(Figure 1) and may equally be treated as a strain with δ_s = 90 and 270° (eq 12). Molecular fields of this symmetry seem still to be important at $x < 0.4_5$, however, if Cu^{2+} clusters above a certain critical size are considered only. Thus the observaton of two types of EPR signals in the intermediate concentration range indicates the presence of clusters above and below this critical size. This latter argument explains reasonably well the discontinuity in the shift of the φ parameters (Figure 11). The change in the elastic forces between the CuF$_6$ polyhedra due to the substitution of Zn^{2+} by Cu^{2+} ions is considerable in this specific host structure, which is related to the perovskite type. Similarly strong variations of the local distortions in dependence on the concentration of the Jahn–Teller cations have been observed in various other mixed-crystal series.[1,24]

The energy of the radial vibrations $\hbar\omega$ is calculated to be $\simeq$200 cm^{-1} for $x = 1$ and $\simeq$250 cm^{-1} for $x < 0.10$ (eq 5). These values seem reasonable in magnitude for metal–ligand vibrations in this type of compound. The angular energy, which induces the thermal fluctuation between the two sublattices can be estimated from eq 14[2] which holds for large values of $4E_{JT}\beta/(\hbar\omega)^2$. For K$_2CuF_4$ one obtains $\hbar\omega' \simeq 125$ cm^{-1}.

$$\hbar\omega' = 3\left(\frac{\beta}{2E_{JT}}\right)^{1/2}\hbar\omega \qquad (14)$$

It is finally interesting to compare the dynamic behavior in the low concentration range with the one described by Silver and Getz.[25] While in our system complete motional narrowing between minima of *equal* energies occurs, there is a small energy difference between them in Cu^{2+}-doped Tutton salts, which is obviously induced by an *orthorhombic* host lattice strain. The **g** tensor is orthorhombic but exhibits a tendency toward tetragonal symmetry with increasing temperature due to extensive thermal population of the higher of the two levels. The EPR spectra of the stochiometric complex Cu(terpy)$_2$Br$_2$·3H$_2$O exhibit a similar behavior with incomplete motional narrowing even at high temperatures.[22] After all Ba$_2$Cu$_x$Zn$_{1-x}$F$_6$ mixed crystals with $x < 0.3$ are the only systems so far described, in which Cu^{2+} occupies a tetragonally compressed site with a pure d$_{z^2}$ ground state.[1,3]

The assignment of the electronic transitions in the ligand field spectra, in particular at low Cu^{2+} concentrations, remains doubtful (Figure 8). The change of φ with increasing x is not reflected by any variation of the intensity distribution or additional splittings, as one would expect on the basis of the EPR results. The same observation was made for the Ba$_2$Zn$_{1-x}$Cu$_x$F$_6$ mixed crystals.

Acknowledgment. We gratefully acknowledge the measuring facilities at the Institut für Angewandte Kernphysik, Kernforschungszentrum Karlsruhe, and thank Dr. S. Klein for recording the neutron diffraction diagrams. D.R. appreciates the hospitality of Professor Hagenmuller and Dr. Tressaud during a sabbatical stay at the University of Bordeaux, in which this paper was written. We also would like to thank Drs. M. A. Hitchman and C. Friebel for valuable discussions.

Registry No. K$_2$ZnF$_4$, 37732-22-2; K$_2$CuF$_4$, 17712-46-8; Rb$_2$ZnF$_4$, 35944-46-8; Rb$_2$CuF$_4$, 17712-47-9.

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Resonance Raman, Excitation Profile, and Electronic Structural Studies of Diruthenium Tetracarboxylate Complexes

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Received October 8, 1980

The resonance Raman spectra of the diruthenium carboxylate complexes Ru$_2$(O$_2$CCH$_3$)$_4$Cl, [Ru$_2$(O$_2$CCH$_3$)$_4$(H$_2$O)$_2$]$^+$BF$_4^-$, Ru$_2$(O$_2$CH)$_4$Cl, Ru$_2$(O$_2$CC$_2$H$_5$)$_4$Cl, and Ru$_2$(O$_2$CC$_3$H$_7$)$_4$Cl have been recorded, at room temperature as well as at ca. 80 K, with exciting lines of wavenumber in the region of the electronic band which lies at ~21 000 cm^{-1} for each complex. The Raman band which is the most resonance enhanced in each case is that at 326–340 cm^{-1}. On the basis of studies of its depolarization ratio and of its lack of sensitivity to ^{18}O substitution in the case of the acetate complex, this band is assigned to the $\nu_1(a_{1g})$ fundamental, the Ru–Ru stretching mode (in D_{4h} nomenclature). A second band, at 369–432 cm^{-1}, has its intensity modified (although to a lesser extent) when the complexes are irradiated in the 21 000-cm^{-1} region. This band is also polarized, and on the basis of its shift (~5–13 cm^{-1}) on ^{18}O substitution of the acetate complex, the band is unambiguously assigned to the $\nu_2(a_{1g})$ fundamental, the symmetric Ru–O stretching mode. The excitation profiles of these two Raman bands of each complex are discussed. These results, together with polarization dispersion results, imply that the resonant electronic transition is electric-dipole allowed in axial (z) polarization, a result which is in agreement with a recent molecular orbital treatment in which the transition was given the assignment $6e_u \rightarrow 6e_g$, O(π) $\rightarrow \pi^*$. Excitation to the π^* state would lead to a decrease in Ru–Ru as well as in Ru–O π bonding and thus to a lengthening of both Ru–Ru and Ru–O bonds in the $6e_g$ excited state. On resonance with the $6e_u \rightarrow 6e_g$ transition, therefore, progressions in ν(RuRu) as well as ν(RuO) would be expected, as observed, for the acetate complex. The other complexes show unexplained differences in this respect since they display $\nu_2 + v_1\nu_1$ but not $v_2\nu_2$ progressions. The observation of these progressions enables both harmonic wavenumbers and anharmonicity constants to be calculated.

Introduction

The dimeric complexes of ruthenium formed with bridging carboxylate ligands, Ru$_2$(O$_2$CR)$_4$Cl, were reported in 1966 by Stephenson and Wilkinson[1] and were formulated as involving mixed +2,+3 oxidation states of ruthenium. The paramagnetism of the complexes is indicative of the presence of three unpaired electrons per dimer. The key structural features of the butyrate complex were established by Cotton et al.[2] to consist of four bridging butyrate groups per dimer,

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the dimeric units (each of approximately D_{4h} symmetry) being linked by bridging chloride groups with the Ru–Cl–Ru angle being 125.4°. The bonding in these complexes has been of considerable interest from the outset, as has the assignment of the intense and characteristic band of the complexes at $\sim$21 000 cm^{-1}. Although this band was initially thought to arise from a $b_{2g} \rightarrow a_{1g}$ ($\delta \rightarrow \sigma_n$) and/or $b_{2g} \rightarrow 2_{2u}$ ($\delta \rightarrow \sigma_n'$) transition,[2] which would be electric-dipole forbidden in D_{4h} symmetry, resonance Raman (RR) studies indicated (for the acetate and butyrate complexes)[3] that it must arise from an electric-dipole-allowed transition with (by implication) axial (z) polarization. By analogy with RR results and electronic band assignments for other metal–metal multiple-bonded species $[Mo_2Cl_8]^{4-}$, $[Re_2Cl_8]^{2-}$, and $[Re_2Br_8]^{2-}$[4–6] (since extended to $[Mo_2Br_8]^{4-}$),[7] of D_{4h} symmetry, the $\sim$21 000-cm^{-1} band was assigned to the $b_{2g} \rightarrow b_{1u}$ ($\delta \rightarrow \delta^*$) transition, which is allowed with the correct (z) polarization and is the lowest possible allowed transition with this polarization.

