[11]

Instrumental Details.—The Raman spectra were recorded using a Spex 1401 spectrometer in conjunction with Coherent Radiation model 52 Ar$^+$ and Kr$^+$ lasers as described in

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[2] W. Kiefer and H. J. Bernstein, *Mol. Phys.*, 1972, **23**, 835.

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[11] T. A. Stephenson and G. Wilkinson, *J. Inorg. Nuclear Chem.*, 1966, **28**, 2285.

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detail elsewhere.[7] The rotating-sample technique [15,16] was employed and spectra were calibrated by reference to the emission lines of neon which were superimposed directly on to the spectra while they were recorded. There was no evidence of irradiation-produced decomposition. The wavenumbers are accurate to ± 0.5 cm^{-1} for sharp bands and ± 1 cm^{-1} for broader bands. Diffuse-reflectance spectra of the powdered solids were obtained by use of a Cary 14 spectrometer. Infrared spectra were recorded on a Perkin-Elmer 225 spectrometer (to 200 cm^{-1}) as Nujol mulls.

RESULTS AND DISCUSSION

Fundamental Frequencies.—When the compounds $[Ru_2Cl(O_2CMe)_4]$ and $[Ru_2Cl(O_2CPr)_4]$ were excited in the solid state with Kr^+ 647.1-nm radiation, which is well removed from the lowest allowed electronic transition of both molecules (ν_e),[12] a normal Raman spectrum was obtained (Figure 1). The wavenumbers of the Raman bands in the fundamental region, together with the i.r. spectral bands and suggested assignments, are given in Table 1.

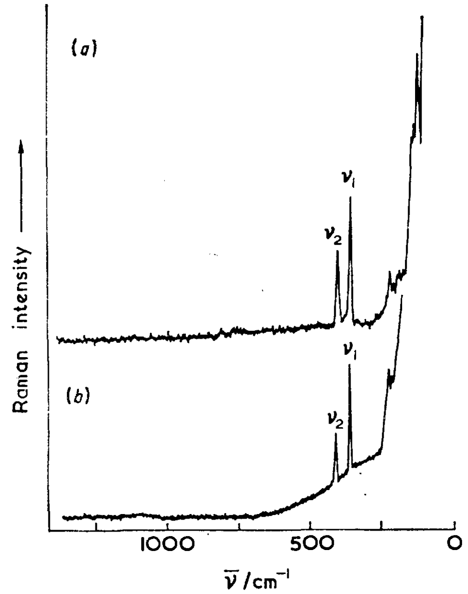

FIGURE 1 Solid-state Raman spectra of (*a*) $[Ru_2Cl(O_2CMe)_4]$ and (*b*) $[Ru_2Cl(O_2CPr)_4]$ obtained with Kr^+ 647.1-nm excitation. Slit widths 2 cm^{-1} for (*a*) and 4 cm^{-1} for (*b*)

The Raman-active a_{1g} ruthenium–oxygen stretching fundamental, designated ν_2, almost certainly gives rise to the band at 369.1 {$[Ru_2Cl(O_2CMe)_4]$} or 376.5 cm^{-1} {$[Ru_2Cl(O_2CPr)_4]$}, these being typical values for metal–oxygen stretching frequencies in compounds of this nature.[17,18] By a similar token, the observed i.r. bands in this spectral region are also assigned as ruthenium–oxygen stretching vibrations.

