Infrared, Resonance-Raman, and Excitation Profile Studies of $[Os_2(O_2CCH_2Cl)_4Cl_2]$, $[Os_2(O_2CC_2H_5)_4Cl_2]$, and $[Os_2(O_2CC_3H_7)_4Cl_2]$: Assignment of Osmium–Osmium, Osmium–Oxygen, and Osmium–Chlorine Stretching Vibrations

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Detailed Raman (1 600—35 cm^{-1}) and Fourier-transform i.r. (3 500—40 cm^{-1}) studies of the diosmium tetracarboxylate complexes $[Os_2(O_2CR)_4Cl_2]$ (R = CH_2Cl, C_2H_5, or C_3H_7), coupled with related earlier studies of $[Os_2(O_2CCH_3)_4Cl_2]$ and $[Os_2(O_2CCD_3)_4Cl_2]$, have provided a basis for the identification of the three Raman-active (a_{1g}) bands ν_1, ν_2, and ν_3 at 236—228, 393—256, and 311—292 cm^{-1} respectively, to the key skeletal fundamentals ν(OsOs), ν(OsO), and ν(OsCl), respectively. Thus, while both ν(OsOs) and ν(OsCl) are relatively insensitive to the carboxylate R group, ν(OsO) is, as expected, highly sensitive thereto. Raman studies at resonance with the intense near-ultraviolet electronic band (406—383 nm) of each complex yield resonance-Raman spectra in each case characterised by the development of three overtone progressions in ν_1. These reach $6\nu_1$, $4\nu_1 + \nu_2$, and $4\nu_1 + \nu_3$ at most. The results are typical of A-term resonance-Raman scattering. The depolarisation ratio of the ν_1 band at resonance with the *ca.* 390 nm band demonstrates that the latter arises from an axially polarised transition, consistent with an earlier assignment $\pi(Cl) \longrightarrow \pi^*(Os_2)$.

X-Ray crystallographic studies of the diosmium tetracarboxylate complexes $[Os_2(O_2CCH_3)_4Cl_2]$, $[Os_2(O_2CC_2H_5)_4Cl_2]$, and $[Os_2(O_2CC_3H_7)_4Cl_2]$[1,2] have demonstrated that all possess the familiar dimetal tetracarboxylate framework (Figure 1) with near D_{4h} symmetry, Os–Os distances of *ca.* 2.310 Å, and Os–Os–O angles of almost exactly 90°. The principal, albeit small, structural difference between the complexes lies in the Os–Cl distances, which decrease in the order $CH_3 > C_2H_5 > C_3H_7$. Recent Raman and i.r. studies of $[Os_2(O_2CCH_3)_4Cl_2]$ and $[Os_2(O_2CCD_3)_4Cl_2]$ have led to the first identification[3] of ν(OsOs), at 229 cm^{-1}, for an osmium–osmium triply bonded species. The present paper represents an extensive study of the Raman, resonance-Raman (1 600—35 cm^{-1}), and Fourier-transform i.r. (3 500—40 cm^{-1}) spectra of three further diosmium tetracarboxylate complexes, *viz.* $[Os_2(O_2CCH_2Cl)_4Cl_2]$, $[Os_2(O_2CC_2H_5)_4Cl_2]$, and $[Os_2(O_2CC_3H_7)_4Cl_2]$. Detailed band assignments are given for the Raman and i.r. bands, as well as for the progressions in ν_1 detected under resonance-Raman conditions. The Raman band excitation profiles, taken at or near resonance with the strongly allowed electronic band near 390 nm of each complex, are typical of scattering which is determined by the A-term scheme for resonance-Raman scattering.[4]

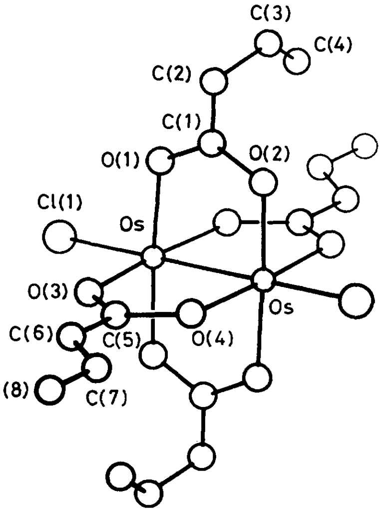

Figure 1. Molecular structure of $[Os_2(O_2CC_3H_7)_4Cl_2]$

Experimental

Complexes.—All complexes were kindly provided in 1982 by the late Dr. T. A. Stephenson and Dr. D. A. Tocher. Elemental analyses for C, H, and Cl were all satisfactory.

