Infrared, Raman, and Resonance-Raman Spectra of $[Mo_2(O_2CCH_3)_4]$ and $[Mo_2(O_2CCD_3)_4]$

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The i.r., Raman, and resonance-Raman spectra of $[Mo_2(O_2CCH_3)_4]$ and $[Mo_2(O_2CCD_3)_4]$ over the range 3 100—50 cm^{-1} have been measured, and the bands assigned. The band shifts on deuteriation are discussed in detail. In particular, ν(Mo–Mo) at 404 cm^{-1} is insensitive (as expected) to deuteriation, but the wavenumbers of many other modes [apart from the obvious ν(CH), CH_3 deformation, and rocking modes], *viz.* ν(CC), ρ_r(COO), and δ(OCO), are sensitive to deuteriation. This implies extensive coupling of the ring co-ordinates. Raman spectra at resonance with transitions in the violet and ultraviolet display short overtone and combination-band progressions involving ν(Mo–Mo), ν(Mo–O), and ρ_r(COO) which indicate that the geometric changes on excitation occur all around the Mo–O–C–O–Mo rings but are small along any one co-ordinate.

Of the many quadruply bonded carboxylate-bridged complexes, dimolybdenum tetra-acetate is perhaps the best known and the one of central importance. Hence it is important that its i.r. and Raman spectra should be well defined and usable as models for the spectra of related compounds. However, this is not yet the case, though Shriver and co-workers[1] have assigned a Raman band at 404 cm^{-1} to ν(Mo–Mo) by metal isotope substitution. This is the highest value for ν(Mo–Mo) in any known dimolybdenum compound, greater even than that of $[Mo_2Cl_8]^{4-}$, [2,3] and is consistent with the uniquely short Mo–Mo bond length in the compound of 2.093 Å.[4] Since the shift in this band from natural-abundance molybdenum ($^{n.a.}$Mo) to ^{92}Mo (+9 cm^{-1}) is close to that predicted for a Mo_2 dimer it has been concluded that mixing of the Mo–Mo stretching with other co-ordinates is small.[1] The most complete of the other vibrational studies of this molecule to date[5–7] has been by Cotton and co-workers[5] with whose reported band wavenumbers (for the main bands) this work is in good agreement. However, nearly twice as many bands have been observed in the present study. This is probably due to a combination of higher resolution (2 cm^{-1}, Raman; 1 cm^{-1}, i.r.), lower sample temperature (20 K, Raman; 80 K, i.r.), and improved spectrometer sensitivity, particularly in the lower-wavenumber region (to 50 cm^{-1}) than in previous studies. In the present paper we report a detailed study of the i.r. and Raman spectra of the compound in its ^{1}H and ^{2}H forms, as well as the results of Raman studies at resonance with two different electronic bands. A preliminary report of part of this work has already appeared.[8]

Experimental

Compounds.—The compound $[Mo_2(O_2CCH_3)_4]$ and its deuteriated analogue were prepared by the method of Holste and Schäfer.[9] [^{2}H$_4$]Acetic acid (99.6%) was obtained from Aldrich Chemical Co., Inc.

Instrumental.—Raman spectra were recorded using a Spex 14018 (R6) spectrometer, in conjunction with Coherent CR 3000 K and 590 dye lasers. Stilbene 3 was the lasing dye used. Raman samples were held as pressed discs side by side at *ca.* 20 K for λ_0 = 514.5 nm (spectral slit width 2 cm^{-1}) on a closed-cycle liquid-helium probe (Displex) and the spectra were measured under identical conditions with < 3 mW laser power to ensure equal sample temperatures. Raman spectra with other exciting lines were taken at 80 K. 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.

Results

The full listings of observed i.r. and Raman band wavenumbers for $[Mo_2(O_2CCH_3)_4]$ and $[Mo_2(O_2CCD_3)_4]$ are given in Tables 1—4 together with, where possible, the band assignments. These have been made on the following bases.

(*i*) Comparison of the vibrational data with those for the free acetate ion. This works best for the higher-wavenumber bands which can often be considered as individual oscillators, *e.g.* C–H stretching, but will tend to break down at lower wavenumbers. Here the vibrations necessarily involve several symmetry co-ordinates and a 'local mode' description becomes invalid; in consequence a different approach becomes necessary.

(*ii*) The use of models, *e.g.* an $M_2(O_2CC)_4$ model, to account for the skeletal vibrations of the molecule.

Table 1. Wavenumbers of bands observed in the Raman spectrum of $[Mo_2(O_2CCH_3)_4]$ at *ca.* 20 K and λ_0 = 514.5 nm

$\tilde{\nu}$/cm^{-1}	Assignment	$\tilde{\nu}$/cm^{-1}	Assignment
3 018vw	ν(C–H)	706vw,br	
3 007vw		692s	δ(OCO)
2 977w		686m	
2 942vw (sh)		633vw	out-of-plane ρ_ω(COO)
2 931w		573vw	in-plane ρ_r(COO)
1 500vw	ν_{asym}(COO)	569vw	
1 460s	$\delta_{asym}(CH_3)$	404m	ν(Mo–Mo)
1 443m		323m	ν(Mo–O)
1 440m		315w	
1 431m	$\delta_{asym}(CH_3)$	306vw (sh)	
1 422vs	ν_{sym}(COO)	301m	
1 403m	$\delta_{asym}(CH_3)$	220vw,br	$\tau(CH_3)$
1 367m	$\delta_{sym}(CH_3)$	204w	δ(O–Mo–O) or δ(Mo–Mo–O)
1 355w		190w	
1 058vw	$\rho(CH_3)$	143w	$\tau(CH_3)$
1 047vw		106vw	
1 036vw		83vw	
949m	ν(C–C)	72vw	
944m		65vw	

Table 2. Wavenumbers of bands observed in the i.r. spectrum of $[Mo_2(O_2CCH_3)_4]$ at *ca.* 80 K

$\tilde{\nu}$/cm^{-1}	Assignment	$\tilde{\nu}$/cm^{-1}	Assignment
3 017w	ν(C–H)	1 355m	$\delta_{sym}(CH_3)$
3 007w		1 352m	
2 975w		1 054m	$\rho(CH_3)$
2 931w		1 046m	
2 465vw,br	1 034 + 1 431	1 034m	
2 430vw,br		937m	ν(C–C)
2 393vw,br	1 454 + 937	676s	δ(OCO)
2 362vw,br	1 420 + 937	636m	out-of-plane ρ_ω(COO)
2 341vw,br		628m	
1 622w	1 046 + 575	583m	in-plane ρ_r(COO)
1 531m (sh)		575w	
1 524m		373m	ν(Mo–O)
1 520m		353m	
1 514s		342m	
1 500s	ν_{asym}(COO)	311w	
1 475w		235w	δ(O–Mo–O) or δ(Mo–Mo–O)
1 454s (sh)		230w	
1 451vs	$\delta_{asym}(CH_3)$	183vw	$\tau(CH_3)$
1 440s	ν_{sym}(COO)	146vw	
1 431m	$\delta_{asym}(CH_3)$	91vw	
1 420m			
1 407vs	$\delta_{asym}(CH_3)$		

Table 3. Wavenumbers of bands observed in the Raman spectrum of $[Mo_2(O_2CCD_3)_4]$ at *ca.* 20 K and λ_0 = 514.5 nm