The most intense Raman band, that at 327.3 {$[Ru_2Cl(O_2CMe)_4]$} (previously reported to be at 337 cm^{-1}) [19] or 330.8 cm^{-1} {$[Ru_2Cl(O_2CPr)_4]$} is assigned as the ν_1 (a_{1g}) (Ru–Ru) stretching vibration for the following reasons: (*a*) in many cases the strongest band in the Raman spectra of metal–metal bonded systems is the metal–metal stretching frequency; and (*b*) the only other possible assignment for this band would be to the totally symmetric ruthenium–chlorine stretching vibration. However, the Ru–Cl bond length is 2.587 Å [12] which is much larger than the value of *ca.* 2.35 Å usually observed for most ruthenium(III) chloro-complexes,[20] and this is indicative of only a weak Ru–Cl interaction. One characteristic feature of carboxylate dimers is this weak interaction between the metal atom and the ligands bonded *trans* to the metal–metal bond [12] and this results in a correspondingly low metal–ligand stretching frequency. For example $[Re_2Cl_2(O_2CMe)_4]$ [17] exhibits the a_{1g} (Re–Cl) stretching fundamental at 199 cm^{-1}, whereas in the $[Re_2Cl_8]^{2-}$ ion[8] $\nu(a_{1g})$ (Re–Cl) occurs at 356.5 cm^{-1}. A value of *ca.* 330 cm^{-1} would thus be highly improbable for a ruthenium–chlorine stretching fundamental; however, it would appear reasonable to assign the bands at 180.5 {$[Ru_2Cl(O_2CMe)_4]$} and 183.7 cm^{-1} {$[Ru_2Cl(O_2CPr)_4]$} to this fundamental.

TABLE 1

Infrared and Raman bands (cm^{-1}) in the spectra of $[Ru_2Cl(O_2CMe)_4]$ and $[Ru_2Cl(O_2CPr)_4]$ in the solid state*

	$[Ru_2Cl(O_2CMe)_4]$		$[Ru_2Cl(O_2CPr)_4]$	
Assignment	Raman	I.r.	Raman	I.r.
ν(Ru–O)		400s		460s
	369.1m		376.5vw	
		345m (sh)		376m
		338s		344m
ν(Ru–Ru)	327.3s		330.8s	
ν(Ru–Cl)	180.5w		183.7w	
Skeletal bends and lattice modes	161w			
	112w			
	106w			
	97w			

* s = Strong, m = medium, w = weak, vw = very weak, and sh = shoulder. Unassigned bands appear at 296vw and 253vw cm^{-1} in the Raman spectrum of $[Ru_2Cl(O_2CMe)_4]$ and 240m cm^{-1} in that of $[Ru_2Cl(O_2CPr)_4]$. Other spectral bands are due to ligand fundamentals.

Resonance Raman Spectra.—The Raman spectrum of the compounds $[Ru_2Cl(O_2CMe)_4]$ and $[Ru_2Cl(O_2CPr)_4]$ in the solid state depended markedly on the wavenumber of the exciting line. With the Kr^+ 647.1-nm exciting line a normal Raman spectrum is obtained as discussed earlier. However, with the Kr^+ 530.9-nm and the Ar^+ 514.5-, 488.0-, 476.5-, and 457.9-nm exciting lines, which are all within the envelope of the lowest allowed electronic transition (Figure 2 shows the diffuse-reflectance spectra of the two compounds under study), a r.r. spectrum was obtained. This spectrum is characterised

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[15] W. Kiefer and H. J. Bernstein, *Appl. Spectroscopy*, 1971, **25**, 501.

[16] R. J. H. Clark, *Spex Speaker*, 1973, **18**, 1.

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[20] T. E. Hopkins, A. Zalkin, D. H. Templeton, and M. G. Adamson, *Inorg. Chem.*, 1966, **5**, 1427, 1431.

by an enormous enhancement in the intensity of the ruthenium–ruthenium totally symmetric stretching fundamental $\nu_1(a_{1g})$ together with the appearance of an overtone progression reaching $5\nu_1$ (previously reported, with approximate frequencies to $3\nu_1$)[19] for $[Ru_2Cl(O_2CMe)_4]$ and $4\nu_1$ for $[Ru_2Cl(O_2CPr)_4]$ (in both cases observed with 514.5-nm excitation). These r.r. spectra are illustrated in Figure 3, and the wavenumbers and half band widths of the ν_1(Ru–Ru) fundamental and its overtones are given in Table 2. The overtones in both cases display the characteristic features[2] of the r.r. effect, *i.e.* continuous increase in half band width (as illustrated in Figure 4) and continuous decrease in band area with increase in the vibrational quantum number (v_1) as observed recently for the spectra of, for example, the $[AuBr_4]^-$ ion[21] and the $[S_3]^-$ ion.[22] In the case of $[Ru_2Cl(O_2CMe)_4]$ a second, much weaker, progression $\nu_2 + v_1\nu_1$ was also evident in the r.r. spectrum, reaching as far as $v_1 = 3$ for 514.5-nm excitation. The frequencies and half band widths for each member of this progression are also given in Table 2. Further progressions have previously been observed for, for example, the $[Mo_2Cl_8]^{4-}$ ion[7] and the $[Re_2Cl_8]^{2-}$ and $[Re_2Br_8]^{2-}$ ions.[8]

