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Infrared, Raman, Resonance Raman, and Excitation Profile Studies of $Rh_2(O_2CCH_3)_4(PPh_3)_2$ and Its ^{18}O and CD_3 Isotopomers

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The resonance Raman spectra of $Rh_2(O_2CCH_3)_4(PPh_3)_2$ and its ^{18}O and CD_3 isotopomers have been recorded at ca. 80 K. A band at 289 cm^{-1}, denoted ν_1, is assigned to ν(Rh–Rh) and is the dominant progression-forming mode. This band also forms combinations with bands attributable to the tetraacetate cage, such as ν(Rh–O) and δ(OCO), as well as with those of the axial PPh_3 ligands. Excitation profiles of ν(Rh–Rh) and several other bands are shown to maximize under the 376-nm electronic absorption band, which, by way of Raman band depolarization ratio measurements, is assigned to an axial (z) polarized transition terminating in σ^*(RhRh). Bands assigned to ν(Rh–O) are shown to be dependent on both ^{18}O and CD_3 substitution. For $Rh_2(O_2CCH_3)_4(PPh_3)_2$, Raman spectra obtained with 514.5-nm excitation are also discussed. FTIR spectra (3500–40 cm^{-1}) of $Rh_2(O_2CCH_3)_4(PPh_3)_2$ and its ^{18}O and CD_3 isotopomers are also presented and assigned. The results provide a firm basis for making vibrational band assignments for other dimetal tetracarboxylates.

Introduction

In an earlier communication the longstanding controversy regarding the assignment of ν(RhRh) in dirhodium tetracarboxylates was discussed and resolved, in the case of $Rh_2(O_2CCH_3)_4(PPh_3)_2$, in favor of the band at 289 cm^{-1} detected in the resonance Raman spectrum.[1] This paper reports more fully on the assignment of the Raman and resonance Raman spectra of $Rh_2(O_2CCH_3)_4(PPh_3)_2$ and its ^{18}O and CD_3 isotopomers. In particular, the wavelength range of the previously reported resonance Raman spectra has been extended, Raman band excitation profiles have been plotted, and detailed infrared spectra (3500–40 cm^{-1}) are included. This comprehensive study now puts the assignment of ν(Rh–Rh), ν(Rh–O), and other skeletal bands on a firm basis and opens the way to clarifying the vibrational band assignments for other dimetal tetracarboxylates.

Experimental Section

Complexes. $Rh_2(O_2CCH_3)_4(PPh_3)_2$ was prepared by the dropwise addition of a saturated methanolic solution of PPh_3 to a methanolic solution of $Rh_2(O_2CCH_3)_4$. The resultant orange precipitate was recrystallized from dichloromethane. Anal. Calcd for $Rh_2(O_2CCH_3)_4(PPh_3)_2$: 54.7, C; 4.38, H; 6.41, P. Found: 54.5, C; 4.39, H; 6.50, P. Samples of ^{18}O- and CD_3-substituted $Rh_2(O_2CCH_3)_4$ were prepared as described previously.[1] Acetic-d_3 acid (99.6% D) was obtained from Aldrich Chemical Co., Inc. Acetic acid (78.5 atom % ^{18}O) was obtained from Miles-Yeda Ltd.

Instrumentation. Raman spectra were recorded with a Spex 14018 (R6) spectrometer, in the double-monochromator mode, in conjunction with Coherent CR 3000 K and CR 12 lasers. The Raman spectra with λ_0 = 514.5 nm were also obtained in the triple-monochromator mode for the low-wavenumber region (<400 cm^{-1}). Raman samples were held as pressed KCl disks at ca. 80 K using a liquid-nitrogen-cooled cell. Infrared spectra were recorded at ca. 80 K as KCl disks (3500–500 cm^{-1}) and as pressed wax disks (660–40 cm^{-1}) at a spectral resolution of 1 cm^{-1} with a Bruker 113 V interferometer. The wax disks were prepared by adding the complex to the melted wax (mp 49 °C, BDH), and then, as the wax was allowed to solidify, vacuum was applied in order to remove any air present in the wax (since this has been found to give rise to high backgrounds). The resulting solid was then pressed between Teflon plates, one of which was wedged at an angle of 1°. Overlap between the mid- and far-infrared regions allowed matching of band intensities, which are quoted on an arbitrary absorbance scale of vw < 0.02, w = 0.02–0.2, m = 0.2–0.6, s = 0.6–0.9, and vs > 0.9; br = broad, sh = shoulder.

Results and Discussion

The resonance Raman spectrum of $Rh_2(O_2CCH_3)_4(PPh_3)_2$ obtained with 356.4-nm excitation is shown in Figure 1, and the band positions are listed in Table I. There are no strong bands in the 170–150-cm^{-1} region; in fact there are no bands observed below 289 cm^{-1}. The very strong band at 289 cm^{-1}, denoted ν_1, displays an overtone progression up to $4\nu_1$ and forms combinations with several other bands.