$\tilde{\nu}$/cm^{-1}	Assignment	$\tilde{\nu}$/cm^{-1}	Assignment
2 258w	ν(C–D)	851vw	$\rho(CD_3)$
2 250w		673w	
2 228m		664m	δ(OCO)
2 201w		659m	
2 113m		555w	in- and out-of-plane ρ(COO)
1 489w	ν_{asym}(COO)	538vw	
1 485w		533w	
1 467w	914 + 555	403m	ν(Mo–Mo)
1 451w	917 + 538	313m	ν(Mo–O)
1 433s		310m	
1 418vs	ν_{sym}(COO)	302w	
1 406vw		293m	
1 393vw		276vw	
1 389vw (sh)		259vw	
1 098w	$\delta_{sym}(CD_3)$	201w	δ(O–Mo–O) or δ(Mo–Mo–O)
1 093w		187w	
1 047w	$\delta_{asym}(CD_3)$	173vw,br	$\tau(CD_3)$
1 042w		124w	$\tau(CD_3)$
1 028vw		109vw	
917vw	$\rho(CD_3)$	99vw	
914vw		74vw	
903m	ν(C–C)	61vw	
900m			

Table 4. Wavenumbers of bands observed in the i.r. spectrum of $[Mo_2(O_2CCD_3)_4]$ at *ca.* 80 K

$\tilde{\nu}$/cm^{-1}	Assignment	$\tilde{\nu}$/cm^{-1}	Assignment
2 897vw		918m	$\rho(CD_3)$
2 513vw	1 423 + 1 091	913m	
2 375vw		893m	ν(C–C)
2 313vw		889m	
2 256vw	ν(C–D)	847m	$\rho(CD_3)$
2 250w		832vw	
2 227w		672w (sh)	
2 110w		648m	δ(OCO)
1 520w (sh)		558w	in- and out-of-plane ρ(COO)
1 494vs	ν_{asym}(COO)	550m	
1 483s (sh)		539w	
1 466w	918 + 550	363m	ν(Mo–O)
1 451m	913 + 539	343m	
1 427vs	ν_{sym}(COO)	321m	
1 423vs		285w	
1 391w		224w	δ(O–Mo–O) or δ(Mo–Mo–O)
1 312vw,br		220w	
1 091w	$\delta_{sym}(CD_3)$	172vw	$\tau(CD_3)$
1 082vw (sh)			
1 050w	$\delta_{asym}(CD_3)$		
1 040w			
1 029m			

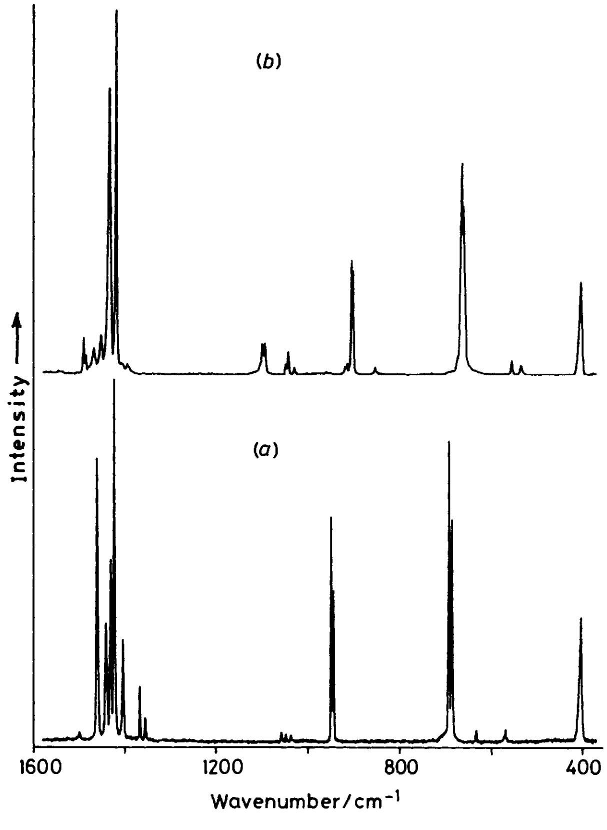

Figure 1. Raman spectra (1 580—370 cm^{-1}) of (*a*) $[Mo_2(O_2CCH_3)_4]$ and (*b*) $[Mo_2(O_2CCD_3)_4]$ as neat solids at *ca.* 20 K with 514.5-nm excitation

(*iii*) Comparison with vibrational data available for other dimeric carboxylates. This approach is limited owing to the small number for which such data are available.

The Raman spectra of $[Mo_2(O_2CCH_3)_4]$ and $[Mo_2(O_2CCD_3)_4]$ at *ca.* 20 K with λ_0 = 514.5 nm are shown for the ranges 1 580—370 and 420—30 cm^{-1} in Figures 1 and 2 respectively. The low-wavenumber range was recorded in the triple monochromator mode in order to minimise Rayleigh scattering. The two very weak peaks at 215 and 100 cm^{-1} in the Raman spectra of $[Mo_2(O_2CCH_3)_4]$ as obtained by Cotton and co-workers,[5] and marked as questionable, have been confirmed in this work; they occur at 220 and 106 cm^{-1}, respectively. The i.r. spectra of the two compounds are shown for the ranges 1 600—600 and 660—140 cm^{-1} in Figures 3 and 4, respectively. The resonance-Raman spectrum of $[Mo_2(O_2CCH_3)_4]$ at *ca.* 80 K is shown in Figure 5 for λ_0 = 445.8, 460.4, and 460.9 nm over the range 1 000—150 cm^{-1}, and in Figure 6 for λ_0 = 337.5 nm over the range 1 000—200 cm^{-1}.

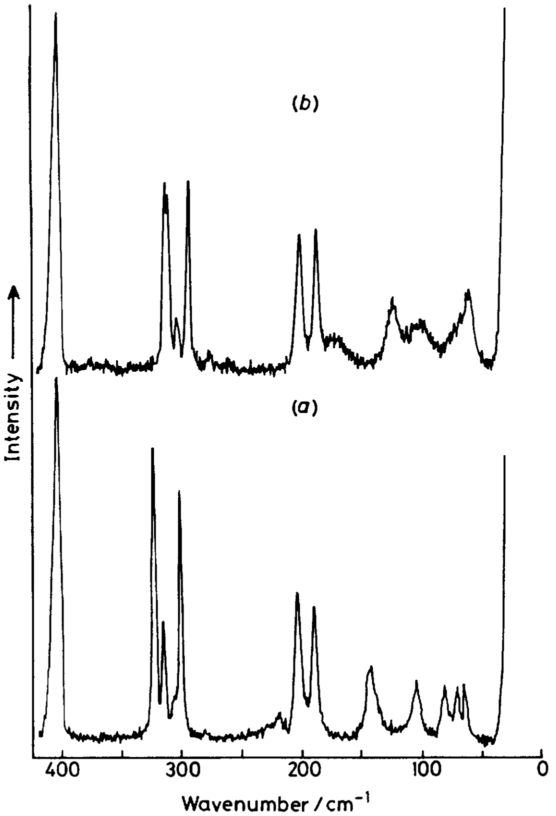

Figure 2. Raman spectra (420—30 cm^{-1}) of (*a*) [$Mo_2(O_2CCH_3)_4$] and (*b*) [$Mo_2(O_2CCD_3)_4$] as neat solids at *ca.* 20 K with 514.5-nm excitation