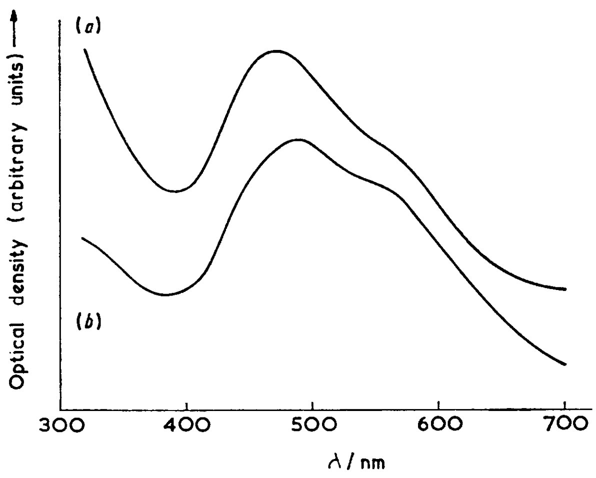

FIGURE 2 Diffuse-reflectance spectra of (*a*) $[Ru_2Cl(O_2CMe)_4]$ and (*b*) $[Ru_2Cl(O_2CPr)_4]$

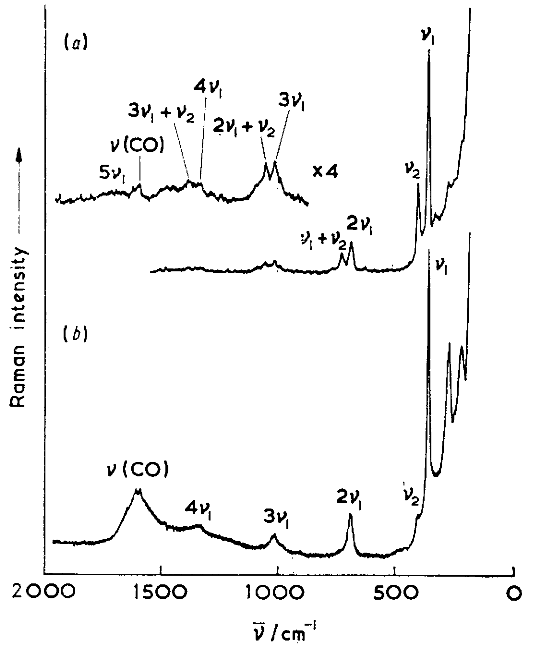

FIGURE 3 Resonance Raman spectra of (*a*) $[RuCl(O_2CMe)_4]$ and (*b*) $[Ru_2Cl(O_2CPr)_4]$ in the solid state, obtained with Ar^+ 514.5-nm excitation. Slit widths 250, 350, and 250 μm (5 cm⁻¹)

TABLE 2

Wavenumbers and half band widths (cm⁻¹) of the ν(Ru–Ru), $\nu_1(a_{1g})$, fundamental and its overtones and members of the $\nu_2 + v_1\nu_1$ progression in the r.r. spectra of the compounds $[Ru_2Cl(O_2CMe)_4]$ and $[Ru_2Cl(O_2CPr)_4]$*

	$[Ru_2Cl(O_2CMe)_4]$		$[Ru_2Cl(O_2CPr)_4]$	
Band	Max	$\Delta\nu_{1/2}$	Max	$\Delta\nu_{1/2}$
ν_1	327.3	10	330.8	10
$2\nu_1$	654.4	18	661.1	23
$3\nu_1$	981.5	30	990.8	37
$4\nu_1$	1 307.5	45	1 320	54
$5\nu_1$	1 634	65		
ν_2	369.1	11	376.5	11
$\nu_2 + \nu_1$	694.7	18		
$\nu_2 + 2\nu_1$	1 020	33		
$\nu_2 + 3\nu_1$	1 345	50		

* Other bands of higher frequency observed in the spectra are due to ligand fundamentals.