Recent self-consistent-field (SCF) scattered-wave, X_α calculations by Norman et al.[8] have reopened the question of the assignment of the $\sim$21 000-cm^{-1} band in the sense that they predict that the $\delta \rightarrow \delta^*$ transition of the free formate complex ion $[Ru_2(O_2CH)_4]^+$, should lie at 8800 cm^{-1} rather than at $\sim$21 000 cm^{-1}. Since the electronic spectrum of $Ru_2(O_2CCH_3)_4Cl$ in D_2O (presumably that of the species $[Ru_2(O_2CCH_3)_4(D_2O)_2]^+$) consists[9] of two bands, one at 23 500 cm^{-1} (ϵ_{max} = 699 M^{-1} cm^{-1}) and the other, much weaker, at $\sim$10 000 cm^{-1} (ϵ_{max} = 60 M^{-1} cm^{-1}), it seemed logical on energy grounds (though hardly on intensity grounds) to assign the $\sim$10 000-cm^{-1} band (despite its weakness) to the $\delta \rightarrow \delta^*$ transition. The much stronger band at $\sim$21 000 cm^{-1} was assigned to an O(π) → π^*, $6e_u \rightarrow 6e_g$ transition, one of whose components, ${}^4B_{2u} \rightarrow {}^4B_{1g}$, is allowed with z polarization. Very recent single-crystal polarized electronic spectra of $Ru_2(O_2CCH_2)_4Cl$, which crystallizes with $[Ru_2(O_2CCH_3)_4]^+$ ions alternately with Cl$^-$ ions as linear chains, have confirmed the z polarization of the $\sim$21 000-cm^{-1} band and have been interpreted[10] to be in agreement with the calculations and assignments of Norman et al.[8] Accordingly, a more detailed RR investigation of a wider range of diruthenium tetracarboxylate complexes is called for in order to establish wheter the RR spectra could be consistent with Norman's assignment of the $\sim$21 000-cm^{-1} band of this class of complexes.

Developments in RR technology, particularly those concerned with the routine holding of samples at liquid-nitrogen temperatures, were expected to lead to much improved RR spectra for the acetate and butyrate complexes studied previously[3] at room temperature only. This has indeed proved to be the case, and in particular the acetate complex yields a very rich and detailed RR spectrum at low temperatures. Many progressions involving both ν_1 and ν_2, the RuRu and RuO symmetric stretching modes, have now been observed; which mode is ν_1 and which is ν_2 has been established definitively by ^{18}O substitution of the acetate, and harmonic wavenumbers and anharmonicity constants have been calculated. The excitation profiles of all Raman bands whose intensities are enhanced at or near resonance with the $\sim$21 000-cm^{-1} band of each complex have now been measured, and the results are discussed in terms of the O(π) → π^* assignment for the resonant electronic transition.

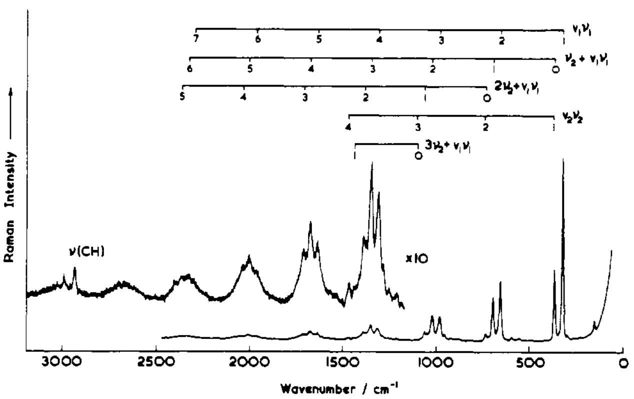

Figure 1. Resonance Raman spectrum of $Ru_2(O_2CCH_3)_4Cl$ at ca. 80 K obtained with 488.0-nm excitation and slit widths of 150/250/150 μm. The assignments of the members of the various progressions are indicated.

Experimental Section

Preparation of Complexes. The complexes $Ru_2(O_2CR)_4Cl$, R = CH_3, C_2H_5, or C_3H_7, were prepared by the modified method of Mitchell et al.,[11] which consistently gives better yields than the original method.[1] $[Ru_2\ (O_2CCH_3)_4(H_2O)_2]BF_4$ was prepared by the method of Cotton et al.[12] $Ru_2(O_2CH)_4Cl$ was prepared by holding $RuCl_3 \cdot H_2O$ (Johnson Matthey Ltd.) under reflux with formic acid for 1 h, this being a slight modification of the method of Mukaida et al.[13,14]

^{18}O isotopically substituted $Ru_2(O_2CCH_3)_4Cl$ was prepared by adding dried $RuCl_3$ (0.024 g) and anhydrous LiCl (0.024 g) to a mixture of acetic acid (0.500 g) and acetic anhydride (0.500 g), both the acetic acid as well as the acetic anhydride containing 78.5 atom % ^{18}O (Miles-Yeda Ltd.). The mixture was held under reflux, initially in an atmosphere of nitrogen and then in one of oxygen, for 4 h. The solution was sealed and cooled to 10 °C overnight, after which the resulting red-brown crystalline complex was filtered off and dried.

Instrumental Section. Raman spectra were recorded on both a Spex 1401 spectrometer (1200 line mm^{-1} Bausch and Lomb gratings) and a Spex 14018 R6 spectrometer (1800 line mm^{-1} Jobin-Yvon holographic gratings) in conjunction with Coherent Radiation CR52 Kr$^+$ and Ar$^+$ lasers and a CR12 UV Ar$^+$ laser. One line (406.7 nm) was obtained by use of a Spectra Physics 170 Kr$^+$ laser in conjunction with a Jobin-Yvon Ramanor spectrometer with 2000 line mm^{-1} gratings (courtesy of Dr. R. E. Hester, York).

Resonance Raman spectra of the solids at room temperature were obtained with use of a rotating-sample device, while spectra at liquid-nitrogen temperature were obtained on solids as KCl disks held by grease onto the low-temperature probe of a cold cell. Solution spectra were recorded with the use of a rotating liquids cell. Raman band excitation profiles were obtained with use of rotating-solids device. The intensity standard was the ν_2(e) band of $KClO_4$ (465 cm^{-1}); this standard was also cross-checked against the intensities of the $\nu_4(t_2)$, $\nu_1(a_1)$, and $\nu_3(t_2)$ bands of $KClO_4$ (630, 942, and 1097 cm^{-1}, respectively) with various exciting lines in order to establish the lack of any significant absorption effects.

Electronic spectra were recorded on a Cary 14 spectrometer with samples dispersed in KCl disks which were held at both 300 and 80 K.

Infrared spectra of complexes as Nujol mulls were recorded on a Perkin-Elmer 225 spectrometer.