Instrumental.—Raman spectra were recorded using a Spex 14018 (R6) spectrometer in conjunction with Coherent CR 3000 K and CR 12 lasers. Samples were held as pressed KCl discs at *ca.* 80 K in a liquid nitrogen cell. The spectrum of $[Os_2(O_2CCH_2Cl)_4Cl_2]$ was also recorded with a Kr^{2+}-pumped CR599 dye laser using stilbene 3 as the lasing dye. Excitation profiles corrected for both frequency factors and spectral response were plotted by measuring the intensities of the Raman bands of the complex relative to that of the band of KNO_3 at 1 049 cm^{-1}.

Infrared spectra were recorded at *ca.* 80 K as KCl discs (3 500—500 cm^{-1}) and as pressed wax discs (660—40 cm^{-1}) at a spectral resolution of 1 cm^{-1} with a Bruker 113 V interferometer. Standard details for disc preparations have been given elsewhere.[5] Overlap between mid- and far-i.r. regions allowed matching of band intensities, which are quoted on an arbitrary intensity scale of vw <0.02, w 0.02—0.2, m 0.2—0.6, s 0.6—0.9, vs >0.9; br = broad, sh = shoulder, ρ_t = twist, ρ_r = rock, ρ_w = wag.

Electronic spectra were recorded as transmission spectra on a Cary 14 spectrometer, the samples being held as KCl discs at *ca.* 20 K on an Air Products closed-cycle Displex system. Band maxima (nm) were observed as follows: $[Os_2(O_2CCH_3)_4Cl_2]$ 246s, 274s, 383s; $[Os_2(O_2CCH_2Cl)_4Cl_2]$ 362(sh), 406s; $[Os_2(O_2CC_2H_5)_4Cl_2]$ *ca.* 240(sh), 275s, 362(sh), 390s; $[Os_2(O_2CC_3H_7)_4Cl_2]$ 278s, 358(sh), 392s.

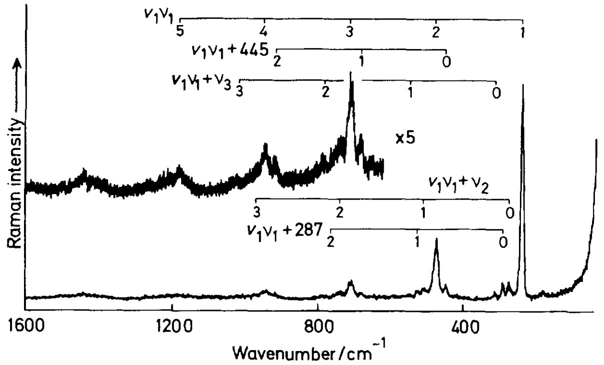

Figure 2. Resonance-Raman spectrum (1 600—60 cm^{-1}) of $[Os_2(O_2CCH_2Cl)_4Cl_2]$ as a KCl disc at *ca.* 80 K with 415.4-nm excitation. Resolution *ca.* 5 cm^{-1}

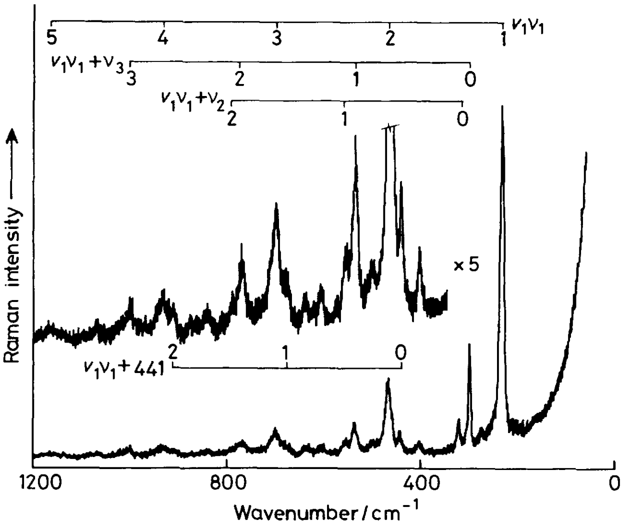

Figure 3. Resonance-Raman spectrum (1 200—60 cm^{-1}) of $[Os_2(O_2CC_2H_5)_4Cl_2]$ as a KCl disc at *ca.* 80 K with 406.7-nm excitation. Resolution *ca.* 5 cm^{-1}