Table I. Wavenumbers/cm^{-1} of Bands Observed in the Resonance Raman Spectrum[a] of $[Rh_2(O_2CCH_3)_4(PPh_3)_2]$ at ca. 80 K

$\tilde{\nu}$	assignt	$\tilde{\nu}$	assignt
289 vs	ν_1, ν(Rh–Rh)	1001 w	p-ring
305 vw	ν(Rh–O)	1012 vw	$\nu_1 + \delta$(OCO)
320 vw	ν(Rh–O)	1038 vw	$2\nu_3$
338 m	ν_2, ν(Rh–O)	1072 vw	d β(C–H)
407 vw	w ϕ(C–C)	1099 w	q X-sens
421 vw	t X-sens	1148 vw, sh	$\nu_1 + \nu_2 + \nu_3$
439 vw	t X-sens	1154 vw	$4\nu_1$
450 vw	t X-sens	1175 vw	
521 m	ν_3, y X-sens	1186 vw	a β(C–H)
578 m	$2\nu_1$	1202 vw	$3\nu_1 + \nu_2$
595 vw	$\nu_1 + 305$	1252 vw	$2\nu_1 + 2\nu_2$
610 vw	$\nu_1 + 320$	1269 vw	e β(C–H)
627 m	$\nu_1 + \nu_2$	1280 vw	e β(C–H)
641 vw		1290 vw	ν_1 + p-ring
675 vw, br	$2\nu_2$	1389 vw	ν_1 + q X-sens
688 vw	r X-sens	1437 vw, br	ν_2 + q X-sens
725 vw	δ(OCO)	1483 vw, br	m ν(C–C)
746 vw	f γ(C–H)	1550 vw	
809 w	$\nu_1 + \nu_3$	1557 vw	
860 vw	$\nu_2 + \nu_3$	1571 vw	l ν(C–C)
866 w	$3\nu_1$	1588 w	k ν(C–C)
881 vw	$2\nu_1 + 305$	1617 vw, br	$2\nu_1 + 2\nu_3$
915 w	$2\nu_1 + \nu_2$	1676 vw	$2\nu_1$ + q X-sens
932 vw		1724 vw, br	$\nu_1 + \nu_2$ + q X-sens
963 vw	$\nu_1 + 2\nu_2$	1771 vw, br	ν_1 + m ν(C–C)
976 vw	h γ(C–H)	1877 vw	ν_1 + k ν(C–C)

[a] 356.4-nm excitation.

The Raman spectrum obtained with 514.5-nm excitation is shown in Figure 2, and the band wavenumbers are listed in Table II. Again, the 289-cm^{-1} band is the strongest, but the overtone and combination bands shown in the 356.4-nm spectrum are no longer apparent apart from a very weak band at 579 cm^{-1}, which may be $2\nu_1$.

There are no bands due to triphenylphosphine in the 400–280-cm^{-1} region;[2] hence, bands in this region must be attributable to the tetraacetate cage itself. Bands attributable to ν(M–O) carboxylate modes are expected in this region; however, the absence of any strong bands in the 170–150-cm^{-1} region of both the resonance Raman and Raman spectra suggests that ν(Rh–Rh) must lie at higher wavenumber than this. In the reported resonance Raman spectra of dimetal tetracarboxylates, it is ν(M–M) that forms the longest progression, although in a few cases, e.g.

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† University College London.
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(1) Clark, R. J. H.; Hempleman, A. J.; Flint, C. D. *J. Am. Chem. Soc.* **1986**, *108*, 518.
(2) Clark, R. J. H.; Flint, C. D.; Hempleman, A. J. *Spectrochim. Acta, Part A* **1987**, *43A*, 805.

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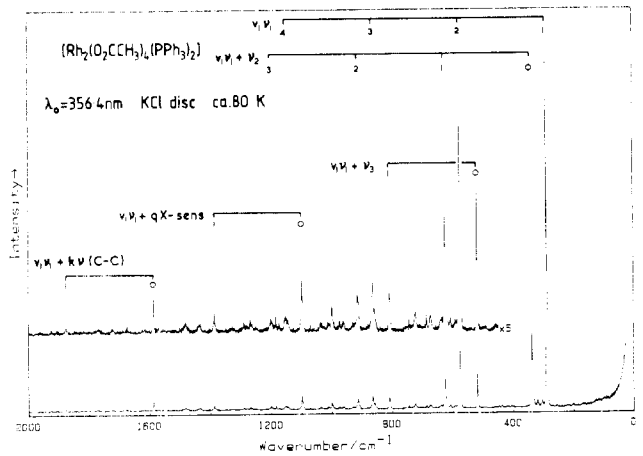

Figure 1. Resonance Raman spectrum (2000–25 cm^{-1}) of $Rh_2(O_2CCH_3)_4(PPh_3)_2$ as a KCl disk at ca. 80 K with 356.4-nm excitation. The resolution is ca. 2.5 cm^{-1}.