Results

$Ru_2(O_2CCH_3)_4Cl$. The RR spectrum of $Ru_2(O_2CCH_3)_4Cl$ at ca. 80 K with 488.0-nm excitation is shown in Figure 1, and

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Table I. Wavenumbers of Members of Progressions Observed in the Resonance Raman Spectrum of the Complex $[Ru_2(O_2CCH_3)_4Cl]$ with 488.0-nm Excitation[a]

band	max/cm^{-1} RT	max/cm^{-1} LT[b]	band	max/cm^{-1}, LT
ν_1	327.3	330.1	$\nu_1 + 2\nu_2$[c]	1068.5
$2\nu_1$	654.5	660.0	$2\nu_1 + 2\nu_2$	1394.5
$3\nu_1$	981.5	989.5	$3\nu_1 + 2\nu_2$	1720
$4\nu_1$	1307.5	1317	$4\nu_1 + 2\nu_2$	2046
$5\nu_1$	1634	1644.5	$5\nu_1 + 2\nu_2$	2370
$6\nu_1$		1971.5	$\nu_1 + 3\nu_2$[c]	1435
$7\nu_1$		2298	$\nu_1 - \nu_L$[d]	304.0
$8\nu_1$		2625	$2\nu_1 - \nu_L$	634.5
$9\nu_1$		2950	$3\nu_1 - \nu_L$	964.5
ν_2	369.2	372.1	$4\nu_1 - \nu_L$	1292
$2\nu_2$		742	$\nu_1 - \nu_x$[d]	269
$3\nu_2$		1110	$2\nu_1 - \nu_x$	599
$4\nu_2$		1476	$3\nu_1 - \nu_x$	928
$\nu_1 + \nu_2$[c]	694.8	700.2	$2\nu_1 + \nu_x$[d]	720
$2\nu_1 + \nu_2$	1020	1028	$3\nu_1 + \nu_x$	1051
$3\nu_1 + \nu_2$	1345	1355	$4\nu_1 + \nu_x$	1377
$4\nu_1 + \nu_2$		1679	$\nu_1 + \nu_y$[d]	490
$5\nu_1 + \nu_2$		2005	$2\nu_1 + \nu_y$	820
$6\nu_1 + \nu_2$		2330	$\nu_1 + \nu_z$[d]	560
			$2\nu_1 + \nu_z$	889
			$3\nu_1 + \nu_z$	~1220

[a] RT = room temperature; LT = liquid nitrogen temperature. Estimated accuracies for the stronger bands are as follows: 0–1000 cm^{-1}, ±0.5 cm^{-1}; 1000–2000 cm^{-1}, ±1 cm^{-1}; over 2000 cm^{-1}, ≥2 cm^{-1}. [b] The ^{18}O (78.5%) substituted form of $Ru_2(O_2CCH_3)_4Cl$ gives rise to the following bands in its RR spectrum: $v_1\nu_1$ progression, ν_1 331.3, $2\nu_1$ 662.2, $3\nu_1$ 993.0, $4\nu_1$ 1323, $5\nu_1$ 1653; $v_2\nu_2$ progression, ν_2 359.3 and 366.8, $2\nu_2$ 718.3 and 732.2, $3\nu_2$ 1077 and 1098; $v_1\nu_1 + \nu_2$ progression, $\nu_1 + \nu_2$ 689.8 and 698.0, $2\nu_1 + \nu_2$ 1020 and 1026 cm^{-1}. [c] Also members of the $\nu_1 + v_2\nu_2$ progression. [d] ν_L is a lattice mode, inferred to lie at 27 ± 1 cm^{-1}. ν_x = band observed at 61 ± 1 cm^{-1}. ν_y = band observed at 161 ± 1 cm^{-1}. ν_z = band observed at 230 ± 1 cm^{-1}. ν(CO) is observed at 1581 cm^{-1} in the room-temperature spectrum but is not observed in that at ca. 80 K. A further very weak band is observed at 182.5 cm^{-1}.

the wavenumbers and assignments of the observed bands at 300 and 80 K are listed in Table I. The spectrum displays many overtone progressions, the main progression $v_1\nu_1$ reaching as far as $v_1 = 9$ and the $v_1\nu_1 + \nu_2$ one reaching as far as $v_1 = 6$. The $v_1\nu_1 + \nu_2$ progression is more intense relative to the $v_1\nu_1$ progression at higher values of v_1 than at lower values. In addition there are weaker, less extensive progressions of the form $v_2\nu_2$ reaching $v_2 = 4$, $v_1\nu_1 + 2\nu_2$ reaching $v_1 = 5$, $\nu_1 + v_2\nu_2$ reaching $v_2 = 3$, $v_1\nu_1 - \nu_L$ reaching $v_1 = 4$, $v_1\nu_1 - \nu_x$ reaching $v_1 = 3$, $v_1\nu_1 + \nu_x$ reaching $v_1 = 4$ (the band corresponding to $v_1 = 1$ is absent in this case), $v_1\nu_1 + \nu_y$ reaching $v_1 = 2$ and $v_1\nu_2 + \nu_z$ reaching $v_1 = 3$ (see Table I). This gives a total of ten progressions in the RR spectrum of $Ru_2(O_2CCH_3)_4Cl$ involving, in all, six different modes.

The weak band observed at 1581 cm^{-1} in the RR spectrum of the complex when held at room temperature is assigned to the ν(CO) stretching mode of the coordinated acetate groups. However, the band could not be observed in the RR spectrum of the complex if the latter were held at ca. 80 K.

The main progression-forming modes, ν_1 and ν_2, have previously been assigned to ν(RuRu) and ν(RuO), respectively (both a_{1g} modes),[3] and in order to substantiate this assignment unambiguously, $Ru_2(O_2CCH_3)_4Cl$ was synthesized with the use of acetic acid and acetic anhydride, both substituted with 78.5 atom % ^{18}O. The results (Table I and Figure 2) clearly show that ν_1 is unaffected by this substitution, fully consistent with its assignment as ν(RuRu). On the other hand, the (single) ν_2 band is shifted from 372.1 cm^{-1} for the ^{16}O species to become a complicated pattern of bands in the 359.3–366.8-cm^{-1} region. The calculated shift in ν_2 from $Ru_2(^{16}O_2CCH_3)_4Cl$ to $Ru_2(^{18}O_2CCH_3)_4Cl$ is 21.3 cm^{-1}, based simply on the factor $(16/18)^{1/2}$, if no coupling between the RuO and other a_{1g} coordinates were occurring. Such behavior is fully consistent with expectation for an a_{1g} ν(RuO) mode, the complicated pattern of bands arising because of the nine different isotopic species present if, as is probable, the distribution of ^{16}O:^{18}O is random; the pattern is further complicated by the possibility of isomers of many of the possible species.[15] Thus the identification of ν_2 and ν(RuO) is definitive.