Results and Discussion

Raman Spectra.—Raman spectra of the diosmium tetracarboxylates $[Os_2(O_2CR)_4Cl_2]$ (Figures 2—4) could only be obtained with exciting lines of wavelengths at or near resonance with the strongly allowed electronic transition ($\lambda_{max.}$ = 406—383 nm) of each complex (see Experimental section). In particular, by use of λ_0 = 406.7 nm excitation, intense resonance-Raman spectra of each complex could be obtained, these being dominated by a strong band at 236—228 cm^{-1} (229,[3] 236, 233, 228 cm^{-1} for R = CH_3,[3] CH_2Cl, C_2H_5, or C_3H_7, respectively), by an associated overtone progression $v_1\nu_1$ (reaching v_1 = 6,[3] 5, 5, and 6, respectively), and by two obvious combination band progressions $v_1\nu_1 + \nu_2$ (reaching v_1 = 3,[3] 3, 2, and 4, respectively) and $v_1\nu_1 + \nu_3$ (reaching ν_1 = 4,[3] 3, 4, and 4, respectively). Two further combination band progressions occur in the case R = CH_2Cl; these are $v_1\nu_1$ + 287 as far as v_1 = 2, where the band at 287 cm^{-1} is probably attributable to a Raman active, albeit non-a_{1g}, OsO stretching mode, and $v_1\nu_1$ + 445 as far as v_1 = 2, where the band at 445 cm^{-1} is assigned to either ρ_r(COO) or δ(CCl). At least two further, weak, combination band progressions can be observed in the case R = C_2H_5, *viz.* $v_1\nu_1$ + 403, as far as v_1 = 2 and $v_1\nu_1$ + 441 as far as v_1 = 2; neither the 403 nor the 441 cm^{-1} bands can be assigned in the absence of isotopic data. Several other weak combination band progressions occur in the case R = C_3H_7; these include $v_1\nu_1$ + 273 to v_1 = 1, $v_1\nu_1$ + 313 to v_1 = 1, $v_1\nu_1$ + 354 to v_1 = 2, $v_1\nu_1$ + 557 to v_1 = 2, $v_1\nu_1$ + 603 to v_1 = 2, the enabling mode being unassigned in each case.

Table 1. Wavenumbers (cm^{-1}) of bands observed in the resonance-Raman spectrum* of $[Os_2(O_2CCH_2Cl)_4Cl_2]$ at *ca.* 80 K

$\tilde{\nu}$	Assignment	$\tilde{\nu}$	Assignment
178vw,br		708w	$3\nu_1$
236vs	ν_1, ν(Os–Os)	738vw	$2\nu_1 + \nu_2$
271w	ν_2, ν(Os–O)	757vw	$2\nu_1$ + 287
287w	ν(Os–O)	788vw	$2\nu_1 + \nu_3$
311vw	ν_3, ν(Os–Cl)	920vw	$2\nu_1$ + 445
445w	ρ_r(COO) or δ(C–Cl)	946w,br	$4\nu_1$
471m	$2\nu_1$	971vw	$3\nu_1 + \nu_2$
505w	$\nu_1 + \nu_2$	1 021vw	$3\nu_1 + \nu_3$
521w	ν_1 + 287	1 180vw,br	$5\nu_1$
548vw	$\nu_1 + \nu_3$	1 444vw,br	
680vw	ν_1 + 445		

* 415.4-nm excitation.

Table 2. Wavenumbers (cm^{-1}) of bands observed in the resonance-Raman spectrum* of $[Os_2(O_2CC_2H_5)_4Cl_2]$ at *ca.* 80 K

$\tilde{\nu}$	Assignment	$\tilde{\nu}$	Assignment
233vs	ν_1, ν(Os–Os)	766w	$2\nu_1 + \nu_3$
271w		785vw	$2\nu_1 + \nu_2$
299m	ν_3, ν(Os–Cl)	837vw	ν_1 + 603
321w	ν_2, ν(Os–O)	871vw	$2\nu_1$ + 403
403w		907vw	$2\nu_1$ + 441
441w		932vw	$4\nu_1$
465m	$2\nu_1$	998vw,br	$3\nu_1 + \nu_3$
500w		1 065vw	
535w	$\nu_1 + \nu_3$	1 164vw	$5\nu_1$
554w	$\nu_1 + \nu_2$	1 234vw	$4\nu_1 + \nu_3$
603vw		1 295vw	$\rho_w(CH_2)$
636vw	ν_1 + 403	1 308vw	
676w	ν_1 + 441	1 435vw	$\delta_{asym}(CH_3)$ and $\delta(CH_2)$
699w	$3\nu_1$	1 452vw	
		1 472vw	

* 406.7-nm excitation.