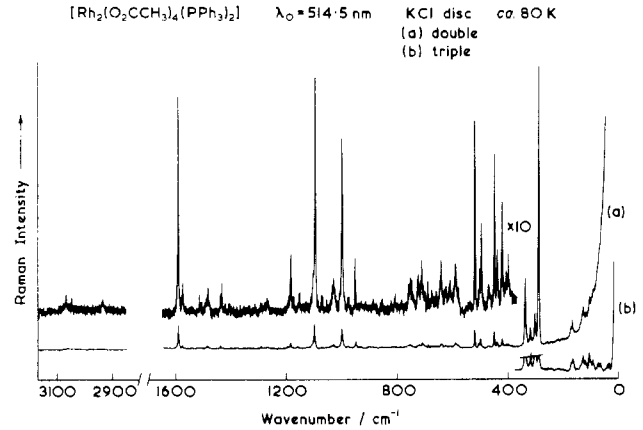

Figure 2. Raman spectrum (3150–2850 and 1650–25 cm^{-1}) of $Rh_2(O_2CCH_3)_4(PPh_3)_2$ as a KCl disk at ca. 80 K with 514.5-nm excitation. The resolution is ca. 3 cm^{-1}. The spectra were obtained (a) in the double- and (b) in the triple-monochromator modes.

$Ru_2(O_2CCH_3)_4Cl$,[3] ν(M–O) also forms a progression—albeit always shorter than that formed by ν(M—M); the length of the ν(M–O) progression is apparently related to the wavenumber separation ν(M–O) – ν(M–M). Moreover, since ν(M–M) is usually the strongest Raman band below 500 cm^{-1}, this suggests that ν(Rh–Rh) is attributable to the strong band at 289 cm^{-1}, an assignment that is consistent with that of Ketteringham and Oldham.[4]

In order to resolve the ambiguity over the assignment conclusively, it was decided to use isotopic substitution. There are no stable isotopes of rhodium apart from ^{103}Rh (100% abundance), thus ruling out the possibility of using the direct method for identifying the metal–metal stretching vibration. Consequently, the technique of assignment by default, as demonstrated for $Mo_2(O_2CCH_3)_4$,[5,6] was applied. However, instead of just a deuteriated acetate sample, a 78.5 atom % ^{18}O-enriched sample was also synthesized. The band at 289 cm^{-1} is virtually unshifted upon this substitution, whereas the 338-cm^{-1} band, denoted ν_2, suffers a shift to lower wavenumber of 6 and 13 cm^{-1} for the ^{18}O and CD_3 isotopomers, respectively. This is consistent with ν_1 being assigned to ν(Rh–Rh) and ν_2 to ν(Rh–O).

The only other possible assignment for ν_1 is ν(Rh–P), but this can be discounted for two reasons. First, ν(M–P) occurs around 200 cm^{-1} for mononuclear complexes: for example, for $Ni(PPh_3)_2Cl_2$, ν(Ni–P) occurs at 189.6 and 164.0 cm^{-1},[7] which is considerably lower than 289 cm^{-1}; indeed ν(Rh–P) might be expected to be even lower than 189 cm^{-1} owing to the Rh–P distance of 2.477 (1) Å being 0.10–0.18 Å longer than that found for mononuclear compounds of rhodium.[8] Second, this band moves to *higher* wavenumber for the analogous $AsPh_3$ and $SbPh_3$ derivatives, 297 and 307 cm^{-1}, respectively.[9,10] This is in the opposite direction from that expected on consideration of both mass and Rh–M bond lengths; viz., for the series $Rh_2(O_2CCH_3)_4(MPh_3)_2$, r(Rh–M) increases in the order 2.477,[8] 2.576,[9] and 2.732 Å[9] for M = P, As, and Sb, respectively.

One surprising result is the magnitude of the shift in ν_2. At 78.5 atom % ^{18}O enrichment the most abundant isotopomer of $Rh_2(O_2CCH_3)_4(PPh_3)_2$ would be the $(^{16}O)_2(^{18}O)_6$ species (30.3%) followed by the $(^{16}O)_3(^{18}O)_5$ and $(^{16}O)_1(^{18}O)_7$ species, 16.6 and 14.4%, respectively. Such substitution corresponds on average to an increase in the mass of the acetate bridge by three atomic mass units. The same mass effect can be achieved by methyl deuteriation, yet this results in twice as large a wavenumber shift for ν_2 as that found for ^{18}O substitution. A simple diatomic calculation regarding the acetate group as a point mass predicts only an 8-cm^{-1} shift for ν(Rh–acetate). The only other similar compound for which 78.5 atom % ^{18}O substitution data are available is $Ru_2(O_2CCH_3)_4Cl$[3] but, unfortunately, in this case the exact magnitude of the shift is not clear, as the band assigned to ν(Ru–O) shifts from 372.1 cm^{-1} to give a doublet at 366.8 and 359.3 cm^{-1} for the ^{18}O isotopomer. This may have been due to

Table II. Wavenumbers/cm^{-1} of Bands Observed in the Raman Spectrum[a] of $[Rh_2(O_2CCH_3)_4(PPh_3)_2]$ at ca. 80 K