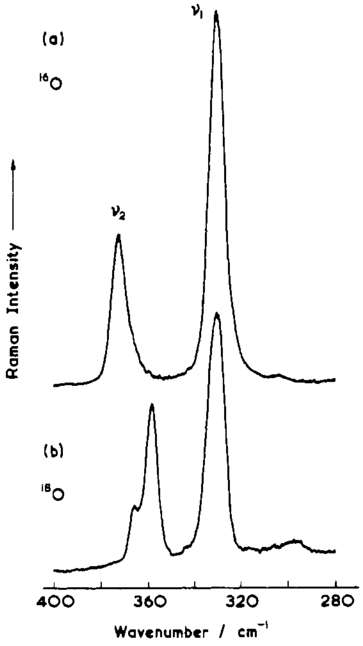

Figure 2. Resonance Raman spectrum of (a) $Ru_2(^{16}O_2CCH_3)_4Cl$ and (b) the same complex formed with 78.5 atom % ^{18}O acetate, each obtained at ca. 80 K with 514.5-nm excitation and slit widths of 50/100/50 μm.

The relative wavenumber order, $\nu(RuO) > \nu(RuRu)$, in these complexes, clearly established above, is to be contrasted with that equally clearly established by metal isotope substitution for $Mo_2(O_2CCH_3)_4$, viz., $\nu(MoMo) > \nu(MoO)$.[16] The difference is presumably associated with the belief that the RuRu bond order is 2.5, whereas the Mo–Mo bond is 4.

The excitation profiles (EP's) of the ν_1, $2\nu_1$, ν(CO), ν_2, and $\nu_1 + \nu_2$ bands of $Ru_2(O_2CCH_3)_4Cl$, measured from spectra of the complex at room temperature, are shown in Figure 3b for the range 457.9–752.5 nm. The EP's of the ν_1, $2\nu_1$, ν(CO), ν_2, and $\nu_1 + \nu_2$ bands all maximize near the maximum of the resonant electronic band (~21 600 cm^{-1}),[3] although that for $2\nu_1$ is ~300 cm^{-1} (i.e., ca. 1 quantum of ν_1) higher than that for ν_1.

The EP of the ν_2 band displays a maximum at ca. 19 000 cm^{-1} and a minimum at ca. 20 500 cm^{-1} and then rises toward the blue and ultraviolet regions, and with 363.8-nm excitation, $I(\nu_2)/I(\nu_1) \geq 1$ (the Raman spectrum of the complex with this line in effect constitutes a "normal" Raman spectrum, and no overtones are observed). This is characteristic of an interference operating for ν_2 between the (weaker) scattering associated with the 21 600-cm^{-1} band and the (more intense) scattering associated with a higher energy intense electronic

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(15) At 78.5 atom % ^{18}O, the species present for a random distribution would be (designating the oxygen isotopic content of $Ru_2(O_2CCH_3)_4Cl$ only) as follows: $(^{16}O)_8$ 0.00%, $(^{16}O)_7(^{18}O)$ 0.01%; $(^{16}O)_6(^{18}O)_2$ 0.17%; $(^{16}O)_5(^{18}O)_3$ 1.24%, $(^{16}O)_4(^{18}O)_4$ 5.68%; $(^{16}O)_3(^{18}O)_5$ 16.59%; $(^{16}O)_2(^{18}O)_6$ 30.29%; $(^{16}O)(^{18}O)_7$ 31.59%; $(^{18}O)_8$ 14.42%.

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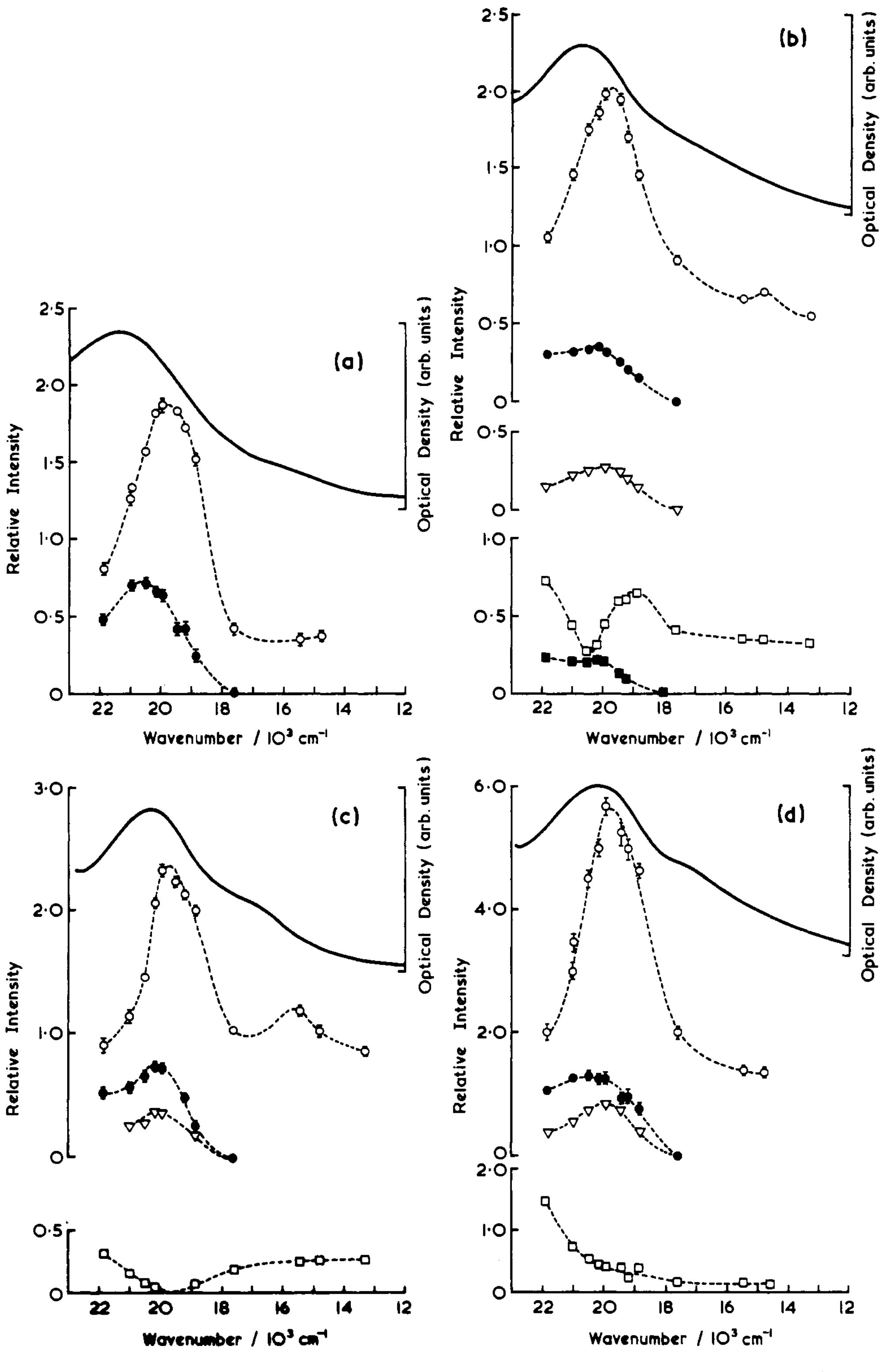

Figure 3. Excitation profiles of ν_1 (○), $2\nu_1$ (●), ν(CO) (▽), ν_2 (□), and $\nu_1 + \nu_2$ (■) for (a) $Ru_2(O_2CH)_4Cl$, (b) $Ru_2(O_2CCH_3)_4Cl$, (c) $Ru_2(O_2CC_2H_5)_4Cl$, and (d) $Ru_2(O_2CC_3H_7)_4Cl$ obtained in each case at ca. 300 K (together with the electronic spectra also at ca. 300 K).

band in the ultraviolet region[17-21] (probably $\sigma \rightarrow \sigma^*$ with respect to the Ru–O bonds). The interference is more apparent in EP's derived from spectra obtained where the sample is held at ca. 300 K rather than at ca. 80 K.