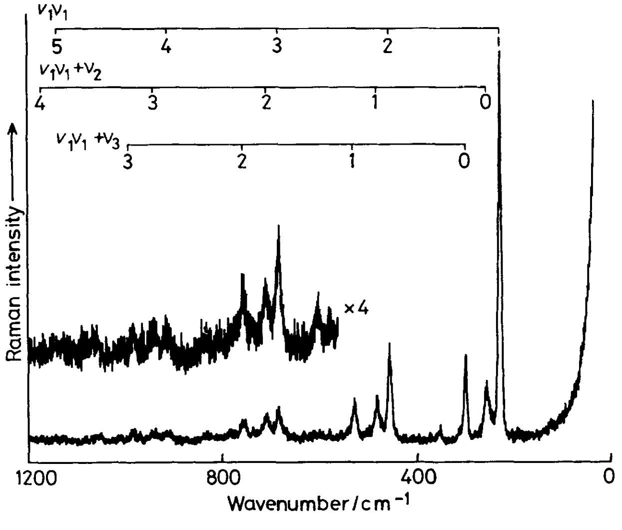

Figure 4. Resonance-Raman spectrum (1 200—35 cm^{-1}) of $[Os_2(O_2CC_3H_7)_4Cl_2]$ as a KCl disc at *ca.* 80 K with 406.7-nm excitation. Resolution *ca.* 5 cm^{-1}

Table 3. Wavenumbers (cm^{-1}) of bands observed in the resonance-Raman spectrum* of $[Os_2(O_2CC_3H_7)_4Cl_2]$ at *ca.* 80 K

$\tilde{\nu}$	Assignment	$\tilde{\nu}$	Assignment
161vw		758w	$2\nu_1 + \nu_3$
192vw		784vw	$\nu_1 + 557$
228vs	ν_1, ν(Os–Os)	808vw	$2\nu_1 + 354$
256m	ν_2, ν(Os–O)	831vw	$\nu_1 + 603$
273w		913vw	$4\nu_1$
299m	ν_3, ν(Os–Cl)	939vw	$3\nu_1 + \nu_2$
313w		961vw	
354w		985vw	$3\nu_1 + \nu_3$
457m	$2\nu_1$	1 011vw	$2\nu_1 + 557$
483m	$\nu_1 + \nu_2$	1 058vw	$2\nu_1 + 603$
501vw	$\nu_1 + 273$	1 137vw	$5\nu_1$
530m	$\nu_1 + \nu_3$	1 163vw	$4\nu_1 + \nu_2$
540w	$\nu_1 + 313$	1 210vw	$4\nu_1 + \nu_3$
557vw		1 278vw	
583vw	$\nu_1 + 354$	1 364vw	$6\nu_1$
603vw		1 417vw	$\delta_{asym}(CH_3)$ and $\delta(CH_2)$
686m	$3\nu_1$	1 436vw	
711w	$2\nu_1 + \nu_2$	1 462vw	
734vw			

* 406.7 nm excitation.

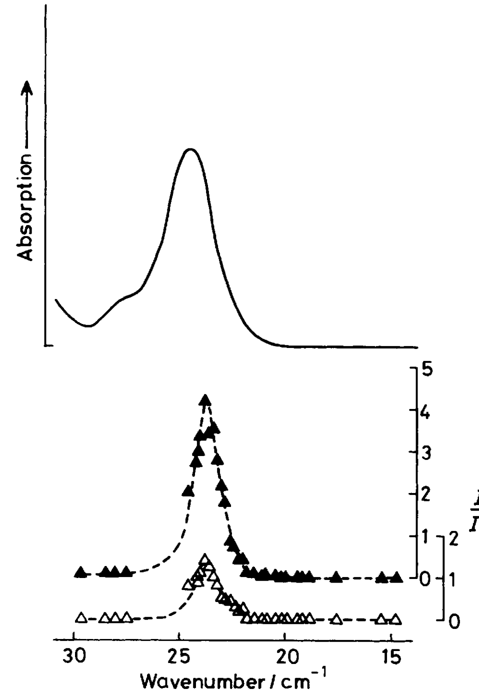

Figure 5. Excitation profiles of ν_1 (▲) and $2\nu_1$ (△) for $[Os_2(O_2CCH_2Cl)_4Cl_2]$ at *ca.* 80 K together with the transmission electronic spectrum recorded as a KCl disc at *ca.* 20 K

The Raman-active fundamental ν_2 occurs over the wide wavenumber range of 393—256 cm^{-1} (393, 271, 321, 256 cm^{-1} for R = CH_3,[3] CH_2Cl, C_2H_5, or C_3H_7, respectively), whereas ν_3 occurs over a much narrower range of 311—292 cm^{-1} (292,[3] 311, 299, 299 cm^{-1} for R = CH_3, CH_2Cl, C_2H_5, or C_3H_7, respectively). Detailed band listings, together with band assignments, are given in Tables 1—3 for the complexes R = CH_2Cl, C_2H_5, and C_3H_7, respectively. No Raman spectra were detected at resonance with the weak transitions (*e.g.* $\delta \longrightarrow \delta^*$, in the visible and near-i.r. regions) thought to originate from the ^3E_u $(\delta^*\pi^*)$ ground state of each complex.[6]