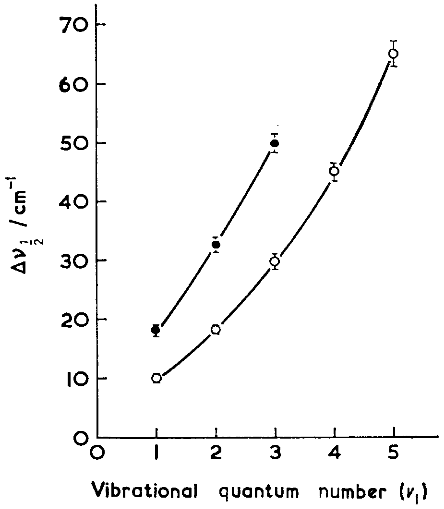

FIGURE 4 Half band widths for the $\nu_1(a_{1g})$ fundamental and for the members of the $v_1\nu_1$ (○) and $\nu_2 + v_1\nu_1$ (●) progressions as deduced from the resonance Raman spectrum of the compound $[Ru_2Cl(O_2CMe)_4]$

By contrast with the solid-state r.r. spectra described above, the signal-to-noise ratio on the r.r. spectrum of $[Ru_2Cl(O_2CPr)_4]$ in ethanol solution was poor. The scattering species is, of course, different in this medium, being the $[Ru_2(O_2CPr)_4]^+$ ion, for which the lowest allowed electronic transition is at 425 nm (23 500 cm⁻¹)

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[21] Y. M. Bosworth and R. J. H. Clark, *J.C.S. Dalton*, 1975, 381.

[22] R. J. H. Clark and M. L. Franks, *Chem. Phys. Letters*, 1975, **34**, 69.

with $\varepsilon = 830$ dm^3 mol^{-1} cm^{-1}. Available exciting lines are accordingly further removed from the band maximum than is the case in the solid state, leading to less effective resonance. Moreover, fluorescence background effects obscured any Raman bands above *ca.* 400 cm^{-1}. Thus only ν(Ru–Ru) at 341 cm^{-1} could be located in solution as a strongly polarised band (ρ 0.12 ± 0.03 at 514.5 nm). It is also worth noting that the 10 cm^{-1} upward shift in ν(Ru–Ru) on going from the solid state to solution is consistent with the removal of the axial bridging chlorine atoms and thus with stronger Ru–Ru bonding, *cf.* the related situation in oxovanadium(IV) species for which co-ordination of a ligand *trans* to the triply bonded $[VO]^{2+}$ entity leads to a lowering in ν(VO).[23]

Harmonic Frequencies and Anharmonicity Constants.—The observation of an overtone progression in the ν_1(Ru–Ru) a_{1g} fundamental for each compound enables a determination of the harmonic frequency (ω_1) and the anharmonicity constant (x_{11}) to be made. The observed wavenumber, $\nu(v_1)$ for any overtone of an anharmonic oscillator is given by expression (1) [24] where $G(v_1)$ is the term

$$\begin{aligned}\nu(v_1) &= G(v_1) - G(0)\\ &= v_1\omega_1 + x_{11}(v_1^2 + v_1) + \ldots \qquad (1)\end{aligned}$$

value of the v_1th vibrational level. The higher terms are considered to be partly responsible for the increase in half band width with increase in vibrational quantum number.[4] Hence ω_1 and x_{11} may be obtained from a plot of $\nu(v_1)/v_1$ against v_1 and the results of the least-squares analysis are shown in Table 3.