These results indicate that ν_1, ν_2, and ν(CO) are all coupled to the resonant electronic transition.

When $Ru_2(O_2CCH_3)_4Cl$ is dissolved in water, in which case the cation present is almost certainly the $[Ru_2(O_2CCH_3)_4(H_2O)_2]^+$ species, the electronic band maximum in the visible region shifts to higher wavenumbers to 23 500 cm⁻¹ (Table II). A polarization dispersion study of this species was carried out from 457.9 to 501.7 nm, the results being illustrated in Figure 4. Off resonance (501.7 nm), the ρ values for ν_1 and ν_2 were

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Table II. Electronic Band Maxima of Diruthenium Tetracarboxylate Species

complex	KCl disk transmission max/nm	aqueous soln[a] max/nm
$Ru_2(O_2CH)_4Cl$	1100 vw	~1100 vw
	595 sh	
	470 s	425 s
		310 vs
$Ru_2(O_2CCH_3)_4Cl$	1100 w	~1100 vw
	560 sh	
	475 s	425 s
		310 vs
$[Ru_2(O_2CCH_3)_4(H_2O)_2]BF_4$	1100 w	1150 vw
	565 sh	960 vw
	470 s	425 s
		310 vs
$Ru_2(O_2CC_2H_5)_4Cl$	1090 w	~1100 vw
	570 sh	
	495 s	425 s
		310 vs
$Ru_2(O_2CC_3H_7)_4Cl$	1090 w	~1100 vw
	580 sh	425 s
	490 s	310 vs

[a] The species present is presumably $[Ru_2(O_2CR)_4(H_2O)_2]^+$ in each case.

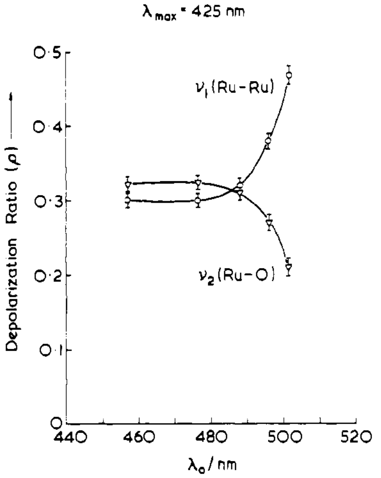

Figure 4. Polarization dispersion of ν_1 and ν_2 for $Ru_2(O_2CCH_3)_4Cl$ in water.

found to be 0.47 and 0.21, respectively, but as the resonance situation was approached, both ρ values approached the value of $^1/_3$. These results demonstrate not only that both ν_1 and ν_2 give rise to polarized bands, and therefore that the modes giving rise to them are totally symmetric, but also that the resonant electronic transition is axially (z) polarized.[22] This result therefore clearly confirms the conclusions of earlier Raman[3] and single-crystal electronic spectral studies[10] as to the polarization of the resonant electronic band.

$[Ru_2(O_2CCH_3)_4(H_2O)_2]BF_4$. The RR spectrum of $[Ru_2(O_2CCH_3)_4(H_2O)_2]BF_4$ is also very detailed, the wavenumbers of the observed bands together with the band assignments being listed in Table III. At resonance with the ~21 000-cm^{-1} band of the complex, the following progressions are observed: $v_1\nu_1$ to $v_1 = 4$, $v_1\nu_1 + \nu_2$ to $v_1 = 2$, $v_2\nu_2$ to $v_2 = 3$ together with bands attributable to ν_3, $\nu_1 + 2\nu_2$, and $\nu_1 - \nu_L$; ν_1 and ν_2 are the ν(RuRu) and ν(RuO) a_{1g} bands by analogy with the results (vide supra) for $Ru_2(O_2CCH_3)_4Cl$, and ν_3 is another Raman-active ν(RuO) mode. Although ν_3 lies between ν_1 and ν_2, it is not resonance enhanced. ν_L is thought to be a lattice mode inferred to lie at ~24 cm^{-1} (again, by analogy with the results for $Ru_2(O_2CCH_3)_4Cl$, for which a lattice mode of ~27 cm^{-1} appeared to be involved in one four-membered progression); alternatively, the 302-cm^{-1} band could arise from an acetate mode. The RR spectrum of $[Ru_2(O_2CCH_3)_4(H_2O)_2]BF_4$ is thus neither as extensive nor as detailed as that of $Ru_2(O_2CCH_3)_4Cl$. No band attributable to ν(CO) was observed in the RR spectrum of this salt.

Table III. Wavenumbers of Members of Progressions Observed in the Resonance Raman Spectrum of the Complex $[Ru_2(O_2CCH_3)_4(H_2O)_2]BF_4$ Held at Ca. 80 K with 488.0-nm Excitation[a]

band	max/cm^{-1}	band	max/cm^{-1}
ν_1	325.7	ν_2	371.0
$2\nu_1$	651.1	$2\nu_2$	738.0
$3\nu_1$	976.1	$3\nu_2$	1103
$4\nu_1$	1301	$\nu_1 + \nu_2$	693.0
$\nu_1 + \nu_L$[b]	301.9	$2\nu_1 + \nu_2$	1015
ν_3	365.1	$\nu_1 + 2\nu_2$	1059

[a] Estimated wavenumber accuracies as for footnote *a* of Table I. [b] ν_L is a lattice mode inferred to lie at ~24 cm^{-1} (assignment uncertain). No band attributable to ν(CO) was observed.

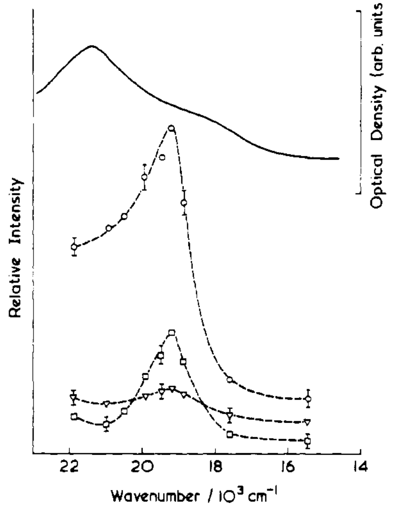

Figure 5. Excitation profiles of ν_1 (○), ν_2 (□), and ν_3 (▽) for $[Ru_2(O_2CCH_3)_4(H_2O)_2]BF_4$ at ca. 80 K.