$\tilde{\nu}$	assignt	$\tilde{\nu}$	assignt
33 vw		609 vw	ν_1 + 319
40 vw		623 vw	out-of-plane ρ_w(COO)
44 vw, sh		639 vw	ν_2 + 303 or 2 × 319
65 vw		655 vw	ν_2 + 319
72 vw		674 vw	$2\nu_2$
91 w		687 vw	r X-sens
98 vw, sh		710 vw	v ϕ(C–C)
104 w		722 vw	δ(OCO)
119 vw		744 vw	f γ(C–H)
128 w		752 vw	
135 vw, sh		851 vw	g γ(C–H)
165 w		883 vw	
170 vw		932 vw	i γ(C–H)
203 vw	δ(O–Rh–O)/ δ(Rh–Rh–O)	952 vw	ν(C–C)
216 vw		975 vw	h γ(C–H)
222 vw	x X-sens	1000 w	p-ring
242 vw		1030 vw	b β(C–H)
256 vw	u X-sens	1073 vw	d β(C–H)
289 vs	ν_1, ν(Rh–Rh)	1098 w	q X-sens
303 w	ν(Rh–O)	1156 vw	c β(C–H)
319 w	ν(Rh–O)	1174 vw	
338 m	ν_2, ν(Rh–O)	1184 vw	a β(C–H)
398 vw	w ϕ(C–C)	1193 vw	
406 vw		1267 vw	e β(C–H)
421 vw	t X-sens	1278 vw	
439 vw		1289 vw	g + t
448 w		1433 vw	n ν(C–C)
470 vw		1481 vw	m ν(C–C)
497 vw	y X-sens	1510 vw	
503 vw		1571 vw	l ν(C–C)
519 w		1587 w	k ν(C–C)
541 vw		2933 vw	ν(C–H) acetate
579 vw	$2\nu_1$	3044 vw	ν(C–H) aromatic
589 vw	in-plane ρ_r(COO)	3062 vw	

[a] 514.5-nm excitation.

(3) Clark, R. J. H.; Ferris, L. T. H. *Inorg. Chem.* **1981**, *20*, 2759.
(4) Ketteringham, A. P.; Oldham, C. *J. Chem. Soc., Dalton Trans.* **1973**, 1067.
(5) Hempleman, A. J.; Clark, R. J. H.; Flint, C. D. *Inorg. Chem.* **1986**, *25*, 2915.
(6) Clark, R. J. H.; Hempleman, A. J.; Kurmoo, M. *J. Chem. Soc., Dalton Trans.* **1988**, 973.
(7) Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th ed.; Wiley: New York, 1986.
(8) Christoph, G. G.; Halpern, J.; Khare, G. P.; Koh, Y. B.; Romanowski, C. *Inorg. Chem.* **1981**, *20*, 3029.
(9) Clark, R. J. H.; Hempleman, A. J.; Dawes, H. M.; Hursthouse, M. B.; Flint, C. D. *J. Chem. Soc., Dalton Trans.* **1985**, 1775.
(10) Clark, R. J. H.; Hempleman, A. J., submitted for publication.

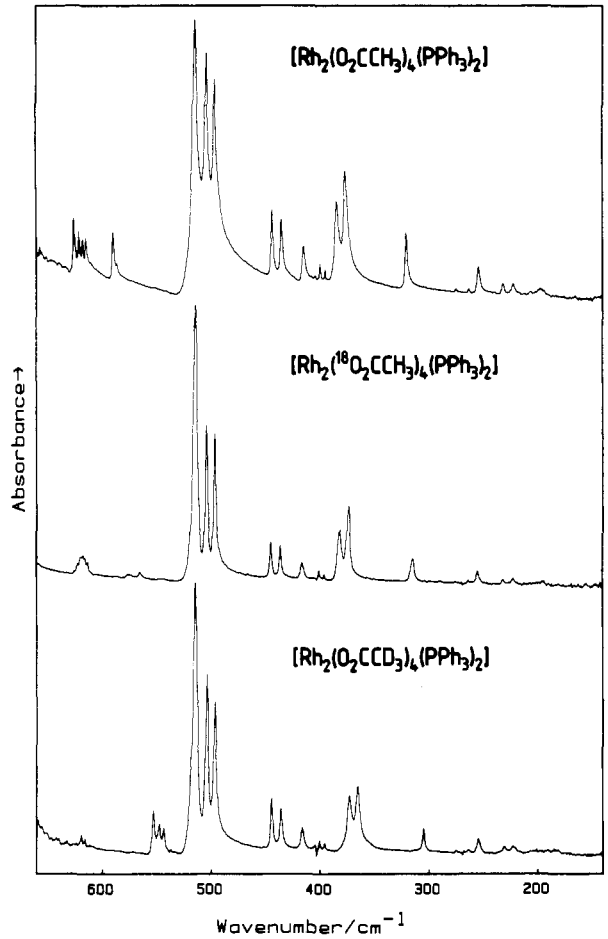

Figure 3. FTIR spectra (660–140 cm^{-1}) of $Rh_2(O_2CCH_3)_4(PPh_3)_2$, $Rh_2(^{18}O_2CCH_3)_4(PPh_3)_2$, and $Rh_2(O_2CCD_3)_4(PPh_3)_2$ as wax disks at ca. 80 K.

the fact that the 372-cm^{-1} band appears asymmetric on the low-wavenumber side and therefore may consist of more than one component. Upon ^{18}O substitution these bands have shifted by differing amounts, resulting in the appearance of a clearly resolved doublet.