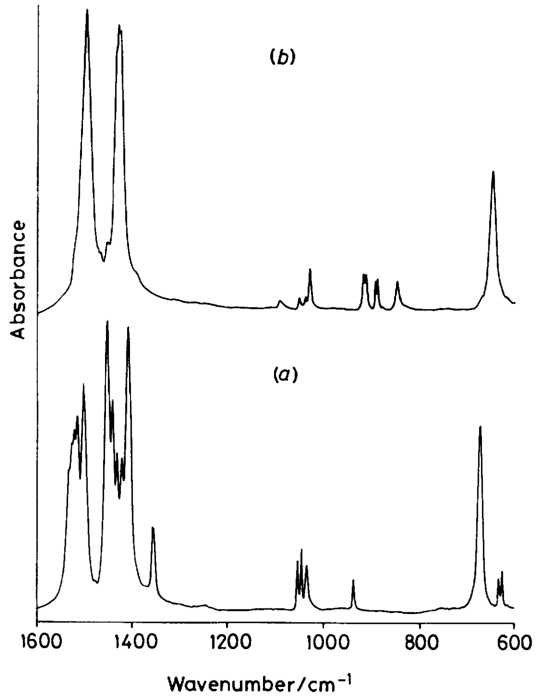

Figure 3. Fourier-transform i.r. spectra (1 600—600 cm^{-1}) of (*a*) [$Mo_2(O_2CCH_3)_4$] and (*b*) [$Mo_2(O_2CCD_3)_4$] as KCl discs at *ca.* 80 K

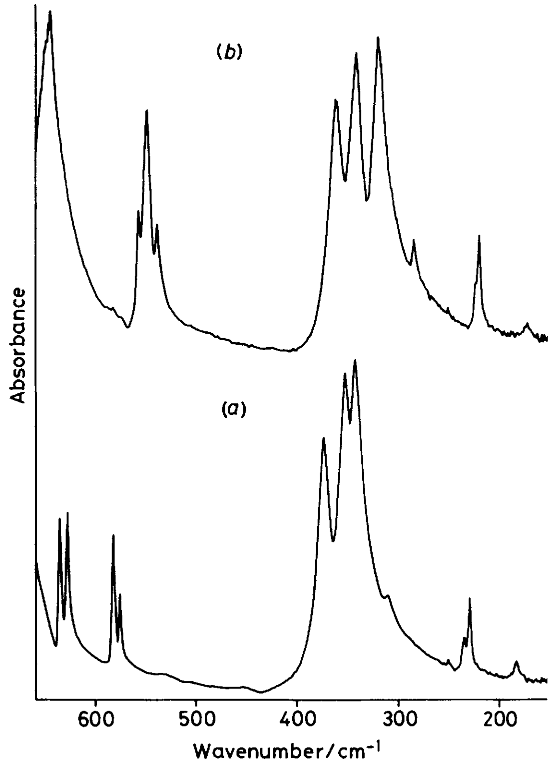

Figure 4. Fourier-transform i.r. spectra (660—140 cm^{-1}) of (*a*) [$Mo_2(O_2CCH_3)_4$] and (*b*) [$Mo_2(O_2CCD_3)_4$] as wax discs at *ca.* 80 K

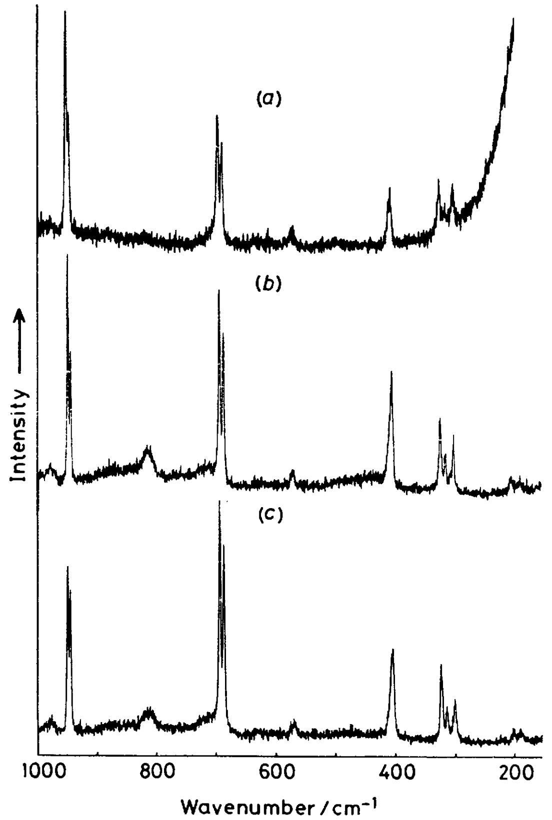

Figure 5. Resonance-Raman spectra of [$Mo_2(O_2CCH_3)_4$] as a neat solid at *ca.* 80 K with λ_0 = 445.8 (*a*), 460.4 (*b*), and 460.9 nm (*c*)

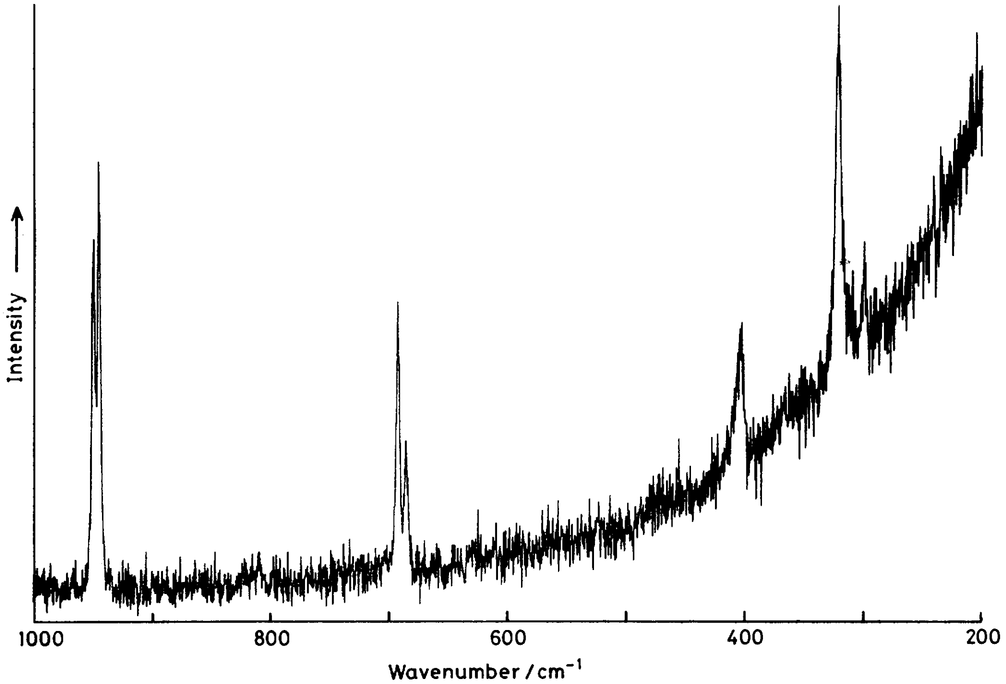

Figure 6. Resonance-Raman spectrum of $[Mo_2(O_2CCH_3)_4]$ as a neat solid at *ca.* 80 K with λ_0 = 337.5 nm

Discussion

(*i*) ν(Mo–Mo) *and the Region below* 500 cm^{-1}.—The band at 404 cm^{-1} attributed to ν(Mo–Mo) might have been thought to be the most intense in the Raman spectrum of $[Mo_2(O_2CCH_3)_4]$ on account of the high Mo–Mo bond order of four. However it is noteworthy that there are several bands in the spectrum which are more intense than that at 404 cm^{-1}. In order to remove any possible ambiguity regarding the assignment of ν(Mo–Mo) we have studied the fully deuteriated analogue and have demonstrated that the band at 404 cm^{-1} suffers a shift of only 1 cm^{-1} to lower wavenumber on deuteriation. This result unambiguously confirms the assignment. The ν(Mo–O) modes, which are known to occur at somewhat lower wavenumbers, suffer a much greater shift on deuteriation than this. The technique of deuteriation rather than metal isotope substitution for providing a basis for assigning ν(M–M) in such complexes is to be preferred where (*a*) there is not sufficient mass difference between any two accessible isotopes and (*b*) there are no metal isotopes available. Effectively, this is assignment by default, *i.e.* identification of a band on the basis that it does *not* shift on substitution.