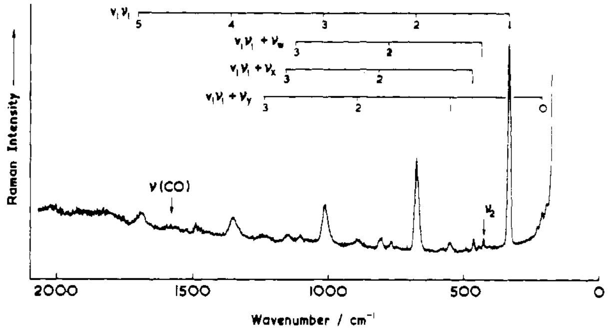

Figure 6. Resonance Raman spectrum of $Ru_2(O_2CH)_4Cl$ at ca. 80 K obtained with 476.5-nm excitation and slit widths of 170/220/170 μm.

The EP's of ν_1, ν_2, and ν_3 are given in Figure 5. The behavior of ν_1 and ν_2 is closely similar to that of the anhydrous acetate except that ν_1 and ν_2 both maximize at ca. 20 000 cm^{-1} and that the interference effect for ν_2 is only slight. The relative enhancement of ν_2 with respect to ν_3 in the resonance

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[22] Mortensen, O. S.; Hassing, S. *Adv. Infrared Raman Spectrosc.* **1980**, *6*, 1.

Table IV. Wavenumbers of Members of Progressions Observed in the Resonance Raman Spectra of the Complexes $Ru_2(O_2CH)_4Cl$, $Ru_2(O_2CC_2H_5)_4Cl$, and $Ru_2(O_2CC_3H_7)_4Cl$ with 488.0-nm Excitation[a]

$Ru_2(O_2CH)_4Cl$		$Ru_2(O_2CC_2H_5)_4Cl$			$Ru_2(O_2CC_3H_7)_4Cl$		
			max/cm^{-1}			max/cm^{-1}	
band	max/cm^{-1}, LT	band	RT	LT	band	RT	LT
ν_1	339.0	ν_1	337.5	339.3	ν_1	330.8	332.6
$2\nu_1$	677.4	$2\nu_1$	672.0	676.7	$2\nu_1$	661.1	664.2
$3\nu_1$	1016	$3\nu_1$	1007.5	1014.0	$3\nu_1$	990.8	995.3
$4\nu_1$	1353	$4\nu_1$	1335	1345.0	$4\nu_1$	1320	1326
$5\nu_1$	1690	$5\nu_1$		1675	$5\nu_1$		1656
		$6\nu_1$		2009	$6\nu_1$		1985
b	408	$7\nu_1$		2342	$7\nu_1$		2313
ν_2	432	ν_2	395.0	397.2	ν_2	376.5	379.6
$\nu_1 + \nu_2$	770	$\nu_1 + \nu_2$		734.5	$\nu_1 + \nu_2$		710.0
$2\nu_1 + \nu_2$	1107	$2\nu_1 + \nu_2$		1069.5	$2\nu_1 + \nu_2$		1040
$\nu_1 + \nu_x$[c]	467.5	$\nu_1 - \nu_L$[c]		312.8	$\nu_1 - \nu_L$[b]		311
$2\nu_1 + \nu_x$	810	$2\nu_1 - \nu_L$		650	$2\nu_1 - \nu_L$		636
$3\nu_1 + \nu_x$	1152						
		$\nu_1 + \nu_z$[c]		598	ν(CO)	1580	1582
$\nu_1 + \nu_y$	552.5						
$2\nu_1 + \nu_y$	895	ν(CO)	1590	1591			
$3\nu_1 + \nu_y$	~1235						
ν(CO)	1580						

[a] See footnote *a* of Table I. [b] The assignment of the very weak band at 408 cm^{-1} in the spectrum of $Ru_2(O_2CH)_4Cl$ is unknown. [c] ν_x, ν_y, and ν_z are the designations given to band inferred to lie at 128.5 cm^{-1} and the bands both observed and inferred to lie at 216 and 260 cm^{-1}, respectively. ν_L is the designation given to a lattice mode inferred to lie at ~25 cm^{-1}.

region shows that ν_3 plays little significant part in the RR spectrum. This result demonstrates that the presence of axial water molecules (with ν(OH) infrared bands at 3440 and 3240 cm^{-1}) does not affect significantly the relative intensities of ν_1 and ν_2. However, the degree of mixing between the RuRu and RuO symmetry coordinates is less for this complex than for the anhydrous acetate, as signified by shorter progressions observed.

$Ru_2(O_2CH)_4Cl$. The RR spectrum of $Ru_2(O_2CH)_4Cl$ is shown in Figure 6, and the wavenumbers of the observed bands together with the band assignments are listed in Table IV. Unlike the RR spectrum of $Ru_2(O_2CCH_3)_4Cl$, for which many progressions appear involving both ν_1 and ν_2, that of the formate is dominated by the $v_1\nu_1$ progression which reaches $v_1 = 5$, together with three other three-membered progressions in ν_1. The very weak band at 432 cm^{-1} appears to be ν_2, ν(RuO) (excited state value 420 cm^{-1})[23] but no progressions involving ν_2 could be observed.

The EP's of ν_1 and $2\nu_1$ (Figure 3a) both maximize near to the resonant electronic band maximum, as in the case of the analogous acetate complex.

$Ru_2(O_2CC_2H_5)_4Cl$. The RR spectrum of $Ru_2(O_2CC_2H_5)_4Cl$ is shown in Figure 7, and the wavenumbers of the observed bands together with the band assignments are given in Table IV. Like the RR spectrum of the formate, that of the propionate is dominated by the $v_1\nu_1$ progression, reaching $v_1 = 7$. Less-intense, shorter progressions in ν_1, viz., $v_1\nu_1 + \nu_2$ to $v_1 = 2$, $v_1\nu_1 - \nu_L$ also to $v_1 = 2$, are also observed. ν(CO) in the RR spectrum of this complex is at 1591 cm^{-1} and is observed in spectra taken at both 300 and 80 K.

The EP's of ν_1, $2\nu_1$, and ν(CO) all maximize (19 750, 20 100, and 20 100 cm^{-1}, respectively) near the maximum of the resonant electronic transition (20 200 cm^{-1}) (Figure 3c). The EP and $2\nu_1$ is thus ~350 cm^{-1} (i.e., ~1 quantum of ν_1) above that of ν_1; tests showed (see Experimental Section) that this effect was not caused by self-absorption. The EP of ν_2 is, however, very different from those described above since it minimizes in the vicinity of the maximum of the resonant electronic transition. As for the similar case of $Ru_2(O_2CCH_3)_4Cl$, this observation is consistent with the operation of interference effects.

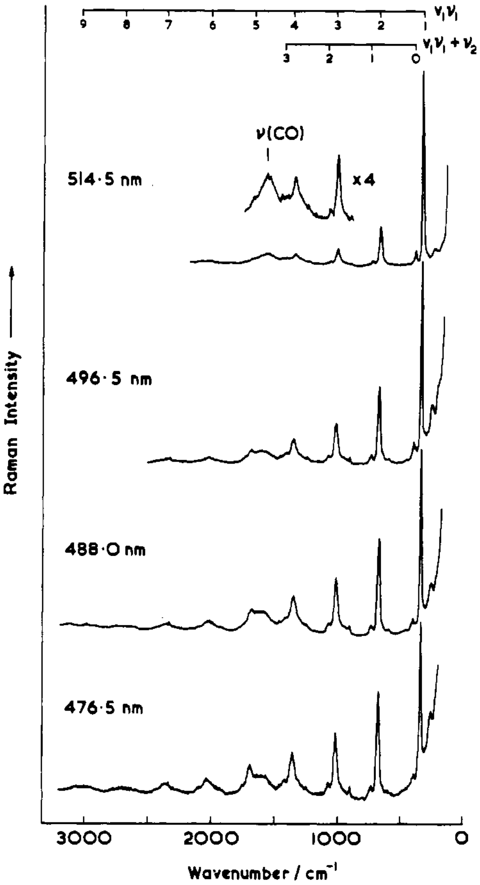

Figure 7. Resonance Raman spectra of $Ru_2(O_2CC_2H_5)Cl$ at ca. 80 K obtained with 514.5-, 496.5-, 488.0-, and 476.5-nm excitation.