Since ν_2 shows such a large sensitivity to deuteriation of the methyl group, the contribution of the methyl group symmetry coordinate to the ν_2 normal coordinate must be large. This was also found to be the case for $Mo_2(O_2CCH_3)_4$, for which the ratio of the ν_2 band wavenumbers $Mo_2(O_2CCD_3)_4/Mo_2(O_2CCH_3)_4$ is 0.97;[5,6] cf. for the ν_2 band of $Rh_2(O_2CCH_3)_4(PPh_3)_2$, where this ratio is 0.96. Quite clearly the description ν(Rh–O) is an approximate one.

Two other very weak bands are observed in this region at 320 and 305 cm^{-1}, which shift upon ^{18}O substitution to 314 and 302 cm^{-1}, respectively, and are also assigned to ν(Rh–O). Their intensities compared to that of ν_2 in the resonance Raman spectrum (Figure 1) are lower than that observed in off-resonance conditions (Figure 2) suggesting that, unlike ν_2, they are attributable to non totally symmetric ν(Rh–O) modes. Upon deuteriation only the highest component is observed, occurring at 307 cm^{-1}, the lower band presumably being obscured by ν(Rh–Rh).

Assignment of the corresponding infrared-active ν(Rh–O) bands is also simplified by the absence of any bands due to triphenylphosphine in the 400–300-cm^{-1} region.[2] Infrared-active ν(M–O) bands in tetraacetate compounds appear at higher wavenumber than their Raman counterparts; cf. the observations for $Mo_2(O_2CCH_3)_4$. In the infrared spectrum of $Mo_2(O_2CCH_3)_4$, bands at 373, 353, 342, and 311 cm^{-1} are assigned to ν(Mo–O), shifting to 363, 343, 321, and 285 cm^{-1}, respectively, upon deuteriation.[6] By comparison, bands at 385, 377, and 321 cm^{-1} in the infrared spectrum of $Rh_2(O_2CCH_3)_4(PPh_3)_2$ (Figure 3) are assigned to ν(Rh–O). Their relative shifts upon ^{18}O and deuterium substitution are 3 and ca. 12 cm^{-1} for the uppermost two bands, respectively, and 6 and 16 cm^{-1}, respectively, for the lowest wavenumber bands. The relative shifts upon deuteriation are similar to those observed for $Mo_2(O_2CCH_3)_4$;[6] i.e., the two uppermost bands shift by less than the lower bands. The observation of three infrared-active bands attributable to ν(Rh–O) is in contradiction to the predictions of the $M_2(O_2CC)_4$ model.[6] Like $Mo_2(O_2CCH_3)_4$,[11] $Rh_2(O_2CCH_3)_4(PPh_3)_2$[8] only possesses one molecule per unit cell, and therefore band splitting cannot arise from factor group coupling but must be due to the low site symmetry, C_i, in the crystal.

Table III. Wavenumbers/cm^{-1} of Bands Observed in the Resonance Raman Spectrum[a] of $[Rh_2(^{18}O_2CCH_3)_4(PPh_3)_2]$ at ca. 80 K

$\tilde{\nu}$	assignt	$\tilde{\nu}$	assignt
289 vs	ν_1, ν(Rh–Rh)	1031 vw	b β(C–H)
302 vw	ν(Rh–O)	1040 vw	$2\nu_3$
314 vw	ν(Rh–O)	1074 vw	d β(C–H)
332 m	ν_2, ν(Rh–O)	1100 w	q X-sens
406 vw	w ϕ(C–C)	1127 vw	
422 vw	t X-sens	1140 vw	$\nu_1 + \nu_2 + \nu_3$
439 vw		1152 vw, sh	$4\nu_1$
449 vw		1157 vw, sh	c β(C–H)
520 m	ν_3, y X-sens	1186 vw	a β(C–H)
577 m	$2\nu_1$	1195 vw	$3\nu_1 + \nu_2$
591 vw	ν_1 + 302	1238 vw, br	$2\nu_1 + 2\nu_2$
602 vw	ν_1 + 314	1269 vw	e β(C–H)
620 m	$\nu_1 + \nu_2$	1280 vw	
663 vw, br	$2\nu_2$	1290 vw	ν_1 + p-ring
688 vw	r X-sens	1329 vw	$\nu_1 + 2\nu_3$ or ν_2 + p-ring
706 vw	δ(OCO)	1389 vw	ν_1 + q X-sens
710 vw, sh		1434 vw, br	ν_2 + q X-sens
715 vw		1482 vw, br	m ν(C–C)
746 vw	f γ(C–H)	1523 vw, br	
753 vw		1558 vw	
759 vw		1571 vw	l ν(C–C)
809 w	$\nu_1 + \nu_3$	1588 w	k ν(C–C)
853 vw	$\nu_2 + \nu_3$	1620 vw, br	$2\nu_1 + 2\nu_3$
864 w	$3\nu_1$	1676 vw	$2\nu_1$ + q X-sens
908 w	$2\nu_1 + \nu_2$	1721 vw, br	$\nu_1 + \nu_2$ + q X-sens
949 vw, br	$\nu_1 + 2\nu_2$	1769 vw, br	ν_1 + m ν(C–C)
975 vw	h γ(C–H)	1807 vw, br	
979 vw, sh	ν_1 + r X-sens	1877 vw	ν_1 + k ν(C–C)
1001 w	p-ring	1919 vw	ν_2 + k ν(C–C)

[a] 356.4-nm excitation.