The group of bands in the 300 cm^{-1} region (Figure 2) shift typically *ca.* 10 cm^{-1} on deuteriation and are thus assigned to ν(Mo–O) modes, in agreement with the conclusions of Shriver and co-workers.[1]

The large metal character of the band at 404 cm^{-1} is implicit in its breadth by comparison with that of the bands in the 300 cm^{-1} region. The uneven spread of isotopes in molybdenum of natural abundance can clearly be inferred from the shape of the band at 404 cm^{-1}, which is asymmetric on the high-wavenumber side.

In order to perform a force-constant analysis[10] on a number of both unbridged and bridged multiply bonded species, Cotton and co-workers[5] used an M_2X_8 model with D_{4h} symmetry (Table 5). While this model accounts for all the vibrations of an $[Mo_2Cl_8]^{4-}$ ion, it can only be used as a first approximation to account for the skeletal vibrations of $[Mo_2(O_2CCH_3)_4]$. The model predicts nine Raman-active bands and two i.r.-active bands and, by virtue of the masses involved, the bands would all be expected to occur below 500 cm^{-1}. The Raman-active modes include three M–O stretching vibrations (a_{1g}, b_{2g}, and e_g) and five bending modes (a_{1g}, b_{1g}, b_{2g}, and $2e_g$), whereas the i.r.-active modes include two M–O stretches (a_{2u} and e_u) and three bending modes (a_{2u} and $2e_u$).

An alternative to the M_2O_8 model is to consider the vibrations of the bridging acetate groups as well. This is obviously a more complicated model but allows more understanding of coupling effects. The $M_2(O_2CR)_4$ structure possesses D_{4h} symmetry, and has 48 normal modes (Table 6). These can be broken down into the following representations, $5a_{1g}$, $2a_{2g}$, $4b_{1g}$, $3b_{2g}$, $5e_g$, a_{1u}, $4a_{2u}$, b_{1u}, $4b_{2u}$, and $7e_u$. Of these, $5a_{1g}$, $4b_{1g}$, $3b_{2g}$, and $5e_g$ are Raman-active, $4a_{2u}$ and $7e_u$ are i.r.-active and $2a_{2g}$, a_{1u}, b_{1u}, and $4b_{2u}$ are inactive. As a consequence of the centre of inversion the rule of mutual exclusion applies and there should be no coincidences between i.r. and Raman bands. However, any separations of the vibrational band wavenumbers corresponding to symmetrical and antisymmetrical vibrations localised mainly in the R groups are likely to be small. As a result the separate vibrations of this type will usually give rise to apparent i.r. and Raman coincidences [see section (*ii*)].

Many of the descriptions of the various normal modes and their symmetries (Table 6) stem from those proposed for the acetate ion.[11,12] The number of M–O stretching vibrations is obviously the same as predicted by the M_2O_8 model, but the difference between the two models is in the number of bending modes predicted.

Effectively the M_2O_8 model overpredicts the number of skeletal bending vibrations (10), whereas with the inclusion of the acetate groups in the $M_2(O_2CC)_4$ model a number of these modes (6) are described in terms of other co-ordinates. Thus for the M_2O_8 model an M–M–O (θ) deformation of a_{1g} symmetry is such that all the oxygen atoms move out of the MO_4 plane in phase and this vibration would be expected to occur at low wavenumber; alternatively in terms of the

Table 5. Symmetry of normal modes and internal co-ordinates for a D_{4h} M_2O_8 unit

	a_{1g}	b_{1g}	b_{2g}	e_g	a_{1u}	a_{2u}	b_{1u}	b_{2u}	e_u
Activity[a]	R	R	R	R		i.r.			i.r.
1 M–M	1								
8 M–O	1	1		1		1		1	1
8 M–M–O (θ)	1[b]	1		1		1[b]		1	1
8 O–M–O (φ)	1[b]		1	1		1[b]	1		1
1 M–M torsion					1				
$\Gamma_{\mathrm{vib}}(24)$	3	2	1	3	1	2	1	2	3

[a] R = Raman-active, i.r. = infrared-active. [b] Symmetry species a_{1g} and a_{2u} contain one redundancy each in the angle bending co-ordinates θ and φ.

Table 6. Symmetry of normal modes and internal co-ordinates for an $M_2(O_2CC)_4$ species*

Description	Raman active	Infrared active	Inactive
M–M stretch	a_{1g}		
M–O stretch	$a_{1g} + b_{1g} + e_g$	$a_{2u} + e_u$	b_{2u}
C–O stretch (sym)	$a_{1g} + b_{1g}$	e_u	
C–O stretch (asym)	e_g	a_{2u}	b_{2u}
C–C stretch	$a_{1g} + b_{1g}$	e_u	
OCO bend	$a_{1g} + b_{1g}$	e_u	
CH_3 rock (in-plane)	e_g	a_{2u}	b_{2u}
CH_3 rock (out-of-plane)	b_{2g}	e_u	a_{2g}
COO rock (in-plane)	e_g	a_{2u}	b_{2u}
COO rock (out-of-plane)	b_{2g}	e_u	a_{2g}
M_2O_8 deformations	$b_{2g} + e_g$	e_u	b_{1u}
M–M torsion			a_{1u}
$\Gamma_{\mathrm{vib}}(^{48})$	22	18	8

* 48 normal modes comprise $5a_{1g}$, $2a_{2g}$, $4b_{1g}$, $3b_{2g}$, $5e_g$, a_{1u}, $4a_{2u}$, b_{1u}, $4b_{2u}$, and $7e_u$ in D_{4h} symmetry.

$M_2(O_2CC)_4$ model it could be described as the a_{1g} OCO bending vibration, on which basis it would be expected to occur at a much higher wavenumber. Both models predict the same number of bands and the same symmetries for the molybdenum–oxygen stretching vibrations, *i.e.* three Raman-active bands of a_{1g}, b_{1g}, and e_g symmetries and two i.r.-active bands of a_{2u} and e_u symmetry. In this study three bands are observed in the Raman spectrum of $[Mo_2(O_2CCH_3)_4]$ at 323, 315, and 301 cm^{-1} which are close to those observed by Shriver and co-workers.[1] However the better resolution obtained here has enabled the observation of a much weaker band occurring on the high-wavenumber side of the band at 301 cm^{-1} at approximately 306 cm^{-1}. Upon deuteriation all four bands show shifts, but to different extents: thus the bands at 323 and 301 cm^{-1} for $[Mo_2(O_2CCH_3)_4]$ shift to 313 and 293 cm^{-1}, respectively for $[Mo_2(O_2CCD_3)_4]$, whereas the band at 315 cm^{-1} and the weak shoulder at 306 cm^{-1} shift to 310 and 302 cm^{-1}, respectively.

Both the M_2O_8 model and the $M_2(O_2CC)_4$ model predict two i.r.-active ν(Mo–O) bands, of e_u and a_{2u} symmetries. However, four bands are so assigned (373, 353, 342, and 311 cm^{-1}), the additional ones arising from site-symmetry effects.[4] The shifts of these bands are much greater than those of the Raman counterparts, being 10 cm^{-1} for the upper two bands and over 20 cm^{-1} for the lower two. The breadth of these i.r. bands (Figure 3) is indicative of the involvement of the molybdenum atoms in the vibrations, as opposed to the situation for their Raman counterparts.