$Ru_2(O_2CC_3H_7)_4Cl$. The RR spectrum of $Ru_2(O_2CC_3H_7)_4Cl$ is very similar to that of the formate and propionate in that it is dominated by the intense $v_1\nu_1$ progression, reaching $v_1 = 7$, together with the less intense and shorter progressions $v_1\nu_1 + \nu_2$ to $v_1 = 2$ and $v_1\nu_1 - \nu_L$ also to $v_1 = 2$. ν(CO) occurs at

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(23) V. Miskowski, personal communication.

Table V. Harmonic Wavenumbers and Anharmonicity Constants for the Diruthenium Tetracarboxylates (cm^{-1})

complex	ω_1	x_{11}	x_{12}	ω_2
$Ru_2(O_2CH)_4Cl$	339.5 ± 0.3	−0.24 ± 0.02	−1.5 ± 1	432[c]
$Ru_2(O_2CCH_3)_4Cl$[a]	330.8 ± 0.3	−0.31 ± 0.02	−2.0 ± 0.2	374.2 ± 0.5
$[Ru_2(O_2CCH_3)_4(H_2O)_2]BF_4$[b]	326.0 ± 0.3	−0.15 ± 0.02	−3.5 ± 1	374.2 ± 0.5
$Ru_2(O_2CC_2H_5)_4Cl$	341.8 ± 0.3	−1.1 ± 0.05	−2.2 ± 0.4	397.2[c]
$Ru_2(O_2CC_3H_7)_4Cl$	333.2 ± 0.3	−0.35 ± 0.02	−2.1 ± 0.3	379.6[c]

[a] For this complex, the following constants could also be determined: $x_{22} = -1.0_6 \pm 0.2$ cm^{-1} and $x_{1L} = 0.8 \pm 0.2$ cm^{-1}, where the latter is the cross term connecting ν_1 with a lattice mode, ν_L, at 27 cm^{-1}. [b] For this complex, $x_{22} = -1.7 \pm 0.2$ cm^{-1}. [c] The value quoted is that for ν_2, not ω_2; only insufficient data points could be established with which to determine ω_2.

1582 cm^{-1} in both 300 and 80 K spectra (Table IV).

The EP's of ν_1, $2\nu_1$, and $\nu(CO)$ all maximize (19 850, 20 250, and 20 200 cm^{-1}, respectively) close to the maximum of the resonant electronic transition (20 400 cm^{-1}), with that of $2\nu_1$ again being of the order of 1 quantum of ν_1 above that of ν_1 (Figure 3d). The EP of ν_2 also minimizes, as in the case of that of the other complexes, in the vicinity of the maximum in the resonant electronic band. This interference effect is less evident in spectra recorded from samples of the complex held at ca. 80 K than from those held at room temperature.

The EP of ν_1 of this complex, and also that of the acetate and propionate, shows a small inflexion near 17 000 cm^{-1}, a wavenumber which is close to that of a shoulder observed in the electronic spectrum of each complex at 17 600 cm^{-1}.

Harmonic Frequencies and Anharmonicity Constants. The observation of a large number of overtone bands under RR conditions permits the determination of various harmonic wavenumbers and anharmonicity constants.[24] The data for $Ru_2(O_2CCH_3)_4Cl$ are particularly extensive, and the following constants could be obtained in this case: ω_1 and x_{11} from the intercept and slope of the plot of $\nu(v_1\nu_1)/v_1$ vs. v_1 (and similarly ω_2 and x_{22}), x_{12} from the difference between the intercept for the plot of $\nu(v_1\nu_1/v)_1$ vs. v_1 and that for the plot of $[\nu(v_1\nu_1 + v_2\nu_2) - \nu(v_2\nu_2)]/v_1$ vs. v_1.

The results of all the analyses on the complexes studied are given in Table V.

The ω_1 values for the four complexes $Ru_2(O_2CR)_4Cl$ are all accurately defined by the data, and three of the four x_{11} values established are very small (≤−0.35 cm^{-1}). The x_{11} for the propionate is larger (−1.1 cm^{-1}) than this, which is difficult to understand, although it might be connected with the fact that this complex alone differs significantly from D_{4h} symmetry (S_4 since the difference between the two crystallographically independent Ru–Ru–O angles is 7° with an esd of 1°).[12] The x_{12} values for the complexes $Ru_2(O_2CR)_4Cl$ (~−2 cm^{-1}) are also similar to one another, although that for the diaquo salt (albeit determined only inaccurately) appears to be rather larger than this.

The wider interest in the RR results presented in the previous section lies in their bearing on the nature of, and assignments for, the resonant electronic transition at ~21 000 cm^{-1} in each complex. The polarization dispersion results on the ν_1 and ν_2 modes of the $[Ru_2(O_2CCH_3)_4(H_2O)_2]^+$ ion confirm the previous Raman results[3] as well as results of the single-crystal electronic spectral study of Martin et al.[10] in that the resonant electronic transition is shown to be allowed and z polarized. Although it was earlier proposed[3] that the resonant electronic transition is the $b_{2g} \rightarrow b_{1u}$ ($\delta \rightarrow \delta^*$ transition), which has the correct polarization, the recent SCF calculations of Norman et al.[8] on the formate complex indicate that it is the $6e_u \rightarrow 6e_g$, $O(\pi) \rightarrow \pi^*$ transition, the $^4B_{2u} \rightarrow {}^4B_{1g}$ component of which is also allowed in z polarization. The present RR results, being much more detailed and extensive than the earlier ones (on account of the complexes being held at ca. 80 rather than 300 K), allow further consideration of this new assignment of the resonant electronic transition to be made.

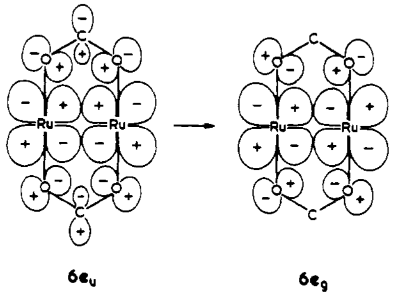

Figure 8. Representation of the $6e_u$ $O(\pi)$ and $6e_g$ π^* orbitals.