The Raman spectrum obtained with 514.5-nm excitation (off-resonance) displays no overtone progressions or combination band involving ν(Rh–Rh) (Figure 2) although there may be a number of very weak combinations involving ν(Rh–O). Unlike the Raman spectrum obtained for $Mo_2(O_2CCH_3)_4$ with 514.5-nm excitation,[6] in which bands attributable to the acetate group are clearly observed, the spectrum for $Rh_2(O_2CCH_3)_4(PPh_3)_2$ is dominated by ν(Rh–Rh). Thus the 514.5-nm spectrum is better described as a preresonance Raman spectrum, in which different bands are detected as compared to the resonance Raman spectrum; however, most of these appear to be due to the axial PPh_3 ligands, and assignment of the acetate group vibrations has to be taken from the infrared spectrum. This is not straightforward owing to overlap with bands due to the axial PPh_3 ligands. The majority of the PPh_3 bands would not be expected to shift upon coordination owing to the close structural similarity between the free and coordinated ligands.[8]

The PPh_3 bands expected to shift upon coordination would be those involving large phosphorus amplitudes, namely, the six X-sensitive vibrations, q, r, y, t, u, and x (Whiffen's nomenclature).[12] For PPh_3[2] these occur in the overall infrared and Raman ranges 1098–1087, 683, 515–491, 434–410, 274–247, and 214–188 cm^{-1}, respectively. The shifts upon coordination, if any, appear to be small and are upward; q, r, y, t, u, and x are found in the ranges 1099–1095, 688–687, 521–497, 450–416, 275–255, and

(11) Cotton, F. A.; Mester, Z. C.; Webb, T. R. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1974**, *30*, 2768.
(12) Whiffen, D. H. *J. Chem. Soc.* **1956**, 1350.

Table IV. Wavenumbers/cm^{-1} of Bands Observed in the Resonance Raman Spectrum[a] of $[Rh_2(O_2CCD_3)_4(PPh_3)_2]$ at ca. 80 K

$\tilde{\nu}$	assignt	$\tilde{\nu}$	assignt
287 vs	ν_1, ν(Rh–Rh)	1072 vw	d β(C–H)
307 w	ν(Rh–O)	1100 w	q X-sens
325 m	ν_2, ν(Rh–O)	1133 vw	$\nu_1 + \nu_2 + \nu_3$
406 vw	w ϕ(C–C)	1147 vw	$4\nu_1$
421 vw	t X-sens	1157 vw	c β(C–H)
439 vw		1169 vw	
449 vw		1186 vw	$3\nu_1 + \nu_2$ or a β(C–H)
456 vw		1222 vw	$2\nu_1 + 2\nu_2$
520 m	ν_3, y X-sens	1262 vw, sh	ν_1 + h γ(C–H)
574 m	$2\nu_1$	1269 vw	e β(C–H)
594 vw	ν_1 + 307	1279 vw	
612 m	$\nu_1 + \nu_2$	1287 vw	ν_1 + p-ring
650 vw	$2\nu_2$	1326 vw	$\nu_1 + 2\nu_3$ or ν_2 + p-ring
687 vw	r X-sens	1387 vw	ν_1 + q X-sens
692 vw		1424 vw, br	ν_2 + q X-sens
697 vw		1433 vw	$5\nu_1$
707 vw	δ(OCO)	1471 vw	$4\nu_1 + \nu_2$
745 vw	f γ(C–H)	1481 vw	m ν(C–C)
807 w	$\nu_1 + \nu_3$	1510 vw, br	$3\nu_1 + 2\nu_2$
845 vw	$\nu_2 + \nu_3$	1553 vw	
860 w	$3\nu_1$	1571 vw	l ν(C–C)
882 vw	$2\nu_1$ + 307	1588 w	k ν(C–C)
899 w	$2\nu_1 + \nu_2$	1616 vw	$2\nu_1 + 2\nu_3$
936 vw	$\nu_1 + 2\nu_2$	1676 vw, br	$2\nu_1$ + q X-sens
976 vw	h γ(C–H)	1712 vw, br	$\nu_1 + \nu_2$ + q X-sens
996 vw	ν_1 + δ(OCO)	1760 vw	$5\nu_1 + \nu_2$
1001 w	p-ring	1796 vw, br	$4\nu_1 + 2\nu_2$
1030 vw	b β(C–H)	1876 vw	ν_1 + k ν(C–C)
1039 vw	$2\nu_3$	1914 vw	ν_2 + k ν(C–C)

[a] 356.4 nm excitation.