The fact that the ν(Mo–O) bands show significant sensitivity to deuterium substitution indicates that their co-ordinates are coupled to motions of the methyl groups. It is proposed in section (*ii*) that the in- and out-of-plane rocking vibrations are coupled to these vibrations. This argument receives support from the following: (*a*) both the in- and out-of-plane rocking vibrations show strong sensitivity to deuteriation, shifting by 50 and 100 cm^{-1}, respectively; (*b*) they are close in wavenumber; and (*c*) they share a common atom, oxygen.

One argument opposing this is that, within the framework of the $M_2(O_2CC)_4$ model, the symmetries of the in- and out-of-plane COO rocking vibrations do not span all of the Mo–O stretching vibrations. However, as shown in section (*ii*) the $M_2(O_2CC)_4$ model only has limited success in accounting for the number of observables, and breaks down for both the COO rocking and Mo–O stretching vibrations. These 'additional' bands are not readily interpretable in terms of overtones, or of combination tones, and the only explanation can be a lifting of the degeneracies of a number of modes due to low site symmetry in the crystal environment; however the centre of inversion appears to be preserved owing to the lack of i.r. and Raman coincidences below 500 cm^{-1}.

The $M_2(O_2CC)_4$ model predicts two Raman-active bending modes of b_{2g} and e_g symmetries and an i.r. band of e_u symmetry, which we expected to occur below 250 cm^{-1}. Once again there are considerably more bands observed than this, eight in the Raman and five in the i.r. spectrum, although one acetate group vibration, the methyl torsion, is also expected to occur in this region. Data on these modes are scarce; in alkanes CH_3–CH_2 torsions occur in the 280—220 cm^{-1} region,[13] whilst the CH_3 torsion in $Na(O_2CCH_3)$ has been tentatively assigned to a band at 247 cm^{-1}.[14] They appear as extremely weak and broad bands at room temperature but would be expected to sharpen on cooling,[15] and also to show strong sensitivity to deuterium substitution. On this basis the Raman bands at 220 and 143 cm^{-1} which appear to have shifted upon deuteriation to 173 and 124 cm^{-1}, respectively, are tentatively assigned to CH_3 torsions. The i.r. counterpart of this vibration could possibly be the band at 183 cm^{-1} shifting to 172 cm^{-1} for $[Mo_2(O_2CCD_3)_4]$.

The two bands at 204 and 190 cm^{-1} in the Raman spectrum of $[Mo_2(O_2CCH_3)_4]$ show no dependence upon ^{92}Mo substitution[1] and only shift 3 cm^{-1} each upon deuteriation, which suggests that they arise from skeletal bending modes. In the Raman spectrum of $[^{\mathrm{n.a.}}Cu_2(O_2CCH_3)_4(H_2O)_2]$[16] in this region, bands occur at 181 and 158 cm^{-1} which show a maximum shift of 2 cm^{-1} over the ^{65}Cu, $H_2{}^{18}O$, D_2O, and CD_3 isotopomers. The former band is assigned to a δ(O–Cu–O) vibration and the latter to a δ(Cu–Cu–O) ring deformation.

In the i.r. spectrum of $[Mo_2(O_2CCH_3)_4]$ the two bands at 235 and 230 cm^{-1} which shift upon deuteriation to 224 and 220 cm^{-1}, respectively, are assigned to skeletal bending modes. These shifts are much larger than those of their Raman counterparts, and the appearance of two bands is again in contradiction to the $M_2(O_2CC)_4$ model.

(*ii*) *The Region above* 500 cm^{-1}.—ν(C–H). The methyl group gives rise to two ν(C–H) bands of *a* and *e* symmetry in the spectra of hydrocarbons, at 2 962 and 2 872 ± 10 cm^{-1}, respectively,[17] while $Na(O_2CCH_3)$ gives rise to three ν(C–H) bands, at 3 013, 2 980, and 2 933 cm^{-1}.[11] In the i.r. spectrum of $[Mo_2(O_2CCH_3)_4]$ four bands are observed at 3 017, 3 007, 2 975, and 2 931 cm^{-1}, which have virtually coincident Raman counterparts except for an additional Raman band at 2 942 cm^{-1}. None of these bands can be attributed to overtones or combinations of bands in the 1 500—1 400 cm^{-1} region since, in the spectra of $[Mo_2(O_2CCD_3)_4]$, there are no bands in the 3 000 cm^{-1} region and, moreover, the same number of bands are observed in the ν(C–D) region for $[Mo_2(O_2CCD_3)_4]$ as in the ν(C–H) region for $[Mo_2(O_2CCH_3)_4]$ (Tables 1—4). The observed shifts on deuteriation are by factors of slightly less than $1/\sqrt{2}$ and close to those observed for $Na(O_2CCH_3)$ [*cf.* $Na(O_2CCD_3)$ 2 264, 2 231,and 2 111 cm^{-1}].[11]

In the 2 500—2 200 cm^{-1} region of the i.r. spectrum of $[Mo_2(O_2CCH_3)_4]$ there are many very weak broad bands which are absent from the spectrum of $[Mo_2(O_2CCD_3)_4]$; these are assigned to combination bands (Table 2).

ν(COO). In the vibrational spectrum of the acetate ion ν_{asym}(COO) and ν_{sym}(COO) occur at 1 578 (1 556 cm^{-1} in solution) and 1 413 cm^{-1}, respectively[11] (*cf.* Spinner,[14] 1 583 and 1 421 cm^{-1}, respectively). The asymmetric stretch gives rise to a strong band in the i.r. spectrum but to no detectable band in the Raman spectrum, whereas the symmetric stretch gives rise to a strong Raman band.

The $M_2(O_2CC)_4$ model predicts an i.r.-active mode of a_{2u} symmetry and a Raman-active mode of e_g symmetry for ν_{asym}(COO). Quite clearly there are no bands in the 1 610—1 550 cm^{-1} region of the i.r. spectrum of $[Mo_2(O_2CCH_3)_4]$ corresponding to the asymmetric stretch. There are however a large number of bands in the 1 530—1 400 cm^{-1} region. Upon comparison of the *X*-ray structures of the free acetate ion[18] and that of $[Mo_2(O_2CCH_3)_4]$[4] the reason for the lowering of this band wavenumber upon co-ordination can be understood. The average C–O distance in $[Mo_2(O_2CCH_3)_4]$ (1.277 Å)[4] is much longer than that of the free acetate ion (1.245 Å)[18] and the O–C–O angle is less, 121.3 compared to 125.7°. The first result implies a weakening of the C–O bond upon co-ordination.

The asymmetric C–O stretch of $Na(O_2CCH_3)$ only shifts 11 cm^{-1} on deuteriation.[11] On the basis of this and the preceding points the strong band at 1 500 cm^{-1} in the i.r. spectrum of $[Mo_2(O_2CCH_3)_4]$ is assigned to ν_{asym}(COO), shifting by only 6 cm^{-1} upon deuteriation. Its Raman counterpart of e_g symmetry is assigned to the very weak band at 1 500 cm^{-1}.