TABLE 3

Harmonic frequencies * and anharmonicity constants (cm^{-1}) for the compounds $[Ru_2Cl(O_2CMe)_4]$ and $[Ru_2Cl(O_2CPr)_4]$

	$v_1\nu_1$ Progression		$\nu_2 + v_1\nu_1$ Progression	
Compound	ω_1	x_{11}	ω_1	x_{11}
$[Ru_2Cl(O_2CMe)_4]$	327.6 ±0.5	−0.13 ±0.02	325.8 ±0.6	−0.14 ±0.02
$[Ru_2Cl(O_2CPr)_4]$	331.4 ±0.5	−0.27 ±0.03		

* Higher terms in the general expression for $\nu(v_1)$ contribute to a change of intercept and they therefore, if significant, restrict the accuracy to which the ω_1 values can be evaluated.

The value of ω_1 derived from the $v_1\nu_1$ progression is slightly larger for $[Ru_2Cl(O_2CPr)_4]$, which has rather bulkier alkyl ligands attached to the metal atom, than it is for $[Ru_2Cl(O_2CMe)_4]$. The difference, however, is very small and is presumably a lattice effect. In the case of $[Ru_2Cl(O_2CMe)_4]$, the second progression allows an additional determination of ω_1 and x_{11}. The value of ω_1 obtained is considerably less than that for the $v_1\nu_1$ progression. This difference is a direct although rather imprecise measure of the cross term x_{12} in the expression for energy: thus x_{12} is *ca.* 2 cm^{-1}. This value is significantly larger than previous values of corresponding cross terms,[7,21,22] even taking into consideration the lower accuracy for data from the $\nu_2 + v_1\nu_1$ progression.

The anharmonicity constants x_{11} are very small, and this appears to be a common feature of fundamentals displaying the r.r. effect. The x_{11} values obtained from the two progressions found for $[Ru_2Cl(O_2CMe)_4]$ are almost identical and in both cases lower than that found for $[Ru_2Cl(O_2CPr)_4]$. It is also worth noting that these values are significantly lower than those found for the $[M_2X_8]^{n-}$ skeleton.[7,8]

Conclusion.—The observation of a r.r. spectrum [specifically a progression in ν(Ru–Ru)] on bringing the excitation frequency into near coincidence with that of the lowest electronic band observed in the diffuse-reflectance spectra of these compounds (464 nm = 21 550 cm^{-1} for the acetate and 490 nm = 20 400 cm^{-1} for the butyrate) makes it clear that this electronic band is electric-dipole allowed. Accordingly it must be assigned to the $b_{1u} \leftarrow b_{2g}$ ($\delta^* \leftarrow \delta$) transition and not to the $\sigma_n \leftarrow \delta$ transition,[12] which would be electric-dipole forbidden. The paramagnetism of the compounds, which is indicative of three unpaired electrons per pair of metal atoms, is thus plausibly accounted for by the following electron configuration for this pair of atoms: $a_{1g}(\sigma)^2 e_u(\pi)^4 b_{2g}(\delta)^2\ b_{1u}(\delta^*)^1 e_g(\pi^*)^2$ (see Figure 5).

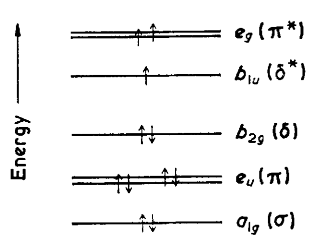

FIGURE 5 Qualitative molecular-orbital diagram for the compound $[Ru_2Cl(O_2CR)_4]$ assuming D_{4h} skeletal symmetry. The distribution of the 11 valence electrons of the Ru_2 moiety is indicated

The existence of 11 valence electrons and a common non-integral oxidation state for the ruthenium atoms of 2.5 is, of course, unaffected by this band reassignment.

The technique of r.r. spectroscopy is thus seen to be a valuable tool, not only for the evaluation of spectroscopic constants of totally symmetric vibrations, but also for the elucidation of assignments of electronic spectral bands.

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[6/350 *Received, 18th February,* 1976]

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