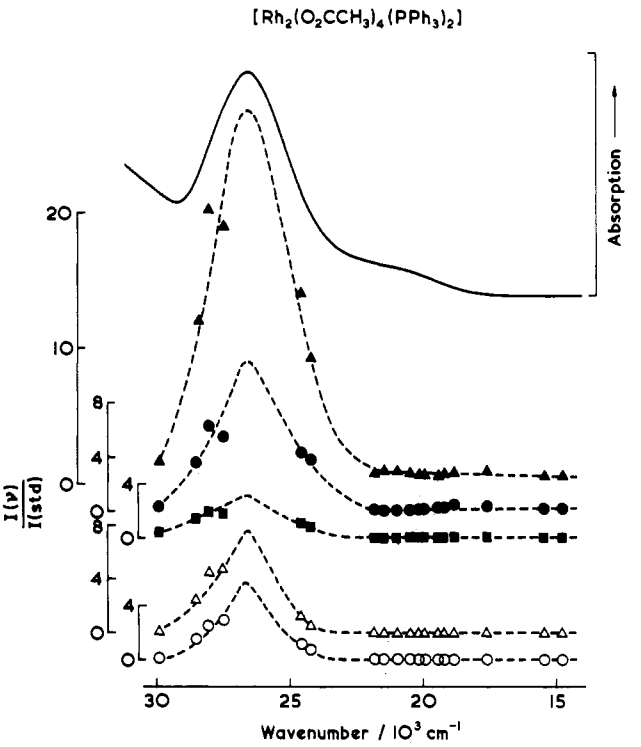

Figure 4. Excitation profiles of ν_1 (▲), ν_2 (●), ν_3 (■), $2\nu_1$ (△), and $\nu_1 + \nu_2$ (○) for $Rh_2(O_2CCH_3)_4(PPh_3)_2$ at ca. 80 K, together with the transmission electronic spectrum at ca. 20 K.

232–222 cm^{-1}, respectively, for $Rh_2(O_2CCH_3)_4(PPh_3)_2$. The smallness of the shifts on coordination is a reflection of the long Rh–P distances and hence weakness of these bonds.

In the resonance Raman spectrum ν(Rh–Rh) forms combinations with ν(Rh–O) and δ(OCO) in a manner similar to that observed for $Ru_2(O_2CCH_3)_4Cl$;[3] however, in addition, ν(Rh–Rh) also forms combinations with the PPh_3 vibrations,[2] y X-sens, p-ring, q X-sens, and m and k ν(C–C). The band assigments for the combinations are not necessarily unique; thus, for the ^{18}O and CD_3 isotopomers, bands at 1329 and 1326 cm^{-1}, respectively, may be assigned to $\nu_1 + 2\nu_3$ or p-ring + ν_2, although there is no such combination band observed for the ^{16}O species. Band listings and assignments for $Rh_2(O_2CCH_3)_4(PPh_3)_2$ and the ^{18}O and CD_3 isotopomers are given in Tables I–IV, respectively.

Table V contains band listings and assignments of the infrared spectra of $Rh_2(O_2CCH_3)_4(PPh_3)_2$ and the ^{18}O and CD_3 isoto-

Table V. Wavenumbers/cm^{-1} of Bands Observed in the Far-Infrared (660–40 cm^{-1}) Spectra of ^{16}O, ^{18}O, and CD_3 Derivatives of $[Rh_2(O_2CCH_3)_4(PPh_3)_2]$ at ca. 80 K

^{16}O		^{18}O		CD_3	
$\tilde{\nu}$	assignt	$\tilde{\nu}$	assignt	$\tilde{\nu}$	assignt
627 w	out-of-plane ρ_w(COO)	622 vw	out-of-plane ρ_w(COO) and s α(C–C–C)	619 vw	s α(C–C–C)
622 w		620 vw, sh		616 vw	
619 vw	s α(C–C–C)	617 vw		553 vw	in- and out-of-plane ρ(COO)
616 vw		616 vw		548 vw	
591 vw	in-plane ρ_r(COO)	613 vw		544 vw	
587 vw		575 vw	in-plane ρ_r(COO)	516 m	y X-sens
515 m	y X-sens	565 vw		504 m	
504 m		515 m	y X-sens	497 m	
497 m		504 m		444 w	t X-sens
494 w, sh		497 m		436 w	
444 w	t X-sens	445 w	t X-sens	416 vw	
436 w		436 w		405 vw	w ϕ(C–C)
416 vw		416 vw		401 vw	
408 vw		405 vw	w ϕ(C–C)	396 vw	
405 vw	w ϕ(C–C)	400 vw		373 w	ν(Rh–O)
400 vw		396 vw		366 w	
396 vw		382 w	ν(Rh–O)	305 vw	
385 w	ν(Rh–O)	374 w		275 vw	u X-sens
377 w		315 vw		263 vw	
321 w		255 vw	u X-sens	254 vw	
275 vw	u X-sens	231 vw	x X-sens	230 vw	x X-sens
264 vw		222 vw		222 vw	
255 vw				124 vw	
232 vw	x X-sens				
222 vw					
207 vw	δ(O–Rh–O) or δ(Rh–Rh–O)				
197 vw					
130 vw					
124 vw					
110 vw					

pomers in the range 700–40 cm^{-1}; full band listings and assignments (3,500–40 cm^{-1}) are included in the supplementary material (Tables VI–VIII). Assignments of the acetate group vibrations are taken from the data gathered for $Rh_2(O_2CCH_3)_4$,[13] where the spectra are much simpler. In common with Mazo et al.,[14] we make the assumption that the vibrations localized mainly in the acetate group show little dependence on the nature of the axial ligand, although many assignments, particularly those in the 1460–1400-cm^{-1} region, remain tentative owing to overlap between such bands and ones due to PPh_3.