The $6e_u$ $O(\pi)$ orbital is described by Norman et al. as mainly Ru–O bonding but with significnat (24%) Ru–Ru π character. From the representation of the $6e_u$ and $6e_g$ orbitals (Figure 8), between which the resonant electronic transition is indicated to take place on the basis of Norman's calculations, it is clear that this transition would lead to a reduction in the Ru–Ru as well as in the Ru–O π bond order. Thus the complex would be expected to increase its Ru–Ru as well as its Ru–O bonds in the $6e_g$ excited state, and this in turn would be expected to lead in its RR spectrum to the appearance of Franck–Condon progressions in $\nu(RuRu)$ as well as $\nu(RuO)$. This is indeed what is observed for $Ru_2(O_2CCH_3)_4Cl$ in its ca. 80 K RR spectrum, and so the RR results on this complex are consistent with Norman's assignment of the resonant electronic transition. Moreover, the fact that the EP of $\nu(CO)$, where observed, also follows the contour of the resonant electronic transition, albeit without the RR spectrum displaying overtones of this mode, is likewise understandable in terms of the change of CO π bond order ($\pi \rightarrow$ nonbonding) indicated in Figure 8 during the $O(\pi) \rightarrow \pi^*$ transition. However, the most obvious confirmatory experiment of irradiating the complexes at ~10 000 cm^{-1}, i.e., within the contour of the very weak band attributed by Norman et al.[8] to the $\delta \rightarrow \delta^*$ transition, is not yet feasible owing to the lack of suitable exciting lines. Such irradiation, if the ~10 000-cm^{-1} band is indeed the $\delta \rightarrow \delta^*$ transition, should lead to a progression in ν_1, the $\nu(RuRu)$ mode only, since the $\delta \rightarrow \delta^*$ orbitals are thought to possess little ligand character, being composed almost entirely of weakly coupled metal d_{xy} orbitals. Norman's calculations indicate that the charge distribution in the δ orbitals is indeed predominantly metal based (71%) and only slightly different from that in the δ^* orbital (84%).

Although Norman's assignment for the resonant electronic transition in the case of $Ru_2(O_2CCH_3)_4Cl$ is fully consistent with the RR results, those for the formate, propionate, and butyrate are less so. In those cases, ν_2 is weak, no overtone of ν_2 is observed, and no progression of the sort $v_1\nu_1 + \nu_2$ reaches beyond $v_1 = 2$. It is difficult to understand why the RR spectra of these three complexes should differ in this respect from that of the acetate since there can be little doubt that the resonant electronic transition has the same assignment

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[24] Campbell, J. R.; Clark, R. J. H. *Mol. Phys.* **1978**, *36*, 1133.

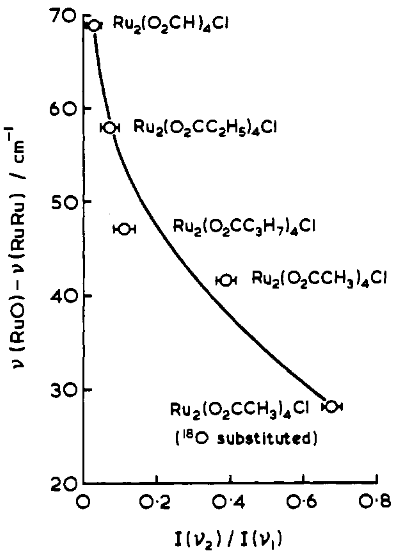

Figure 9. Relationship between ν(RuO) − ν(RuRu) and $I(\nu_2)/I(\nu_1)$ for the carboxylate complexes of the type $Ru_2(O_2CR)_4Cl$ (R = CH_3, C_2H_5, or C_3H_7) at 514.5-nm excitation.

in all cases. The explanation of this unexpected observation may lie in the fact that ν(RuRu) and ν(RuO) are closest in wavenumber in the case of the acetate and, therefore, that the RuRu and RuO symmetry coordinates are coupled most strongly in this case. This would, of course, lead to the greatest intensity borrowing for ν_2 and associated modes of the acetate complex, a situation made clear in Figure 9 for the various complexes of the sort $Ru_2(O_2CR)_4Cl$; note especially that for the ^{18}O-substituted acetate complex, $I(\nu_2)/I(\nu_1)$ is much higher than that for the unsubstituted complex, a particularly compelling result in this context.

Although the observation of combination-band progressions of the sort $v_1\nu_1 + v_2\nu_2$ is not, of itself, a consequence of the Duschinsky effect (the change in composition of the Q_1 and Q_2 normal coordinates, in terms of their constituent symmetry coordinates, on electronic excitation),[25-27] the possibility that the change, with v_1, of the relative intensities of members of the $v_1\nu_1$ and $\nu_2 + v_1\nu_1$ progressions is so (Figure 1), requires further consideration.

Acknowledgment. We thank the Science Research Council and the University of London for financial support and Dr. T. J. Dines for useful discussions.

Registry No. $Ru_2(O_2CCH_3)_4Cl$, 55598-01-1; $Ru_2(O_2CH)_4Cl$, 77904-04-2; $[Ru_2(O_2CCH_3)_4(H_2O)_2]BF_4$, 71106-46-2; $Ru_2(O_2CC_2H_5)_4Cl$, 71106-47-3; $Ru_2(O_2CC_3H_7)_4Cl$, 53370-31-3; ^{18}O, 14797-71-8.

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The Problem of π-Electron Delocalization in Group 4 Acetylacetonate Complexes, $M(acac)_2X_2$, As Studied from the Optical Spectra

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Received December 1, 1980

Absorption and reflectance spectra of *cis*-dihalobis(2,4-pentanedionato) complexes of Ti(IV), Zr(IV), Ge(IV), and Sn(IV) have been measured under water- and alcohol-free conditions. The majority of absorption maxima in the vis–UV region is assigned to π–π* transitions of the acetylacetonate ligands which are subject to the effect of different degrees of metal–ligand π-electron bonding. Significant π bonding, as realized in the titanium compounds, leads to electron delocalization over the complex molecule and increases the splitting of the various π–π* band components. Ligand to metal charge-transfer transitions are likely only for the iodo complexes. However, π-bonded acetylacetonate intermixes ligand–metal charge-transfer states into π,π* excited states which is particularly effective in Ti(IV) complexes. Halogen ligands are able to perturb this mechanism more effectively when π-electron delocalization is large. The intermixing of charge-transfer states is important for relatively large metal optical electronegativities which are a measure of the availability of these energy levels.

Introduction

β-Diketones can bind in a variety of ways to metallic ions.[1] In the most common species the diketone is present as an enolate anion acting as a bidentate ligand via the oxygen atoms. Optical spectra in absorption and emission have been measured frequently although in many cases the bands could not be assigned with confidence, since comparison with theoretical results could not be made, due to the lack of reliable calculations. Because of its metal–ligand π-bonding capability,[2] questions concerning the ring current[3] (aromaticity) in the chelate are raised, and the problem of delocalization of ligand π-electrons over the whole complex is pertinent. Early theoretical work[4,5] starts with assumption of delocalized electrons, by applying convenient Hückel MO theory. However, a closer analysis of spectra, performed with a theoretical procedure of higher sophistication which uses a localized model, results in a better understanding of experimental findings on closed-shell as well as open-shell metal tris(acetylacetonates).[6] The application of the latter model is also easy for the very simple spectrum of closed-shell complex compounds, which is characteristic of many acetylacetonates. The result agrees well with the assignment obtained from the CD spectrum of the complex ion[7] $[Si(acac)_3]^+$ which allows

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