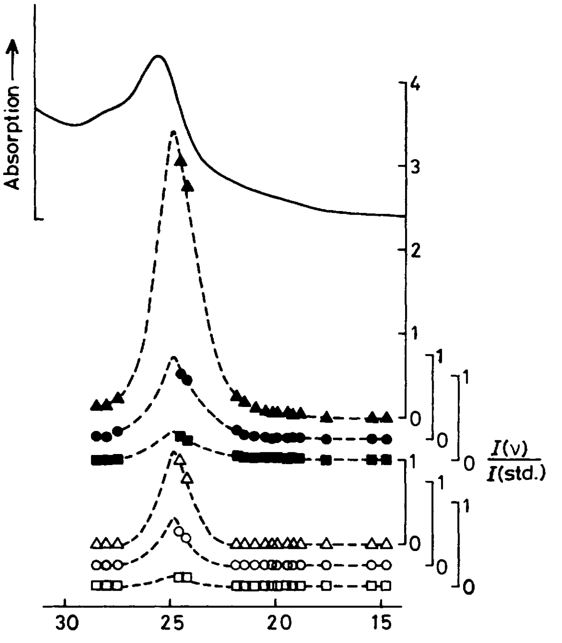

Figure 6. Excitation profiles of ν_1 (▲), ν_2 (■), ν_3 (●), $2\nu_1$ (△), $\nu_1 + \nu_2$ (□) and $\nu_1 + \nu_3$ (○) for $[Os_2(O_2CC_2H_5)_4Cl_2]$ at *ca.* 80 K together with the transmission electronic spectrum recorded as a KCl disc at *ca.* 20 K

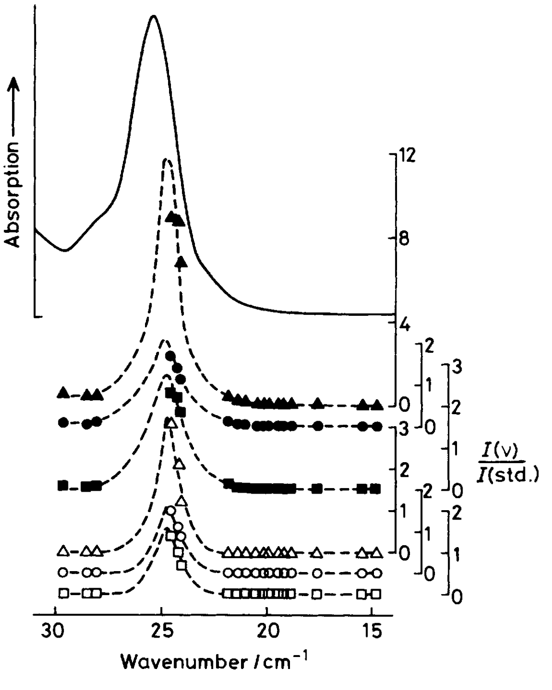

Figure 7. Excitation profiles of ν_1 (▲), ν_2 (●), ν_3 (■), $2\nu_1$ (△), $\nu_1 + \nu_2$ (○) and $\nu_1 + \nu_3$ (□) for $[Os_2(O_2CC_3H_7)_4Cl_2]$ at *ca.* 80 K together with the transmission electronic spectrum recorded as a KCl disc at *ca.* 20 K

Excitation profiles have been constructed for the ν_1 and $2\nu_1$ bands of $[Os_2(O_2CCH_2Cl)_4Cl_2]$ (Figure 5) and for the ν_1, ν_2, ν_3, $2\nu_1$, $\nu_1 + \nu_2$, and $\nu_1 + \nu_3$ bands of $[Os_2(O_2CC_2H_5)_4Cl_2]$ and $[Os_2(O_2CC_3H_7)_4Cl_2]$ (Figures 6 and 7). In all cases the excitation profiles maximise within the electronic band contour