The wavenumber of ν_{asym}(COO) in carboxylate salts has been shown to be determined largely by substituent effects. Reasonable correlations have been obtained with Hammett σ-type values and the value of ν_{asym}(COO) for substituted benzoates.[19] Spinner[14] has shown that, for a number of different salts of the type $Na(O_2CR)$, ν_{asym}(COO) increases very markedly with the electron-withdrawing effect of R and shows no mass effect. By contrast ν_{sym}(COO) is not noticeably affected by polar groups but decreases markedly as the mass of R increases, *e.g.* 1 336 $[Na(O_2CCBr_3)]$ and 1 413 cm^{-1} $[Na_2(O_2CCH_3)]$, although an exception to this is sodium formate where ν_{sym}(COO) occurs at 1 366 cm^{-1}.[11] The fact that no correlations can be achieved between ν_{sym}(COO) values signifies that the COO co-ordinate is involved in coupling to a much greater extent than is ν_{asym}(COO). This is further confirmed by the breakdown of Hammett σ-type correlations when the mean values of ν_{sym} and ν_{asym}(COO) are used.[19]

Assignment of ν_{sym}(COO) is difficult for $[Mo_2(O_2CCH_3)_4]$ as there are a large number of strong bands in the appropriate region in both the i.r. and Raman spectra. Again acetate deuteriation considerably helps in making the assignment as a number of the bands are due to C–H deformations, which are shifted to lower wavenumber upon deuteriation.

The $M_2(O_2CC)_4$ model predicts two Raman-active bands of a_{1g} and b_{1g} symmetries and one i.r.-active band of e_u symmetry in the ν_{sym}(COO) region. The Raman-active modes would be expected to give rise to strong bands, and thus the strong bands at 1 418 and 1 422 cm^{-1} in the Raman spectra of $[Mo_2(O_2CCD_3)_4]$ and $[Mo_2(O_2CCH_3)_4]$, respectively, are assigned to one of the ν_{sym}(COO) components. The shift of 4 cm^{-1} upon deuteriation is comparable to that of 7 cm^{-1} observed for $Na(O_2CCH_3)$.[11] The assignment of the other Raman-active ν_{sym}(COO) band is not clear, and would benefit from ^{18}O studies. Interestingly, the Raman spectrum of $[Mo_2(O_2CH)_4]$[20] also has only one band in this region, at 1 325 cm^{-1}, and this is very strong compared to the rest of the observed bands.[20] This band is assigned to ν_{sym}(COO), *cf.* for the formate ion ν_{sym}(COO) 1 351 cm^{-1} in solution, 1 366 cm^{-1} for the sodium salt.[11]

In the i.r. spectrum only one band of e_u symmetry is expected, the strong band centred at 1 427 cm^{-1} for $[Mo_2(O_2CCD_3)_4]$ being so assigned. Its counterpart in the spectrum of $[Mo_2(O_2CCH_3)_4]$ is difficult to assign, again owing to the large number of strong bands in this region; the band at 1 440 cm^{-1} is tentatively so assigned. An alternative assignment[21] for ν_{asym}(COO) and ν_{sym}(COO) is considered to be incorrect, the observed bands being presumed to result from the decomposition of $[Mo_2(O_2CCH_3)_4]$. Moreover, the results obtained in this study are consistent with those of other workers.[5,22,23]

The only other $M_2(O_2CR)_4$ system for which detailed vibrational data are available is $[Cu_2(O_2CCH_3)_4(H_2O)_2]$ and its isotopomers.[16] Here the i.r. bands at 1 605 and 1 425 cm^{-1} are assigned to ν_{asym} and ν_{sym}(COO), respectively. The much higher value of ν_{asym}(COO) as compared to that for $[Mo_2(O_2CCH_3)_4]$ is consistent with the much shorter C–O distance of 1.260 Å,[24] compared to that of 1.277 Å as found for $[Mo_2(O_2CCH_3)_4]$.[4]

Methyl group deformations. Two deformation vibrations, a symmetric and an asymmetric, occur for a methyl group and so for $[Mo_2(O_2CCH_3)_4]$ eight bands would be expected in total. Assuming the centre of symmetry is preserved then a maximum of four bands would be expected in each spectrum. As mentioned earlier the coupling between the vibrations of the individual methyl groups would be small, so one aid to assignment would be the expected near coincidence of i.r. and Raman bands. Assignments of the symmetric deformation are considered first.

The symmetric methyl deformation is a useful group wavenumber occurring in the range 1 385—1 368 cm^{-1} for alkanes, the shifts therefrom being small when the methyl groups are joined to carbon atoms.[25] The two bands at 1 355 and 1 352 cm^{-1} in the i.r. spectrum, and at 1 367 and 1 355 cm^{-1} in the Raman spectrum, of $[Mo_2(O_2CCH_3)_4]$ are thus assigned to $\delta_{sym}(CH_3)$. In the spectrum of $Na(O_2CCD_3)$, $\delta_{sym}(CD_3)$ occurs at 1 085 cm^{-1}, a shift of 259 cm^{-1} to lower wavenumber from that observed for $Na(O_2CCH_3)$; hence the i.r. bands at 1 091 and 1 082 cm^{-1} and the Raman bands at 1 098 and 1 093 cm^{-1} are assigned to this vibration. It is interesting that the two i.r. bands in this region have decreased in intensity relative to those of the COO stretching vibrations.

Asymmetric CH_3 deformations give rise to absorption bands close to 1 450 cm^{-1}, variations of more than 10—20 cm^{-1} from this value occurring only when a strongly electronegative atom causes a significant change in the charge distribution on the carbon atom.[17] For $Na(O_2CCH_3)$ $\delta_{asym}(CH_3)$ occurs at 1 456 cm^{-1}, shifting down by 382 cm^{-1} upon deuteriation; however, for $[Mo_2(O_2CCH_3)_4]$ assignment is difficult due to the large number of bands in this region, but it is easier for $[Mo_2(O_2CCD_3)_4]$. For this species the Raman bands at 1 028, 1 042, and 1 047 cm^{-1}, and the i.r. bands at 1 029, 1 040, and 1 050 cm^{-1} are readily assigned to $\delta_{asym}(CD_3)$ vibrations.

For $[Mo_2(O_2CCH_3)_4]$ the i.r. bands at 1 451, 1 431, and 1 407 cm^{-1} with Raman counterparts at 1 460, 1 431, and 1 403 cm^{-1} are tentatively assigned to $\delta_{asym}(CH_3)$. These assignments are different from those for $[Cu_2(O_2CCH_3)_4(H_2O)_2]$ (although the reported data differ here), Shriver and co-workers[16] assigning the i.r. and Raman bands at 1 460 and 1 450 cm^{-1}, respectively, and Heyns[26] the four i.r. bands at 1 460, 1 455, 1 445, and 1 440 cm^{-1} to $\delta_{asym}(CH_3)$.

ν(C–C). As opposed to double and triple carbon–carbon bonded species there are no characteristic group wavenumbers for single bonded species. This is because the CC co-ordinate couples strongly with others within a molecule. For $Na(O_2CCH_3)$ ν(C–C) has been assigned to a band at 926 cm^{-1}, which shifts by 43 cm^{-1} to 883 cm^{-1} upon deuteriation.[11] The $M_2(O_2CC)_4$ model predicts two Raman-active bands of a_{1g} and b_{1g} symmetries and one i.r.-active band of e_u symmetry. For $[Mo_2(O_2CCH_3)_4]$ the two Raman bands at 949 and 944 cm^{-1} and the i.r. band at 937 cm^{-1} are assigned to ν(C–C), the number of bands predicted by the $M_2(O_2CC)_4$ model being in agreement with those observed and the band wavenumbers being close to those observed for $Na(O_2CCH_3)$. Upon deuteriation the Raman bands shift to 903 and 900 cm^{-1}, the magnitude of this shift being almost identical to that observed for $Na(O_2CCH_3)$. The assignment of ν(C–C) in the i.r. spectrum of $[Mo_2(O_2CCD_3)_4]$ is less straightforward, due to the presence of other bands in the 920—850 cm^{-1} region; however, by comparison with the Raman spectrum the bands at 893 and 889 cm^{-1} are attributed to ν(C–C). The degeneracy of this vibration may have been lifted for $[Mo_2(O_2CCD_3)_4]$

Methyl group rocking. Methyl rocking gives rise to two bands in the vibrational spectrum of $Na(O_2CCH_3)$ at 1 052 and 1 020 cm^{-1}. The former band is assigned to an out-of-plane and the latter to the in-plane rock.[11] The $M_2(O_2CC)_4$ model predicts two Raman-active bands of b_{2g} and e_g symmetries and two i.r. bands of e_u and a_{2u} symmetries, corresponding to out-of- and in-plane CH_3 rocking vibrations, respectively. These symmetries span those of the COO rocking vibrations and some coupling between the two vibrations is expected. In a methyl rock the CH_3 group does not internally deform but moves as a whole and must be compensated for by motions of the rest of the molecule; hence as the rest of the molecule is mechanically involved in these vibrations, the CH_3 rocking vibration covers a range of wavenumbers.[27] For example in the i.r. spectra of hydrocarbons the CH_3 rocking vibration absorbs weakly at 1 150—1 120 and at 900—890 cm^{-1},[27] which is considerably different from the values for $Na(O_2CCH_3)$.[11] Their wavenumber is similar to that observed for ν(C–C) but their Raman intensities are considerably different, CH_3 rocking vibrations giving rise to weak bands in contrast to the C–C stretching vibrations which give rise to intense ones. Thus assignment is best achieved by first examining the Raman spectrum and, on this basis, the bands at 1 058, 1 047, and 1 036 cm^{-1} are assigned to methyl rocking, their i.r. counterparts being at 1 054, 1 046, and 1 034 cm^{-1}, respectively.

To assign the methyl rocking vibrations for $[Mo_2(O_2CCD_3)_4]$ it is also best to examine the Raman spectrum first. Now, for $Na(O_2CCH_3)$ the shifts upon deuteriation for the in-and out-of-plane rock are 188 and 112 cm^{-1}, respectively.[11] Thus, by comparison, the weak bands at 917, 914, and 851 cm^{-1} in the Raman spectrum and at 918, 913, and 847 cm^{-1} in the i.r. spectrum are assigned to $\rho_r(CD_3)$. Upon deuteriation the shifts of the upper two bands in the spectra of $[Mo_2(O_2CCH_3)_4]$ are approximately 135 cm^{-1} each, while the lower band shifts approximately 185 cm^{-1}.

OCO *Bend.* The OCO bending vibration occurs at 650 cm^{-1} for $Na(O_2CCH_3)$[11] and is likely to be coupled to the C–C stretching vibration which is close in wavenumber and possesses the same symmetry. This is confirmed by its 31 cm^{-1} shift to 619 cm^{-1} for $Na(O_2CCD_3)$, and by comparison with $Na(O_2CH)$ where δ(OCO) occurs at 762 cm^{-1}.[11] The $M_2(O_2CC)_4$ model predicts two Raman bands of a_{1g} and b_{1g} symmetries and one i.r. band of e_u symmetry, their symmetries being coincident with those of the C–C and C–O (symmetric) stretching vibrations. The two intense Raman bands at 692 and 686 cm^{-1} are assigned to a_{1g} and b_{1g} modes, though not necessarily in this order, and the strong broad band at 676 cm^{-1} in the i.r. spectrum is assigned to the e_u vibration. Their counterparts for $[Mo_2(O_2CCD_3)_4]$ are at 664 and 659 cm^{-1} in the Raman spectrum and at 648 cm^{-1} in the i.r. spectrum. These shifts are similar in wavenumber to those observed for $Na(O_2CCD_3)$.[11] There is no obvious correlation between the wavenumber of δ(OCO) and the OCO angle. In the series $Li(O_2CCH_3)$,[18] $[Cu_2(O_2CCH_3)_4(H_2O)_2]$,[24] and $[Mo_2(O_2CCH_3)_4]$,[4] the OCO angle decreases, being 125.7, 124.9, and 121.3°, respectively, whereas δ(OCO) {using the average of the Raman values for $[Mo_2(O_2CCH_3)_4]$} occurs at 650, 702, and 689 cm^{-1}, respectively.

COO *Rocking.* The $M_2(O_2CC)_4$ model also predicts eight vibrations due to rocking motions of the COO group. These can be further broken down into in-plane rocking (ρ_r) and out-of-plane rocking (ρ_ω). The in-plane COO rocking vibrations have the same symmetries as the in-plane CH_3 rocking vibrations, the same being true of the out-of-plane motion (Table 6). In the far-i.r. spectrum of $[Mo_2(O_2CCH_3)_4]$ (Figure 3) there are two groups of bands at 636 and 628 and at 583 and 575 cm^{-1} which are, by analogy to those of $Na(O_2CCH_3)$, assigned to out-of-plane and in-plane COO rocking, respectively. The assignment of the higher-wavenumber bands to the out-of-plane motion is consistent with those for $Na(O_2CCH_3)$.[11] The wavenumber of the out-of-plane vibrations is close to that observed for $Na(O_2CCH_3)$, in contrast to the in-plane vibrations which are nearly 100 cm^{-1} higher than that observed for $Na(O_2CCH_3)$. The Raman counterparts to the out-of-plane and in-plane COO rocking vibrations occur at 633 and 573, 569 cm^{-1}, respectively. Both sets of bands show shifts upon acetate deuteriation which are closely comparable to those observed for $Na(O_2CCH_3)$, namely 100 and 50 cm^{-1}, respectively. In the i.r. spectrum of $[Mo_2(O_2CCD_3)_4]$ this actually results in the coincidence of these two sets of bands. A triplet of bands is observed at 558, 550, and 539 cm^{-1}, the middle band being of much greater intensity than the other two, and is presumably a superposition of two of the four bands observed for $[Mo_2(O_2CCH_3)_4]$. The reason that the in-plane COO rocking is at higher wavenumber than in the acetate ion may be due to coupling with the Mo–O stretching vibrations.

(*iii*) *Resonance-Raman Spectra.*—In this section the results obtained by excitation within the two electronic bands of $[Mo_2(O_2CCH_3)_4]$ of lowest wavenumber are presented. The data shown are for $[Mo_2(O_2CCH_3)_4]$ although similar spectra were obtained for $[Mo_2(O_2CCD_3)_4]$.

The electronic structure of $[Mo_2(O_2CR)_4]$ compounds is the subject of much debate, and their electronic spectra have been the focus of more studies than for any other multiply bonded metal dimer.[22,28–30] The electronic configuration of the metal bonding orbitals for $[Mo_2(O_2CH)_4]$ has been predicted by theoretical studies and appears to be the same as that for $[Mo_2Cl_8]^{4-}$,[31] namely $\sigma^2\pi^4\delta^2$. However, unlike the $[M_2X_8]^{n-}$ species there is no absorption in the 21 000—14 000 cm^{-1} region, the first band in these compounds being weak and centred at 22 700 cm^{-1} ($\varepsilon_{max.} \sim 100$ dm^3 mol^{-1} cm^{-1}).[32] In the solid state at low temperatures this band shows considerable vibrational fine structure, and its lack of sensitivity to the R group suggests a transition between metal-localised orbitals. Originally this was assigned to the dipole-forbidden transition, $\delta \longrightarrow \pi^*$ ($2b_{2g} \longrightarrow 5e_g$),[28] but a more recent examination of the single-crystal spectrum by Martin *et al.*[29] favours the dipole-allowed $\delta \longrightarrow \delta^*$ ($2b_{2g} \longrightarrow 2b_{1u}$) assignment. Matrix-isolation studies by Manning and Trogler[30] have established that two distinct electronic transitions contribute to this band.