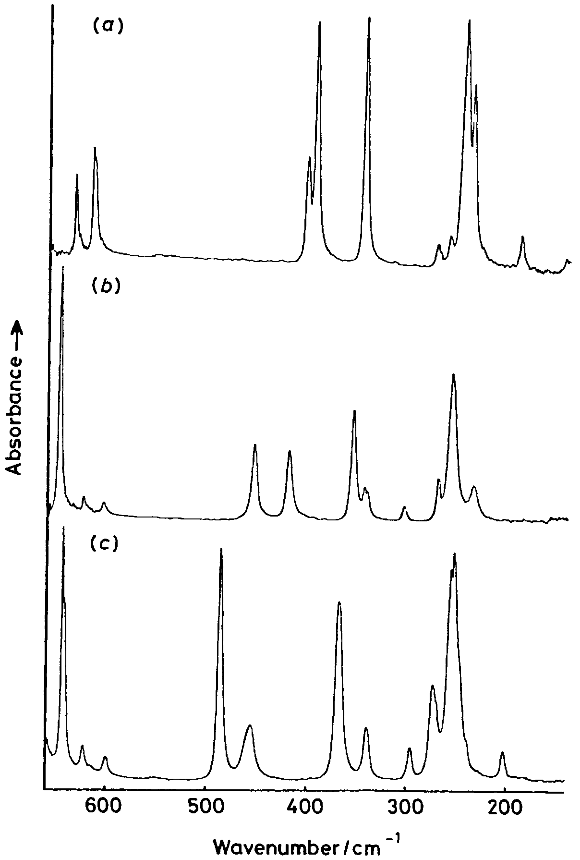

Figure 8. Fourier-transform i.r. spectra (660—140 cm^{-1}) of $[Os_2(O_2CR)_4Cl_2]$, where R = CH_3 (*a*), C_2H_5 (*b*) or C_3H_7 (*c*), as wax discs at *ca.* 80 K

(but just on the low wavenumber side) of the band at *ca.* 390 nm. The excitation profile maxima are particularly well defined in the case of the ν_1 and $2\nu_1$ bands of $[Os_2(O_2CCH_2Cl)_4Cl_2]$ for which the electronic band maximum is at 406 nm (24 600 cm^{-1}), *i.e.* within the compass of the lasing dye stilbene 3 (Kr^{2+} pumped). Use of this dye has enabled the excitation profile maximum to be defined to be 23 800 cm^{-1}. Clearly, ν_1, ν_2, and ν_3 are all strongly coupled to the *ca.* 390 nm electronic band; this has, in the case of R = CH_3, recently been assigned to the $\pi(Cl) \longrightarrow \pi^*(Os_2)$ transition, a transition which would, as found experimentally, be axially polarised.[6]

The ν_1, ν_2, and ν_3 bands (all of which are polarised) have been identified with the key skeletal (a_{1g}) fundamentals ν(OsOs), ν(OsO), and ν(OsCl) on bases which will now be outlined.

ν(OsOs). The band at 236—228 cm^{-1} is assigned to ν(OsOs) on the grounds that (*a*) it is almost insensitive, as would be expected for such a mode, to change in the R group, *cf.* ν(RhRh) of $[Rh_2(O_2CR)_4(PPh_3)_2]$ (R = H, CH_3, C_2H_5, or C_3H_7) only varies by 13 cm^{-1} with change of R group,[7] and (*b*) it is the principal progression-forming mode in each case in the resonance-Raman spectra; this feature is typical of Raman spectra of metal–metal multiply bonded species at resonance with electronic transitions of substantial metal character.[4,8,9] It is significant that ν(OsOs) is insensitive to deuteriation in the case R = CH_3.[3]

ν(OsO). For the dirhodium tetracarboxylate series $[Rh_2(O_2CR)_4(PPh_3)_2]$, ν_2, ν(RhO), is highly sensitive to the mass of R, decreasing in the order 402, 338, 310, 289 cm^{-1} for R = H, CH_3, C_2H_5, or C_3H_7, respectively.[7] A more complicated relationship is evident for the corresponding diruthenium chain complexes[10,11] $[Ru_2(O_2CR)_4Cl]$, but nevertheless, ν(RuO) is certainly strongly dependent on the nature and/or mass of R. Thus, ν_2, ν(OsO), would be expected to depend on R; accordingly the band occurring at 271, 321, and 256 cm^{-1} for R = CH_2Cl, C_2H_5 or C_3H_7, respectively, is assigned to ν_2, ν(OsO), *cf.* the corresponding band for R = CH_3 or CD_3 which occurs at 393 and 375 cm^{-1}, respectively. No overtones of ν_2 are observed under resonance conditions.

Table 4. Wavenumbers (cm^{-1}) of bands observed in the infrared spectrum of $[Os_2(O_2CCH_2Cl)_4Cl_2]$ at *ca.* 80 K

$\tilde{\nu}$	Assignment	$\tilde{\nu}$	Assignment
2 999vw	ν(C–H)	809m	ν(C–Cl)
2 947w		803m	
1 731w,br		794m(sh)	
1 668w,br		725w	δ(OCO)
1 627w,br		712m	
1 609w,br		698w	
1 554w		609w	δ(C–Cl)
1 497w		606w	
1 487w		587w	ρ_w(COO)
1 463m	ν_{asym}(COO)	584w	
1 436vs		460w	δ(C–Cl) and ρ_r(COO)
1 426s(sh)		454w	
1 396s	ν_{sym}(COO)	448w	
1 392m	δ(C–H)	430w	
1 382m		332w	ν(Os–O)
1 378m(sh)		329w(sh)	
1 330w,br		316w	
1 267m	δ(C–H)	308w	
1 260m		278w	
1 219w	$\rho_t(CH_2)$	268w	
1 210w		256w	ν(Os–Cl)?
1 192w	$\rho_w(CH_2)$	200w	δ(O–Os–O) or δ(Os–Os–O)
1 187w		197w	
953w	ν(C–C)	160w	
918w	$\rho_r(CH_2)$	118vw	
911w		111vw	