Gray and co-workers[28] measured the electronic spectrum of the band at 22 700 cm^{-1} for both $[Mo_2(O_2CCH_3)_4]$ and $[Mo_2(O_2CCD_3)_4]$. The 15-K spectra of sublimed films on quartz discs display vibronic structure which is better resolved than in the single-crystal spectra. The dominant progressions in both spectra have the same spacing, *ca.* 370 cm^{-1}. From the data collection in section (*i*) it was shown that, in the ground state, ν(Mo–Mo) is insensitive to deuteriation as opposed to the behaviour of most other bands in the spectrum, therefore this result unequivocally confirms the progression to be in v′(Mo–Mo). The drop of 34 cm^{-1} in the Mo–Mo stretching wavenumber implies a weakening and hence lengthening of the Mo–Mo bond on electronic excitation, and several workers [28,29] have calculated this lengthening from the electronic spectrum to be around 0.1 Å.

Until this work there had been no reports of excitation within the contour of the band at 22 700 cm^{-1}; the appropriate excitation is provided by Kr^{2+}-pumped stilbene 3 which allows tunable output between 480—406 nm. Three different excitation wavelengths were used, 21 699 (460.9), 21 719 (460.4), and 22 432 cm^{-1} (445.8 nm). For $[Mo_2(O_2CCH_3)_4]$ the first and third wavelengths correspond to the band origin A_0, and to its third member A_2, respectively, while the second wavelength corresponds to the band origin reported for $[Mo_2(O_2CCD_3)_4]$.[28]

The three Raman spectra obtained for $[Mo_2(O_2CCH_3)_4]$ are shown in Figure 5. The spectra were difficult to obtain because of (*a*) the very low oscillator strength of this absorption as well as possible self-absorption effects, (*b*) the fact that the laser power could not be increased greatly to compensate for this as sample decomposition was then encountered, and (*c*) the spectral response of the instrument is low in this region. Gray and co-workers [28] found the oscillator strength of the band at 22 700 cm^{-1} in the absorption spectrum of $[Mo_2(O_2CCF_3)_4]$ in acetonitrile solution at 298 K to be 0.0011, which is an order of magnitude less than they obtained for the δ–δ* band at 19 300 cm^{-1} for $K_4[Mo_2Cl_8]$.

The Raman spectrum obtained with 460.9-nm excitation appears at first to be broadly similar to that obtained with 514.5 nm in terms of the relative intensities of v(C–C), δ(OCO), v(Mo–Mo), and v(Mo–O). However, the two bands at 204 and 190 cm^{-1} assigned as skeletal bending vibrations have both decreased in intensity by comparison to their intensities for the 514.5-nm spectrum, the out-of-plane COO rock is not observed, and there appear to be several additional bands. These are assigned as 2 × v(Mo–Mo) (812 cm^{-1}), v(Mo–Mo) + v(Mo–O) (323 cm^{-1} component) (~725 cm^{-1}), and v(Mo–Mo) + in-plane ρ_r(COO) (977 cm^{-1}). Confirmation of these assignments comes from the spectrum of $[Mo_2(O_2CCD_3)_4]$ where corresponding bands are observed at 811 (2 × 403), 711 (403 + 311), and 941 cm^{-1} (403 + 532), respectively.

The lack of a long overtone progression in v(Mo–Mo) and the observation of several ligand vibrations in the spectrum suggests that the displacements to the excited-state geometry, rather than being just along the Mo–Mo bond, occur all around the Mo–O–C–O–Mo ring. One result obtained by Yoo and Zink [33] supports this. They estimated the excited-state distortions for $[Mo_2(O_2CCF_3)_4]$ by calculating the absorption spectrum from the Raman intensities, finding that the Mo–Mo bond elongation is only 0.045 Å. Using a localised bond-stretching model which neglects coupling to other normal modes, they estimated the other bond lengthenings to be 0.03 (Mo–O) and 0.006 Å (C–O). However, in the light of the results presented in sections (*i*) and (*ii*) the 'no coupling' assumption does not hold for this compound, and we believe that the Mo–Mo bond extension may be smaller than the value calculated by Yoo and Zink.[33]

For $[Mo_2(O_2CCH_3)_4]$ in addition to v(Mo–Mo), a number of other vibrations in the excited state may be assigned. There are several other v′(Mo–Mo) progressions in the electronic spectrum whose origins have been labelled B_0, C_0, D_0, E_0, F_0, and G_0.[29] Unfortunately the electronic spectrum of $[Mo_2(O_2CCD_3)_4]$ helps little in their assignment as the vibrational structure is not well resolved owing to overlapping bands. Martin *et al.*[29] assigned the B_0 band, which occurs 175 cm^{-1} above A_0, as arising from a Mo–Mo–O bending vibration, presumably one of the bands observed at 204 or 190 cm^{-1} for this molecule in the ground state. However, they expressed some doubt about this on the grounds that such vibrations are not as effective as a Mo–O stretch in the vibronic process. Manning and Trogler [30] have more recently shown that B_0 arises from a different electronic transition, a result which to some extent receives support from the data presented here where the bands at 204 and 190 cm^{-1} have decreased in intensity relative to their intensities in the 514.5-nm spectrum. Origin C_0 occurs 275 cm^{-1} above A_0 and presumably arises from one of the Raman-active Mo–O stretches observed at 323, 315, and 301 cm^{-1} in Figure 5, and D_0 at 320 cm^{-1} may arise from one of the i.r.-active Mo–O stretches. The remaining three origins E_0, F_0, and G_0 are 545, 590, and 865 cm^{-1} above A_0 and are assigned to the in-plane COO rock, δ(OCO), and v(C–C), respectively.

The next lowest electronic transition of $[Mo_2(O_2CCH_3)_4]$ has been previously assigned as the $2b_{2g} \longrightarrow 2b_{1u}$ ($\delta \longrightarrow \delta^*$) transition on the basis of its insensitivity to the carboxylate R group and of its oscillator strength being comparable to that found for the $\delta \longrightarrow \delta^*$ transition in $[Re_2Cl_8]^{2-}$ and $[Mo_2Cl_8]^{4-}$, although no reassignment has appeared to date. It occurs at 30 800 cm^{-1} in the electronic spectrum of $[Mo_2(O_2CH)_4]$ and has an oscillator strength of 0.03.[31] The shortest laser wavelength available to us, 337.5 nm (29 629 cm^{-1}), falls within this band and the resultant spectrum is shown in Figure 6. By contrast to the spectra obtained by excitation within the band at 22 700 cm^{-1}, the most intense feature is the Mo–O stretching vibration at 323 cm^{-1}. This implies that the transition is not metal based, although the spectrum obtained may be dominated by the much more intense transition to higher wavenumber. This band is the most intense feature in the electronic spectra of molybdenum carboxylates and is centred at 33 500 cm^{-1} ($\varepsilon_{max.}$ ~ 7 000 dm^3 mol^{-1} cm^{-1}) for $[Mo_2(O_2CH)_4]$.[32] On the basis of intensity and sensitivity to the carboxylate R group, this band has been assigned to a metal-to-ligand charge-transfer band, $2b_{2g} \longrightarrow 7e_u$ ($\delta \longrightarrow \pi^*$ CO).[32]

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