ν(OsCl). The ν_3 band is assigned to ν(OsCl) on the grounds that its wavenumber is (*a*) relatively insensitive to change of R (292,[3] 311, 299, and 299 cm^{-1} for R = CH_3, CH_2Cl, C_2H_5, or C_3H_7, respectively) and (*b*) in the same region as that of other established values for ν(OsCl), *viz.* $[Os(CO)_4Cl_2]$ (298, 328 cm^{-1})[12] and $[Os(CO)_4(HgCl)Cl]$ (320 cm^{-1}).[13] The increase in ν_3 in the order $CH_3 < C_2H_5 = C_3H_7$ parallels, but is significantly less than, that which might have been expected as a consequence of the OsCl bond length decreases [2.448(2), 2.430(5), or 2.417(3) Å][1,2] in this order. This insensitivity may arise from coupling between the OsOs and OsCl symmetry co-ordinates; this is expected to be strong owing to the facts that they have the same symmetry, share a common atom, are co-axial, and occur in similar spectral regions. No overtones of ν_3 (or of ν_2, see above) are observed under resonance conditions (unlike the situation for analogous dirhodium complexes[7]); this implies that the principal structural change by far on excitation to the resonant excited state is along the OsOs co-ordinate, with only minor associated structural changes along the OsO and OsCl co-ordinates (as witnessed by the observation of weak overtone progressions of the sort $v_1\nu_1 + \nu_2$ and $v_1\nu_1 + \nu_3$).

Depolarisation Ratios.—Solution studies were confined to $[Os_2(O_2CC_2H_5)_4Cl_2]$ and $[Os_2(O_2CC_3H_7)_4Cl_2]$ as these were the only two complexes which were sufficiently soluble for measurements of the Raman band depolarisation ratios (ρ) to be carried out. The ρ values of the ν_1 bands of these two complexes were determined to be 0.38 and 0.37, respectively, for 406.7 nm excitation. This not only demonstrates that ν_1 must

Table 5. Wavenumbers (cm^{-1}) of bands observed in the infrared spectrum of [Os$_2$(O$_2$CC$_2$H$_5$)$_4$Cl$_2$] at *ca.* 80 K

$\tilde{\nu}$	Assignment	$\tilde{\nu}$	Assignment
3 010w	ν(C–H)	1 089w	ν(C–C)
2 997w		1 078w	
2 990w		1 068m	ρ(CH$_3$)
2 977w		1 015m	
2 957w		999vw	
2 953w(sh)		896vw	ν(C–C)
2 934vw		890vw	
2 929vw		808m	ρ_r(CH$_2$)
2 918vw,br		805m(sh)	
2 891w		746w	
1 493w(sh)		705m	δ(OCO)
1 481m	ν_{asym}(COO)	674m	
1 473m	δ_{asym}(CH$_3$) and δ(CH$_2$)	648m	ρ_w(COO)
1 464m		624vw	
1 457m(sh)		604vw	
1 452m		454w	ρ_r(COO)
1 446s		419w	
1 440vs		355w	ν(Os–O)
1 436vs		344vw	
1 424m	ν_{sym}(COO)	341vw	
1 403m	δ_{asym}(CH$_3$) and δ(CH$_2$)	304vw	
1 377m(sh)	δ_{sym}(CH$_3$)	270vw	
1 374m		257w	ν(Os–Cl)
1 369m		235vw	
1 306m	ρ_w(CH$_2$)	149vw,br	
1 295m		129vw	
1 265vw		124vw	
1 237w	ρ_w(CH$_2$)	97vw	
1 235w(sh)		91vw	

arise from an a_{1g} mode, but that the resonant electronic transition must be axially (z) polarised. This follows from the fact that, for a molecule of D_{4h} symmetry, the ρ value of an a_{1g} mode should tend to $\frac{1}{3}$ if the resonant transition is z-polarised but to $\frac{1}{8}$ if it is x, y polarised.[4,14] These results are consistent with the π(Cl) $\longrightarrow$ π^*(Os$_2$) assignment given to the *ca.* 390 nm electronic band ($\varepsilon_{max.} \approx$ 13 000 dm^3 mol^{-1} cm^{-1}) by Miskowski and Gray[6] on the basis of single-crystal transmission electronic spectroscopy.

Infrared Spectra.—The i.r. spectra of the complexes with R = CH$_3$, C$_2$H$_5$, and C$_3$H$_7$ as wax discs at *ca.* 80 K are illustrated in Figure 8 for the 660—140 cm^{-1} region, and the band assignments (3 500—40 cm^{-1}) are given in Tables 4—6. The assignments for the chloroacetate follow those given previously for the related complexes [Mo$_2$(O$_2$CCH$_2$Cl)$_4$],[15] [Rh$_2$(O$_2$CCH$_2$Cl)$_4$(C$_2$H$_5$OH)$_2$],[16] *etc.*, but are more detailed and more complete than these. The propionate and butyrate spectra are very complicated, as expected for molecules with a large number of atoms. Further studies involving ^{18}O as well as partly and/or completely deuteriated samples would be of assistance in further refining the band assignments, which nevertheless seem, except for ν_{asym}(OsCl), to be sufficiently straightforward as not to require comment. Thus ν_{asym} (OsCl) occurs in the region *ca.* 256 cm^{-1}, *i.e.* it lies below ν_{sym}(OsCl) (ν_3) at 311—292 cm^{-1}. This situation is not unusual for vibrations of heavy metal complexes.[3] The ν_{asym}(OsCl) band usually shows shoulders or multiple features which are presumed to be due to site/factor group effects and to the effects of chlorine isotopic splittings.

Conclusions

All three complexes studied, like [Os$_2$(O$_2$CCH$_3$)$_4$Cl$_2$] and [Os$_2$(O$_2$CCD$_3$)$_4$Cl$_2$],[3] display rich resonance-Raman spectra dominated by three progressions in ν_1, ν(OsOs), at *ca.* 230 cm^{-1}, *viz.* $v_1\nu_1$, $v_1\nu_1 + \nu_2$, and $v_1\nu_1 + \nu_3$, where ν_2 is ν(OsO) and ν_3 is ν(OsCl). ν_1 is virtually insensitive (to within ± 4 cm^{-1}) to the carboxylate alkyl group. From the wavenumbers of bands observed in the $v_1\nu_1$ progression, it is evident that ν_1 is harmonic (x_{11} = 0.0 $\pm$ 0.1 cm^{-1}) to within experimental error. The progressions observed in ν_1 indicate that the molecule undergoes a structural change principally along the OsOs co-ordinate upon excitation to the π^*(Os$_2$)^4 state associated with the *ca.* 390 nm electronic band. The ρ value (*ca.* 0.37) of the ν_1 band at resonance with the *ca.* 390 nm band demonstrates that the resonant transition is z polarised, consistent with recent measurements of the electronic spectrum of single crystals of [Os$_2$(O$_2$CCH$_3$)$_4$Cl$_2$] and [Os$_2$(O$_2$CC$_3$H$_7$)$_4$Cl$_2$].[6] The electronic and resonance-Raman results are, taken together with magnetic results indicating that the electronic configuration of these complexes in the ground state is $\sigma^2\pi^4\delta^2\pi^*\delta^*$, consistent with the assignment π(Cl) $\longrightarrow$ π^*(Os$_2$) for the *ca.* 390 nm electronic band.

Table 6. Wavenumbers (cm^{-1}) of bands observed in the infrared spectrum of [Os$_2$(O$_2$CC$_3$H$_7$)$_4$Cl$_2$] at *ca.* 80 K

$\tilde{\nu}$	Assignment	$\tilde{\nu}$	Assignment
3 014vw	ν(C–H)	1 044vw	ρ(CH$_3$)
2 983w		1 040vw(sh)	
2 971w		955vw	
2 964m		942vw	
2 949w(sh)		901vw	ν(C–C)
2 941w		898vw(sh)	
2 926w		889vw	
2 904w		880vw	
2 880w		878vw	
2 869w		864vw	
1 477m	ν_{asym}(COO)	802m	ρ_r(CH$_2$)
1 469m(sh)	δ_{asym}(CH$_3$) and δ(CH$_2$)	754w	
1 465m		729m	
1 462m(sh)		716w	
1 461m		671m	δ(OCO)
1 449m(sh)		643m	ρ_w(COO)
1 441vs		623vw	
1 431m(sh)		601vw	
1 421s	ν_{sym}(COO)	486m	ρ_r(COO)
1 400s	δ_{asym}(CH$_3$) and δ(CH$_2$)	459w(sh)	
1 384m	δ_{sym}(CH$_3$)	455w	
1 381m		368w	ν(Os–O)
1 353m	ρ_t(CH$_2$)	367w(sh)	
1 330m		340vw	
1 310m	ρ_w(CH$_2$)	296vw	
1 299w		273w	
1 274w(sh)		258m(sh)	ν(Os–Cl)
1 266m		256m	
1 255w		253m	
1 238vw		247w(sh)	
1 205w	ρ_w(CH$_2$)	240vw(sh)	
1 201w		203vw	
1 113w		104vw	
1 102m		99vw	
1 094w(sh)	ν(C–C)	93vw	
1 080vw			

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