The observation of differing numbers of bands in both the infrared and resonance Raman spectra of $Rh_2(O_2CCH_3)_4(PPh_3)_2$ and its isotopomers is a consequence of two factors. First, many bands observed are very weak; hence, slight differences in signal-to-noise ratio between spectra affect the number of observables. Second, isotopic band shifts can reveal or obscure other bands.

Excitation profiles (EP's) have been constructed for the ν_1, ν(Rh–Rh), ν_2, ν(Rh–O), and ν_3 y X-sens bands and also for the combination bands $2\nu_1$ and $\nu_1 + \nu_2$. These are shown in Figure 4. Quite clearly, the EP's of all the bands measured maximize within the contour of the 376-nm electronic absorption, although exact EP maxima were not achievable owing to the lack of a complete set of suitable exciting lines within this region. This absorption band has been assigned to the electric dipole allowed $\sigma \rightarrow \sigma^*$ transition of the Rh–Rh bond.[15] Excitation within the contour of this band should lead primarily to a change in the metal–metal bond length, and hence, the resonance Raman spectrum would be expected to be dominated by a band progression in the metal–metal stretching vibration.[16,17] This is the case here, with an overtone progression up to $4\nu_1$ being observed. However, very recently a different assignment has been proposed[18] for the near-UV band of dirhodium tetraacetate complex ions of the sort $[Rh_2(O_2CCH_3)_4L_2]^{2-}$ (L = Cl^-, Br^-, I^-), viz. that it is the σ(Rh–L) $\rightarrow \sigma^*$(Rh–Rh) transition. This assignment is strongly suggested for the above ions by the fact that the band maximum moves progressively toward the visible region in the wavenumber order Cl > Br > I, as would be expected for a LMCT transition. The problem with this assignment in the case of the complex $Rh_2(O_2CCH_3)_4(PPh_3)_2$ is that Raman spectra taken at resonance with the 376-nm transition might then have been expected to yield a considerably intensified ν(Rh–P) band together with, depending on the extent of the Rh–P bond length change on excitation, a progression in ν(Rh–P). Yet no band could be found that could even be attributed to ν(Rh–P) itself. Paradoxically, however, a number of X-sensitive modes act as enabling modes for readily observed progressions in ν_1. The present results do not allow a firm distinction to be drawn between these alternative assignments[15,18] for the 376-nm band except that it is z-polarized and undoubtedly involves a transition terminating in σ^*(Rh–Rh).

Further confirmation for the polarization comes from the depolarization ratio of the ν_1 band of $Rh_2(O_2CCH_3)_4(PPh_3)_2$. The polarizability tensor for a totally symmetric mode of a molecule of D_{4h} symmetry associated with a nondegenerate electronic transition will be dominated by its α_{zz} element on resonance. Consequently the ρ value of such a band will approach $^1/_3$ on-resonance, while any value between 0 and $^3/_4$ is expected off-resonance, depending on the relative sizes of the various tensor elements.[16,17] In agreement with this, the depolarization ratio was found to be 0.34 when the band was excited with 363.8-nm radiation, confirming the axial (z) polarization of the electronic transition. Problems were encountered with sample decomposition due to the light-sensitive nature of the solutions. Consequently, the depolarization ratios were obtained by a technique of bracketing the measurements; i.e., first $\rho_\parallel$ was recorded, followed by $\rho_\perp$, and then $\rho_\parallel$ was measured again. The two $\rho_\parallel$ values were then averaged. Obviously, this is not entirely satisfactory, and better results may be achieved by the development of a jet-flow system. Unfortunately, reliable depolarization ratios could not be obtained for ν_2 and ν_3 owing to their low band intensities; however, by virtue of the resonance enhancement of ν_2 and ν_3, they are assumed to arise from totally symmetric fundamentals. It is significant, moreover, that independent work on the analogous $SbPh_3$ complex[10] clearly indicates both ν_2 and ν_3 to be polarized. Attempts were also made to obtain off-resonance depolarization ratios, but surprisingly, even when 647.1-nm radiation was used, the sample decomposed.

Conclusions

The results obtained provide a firm basis for making vibrational band assignments for other dirhodium tetracarboxylates. The use of ^{18}O and CD_3 derivatives has been necessary in order to distinguish between several of the key and close-lying skeletal modes. The principal progression-forming mode under resonance Raman conditions, ν_1, is almost harmonic, with the anharmonicity constant $x_{11} \leq 0.2$ cm^{-1}; ν_1 acts as the progression-forming mode in at least 10 progressions, the enabling modes being other, presumably totally symmetric, fundamentals or overtones.

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Registry No. $Rh_2(O_2CCH_3)_4(PPh_3)_2$, 39773-08-5; $Rh_2(^{18}O_2CCH_3)_4(PPh_3)_2$, 99829-59-1; $Rh_2(O_2CCD_3)_4(PPh_3)_2$, 99829-60-4; ^{18}O, 14797-71-8; D_2, 7782-39-0.

Supplementary Material Available: Tables VI–VIII, containing full band listings and assignments for the infrared spectra of $Rh_2(O_2CCH_3)_4(PPh_3)_2$ and its ^{18}O and CD_3 isotopomers (6 pages). Ordering information is given on any current masthead page.

(13) Clark, R. J. H.; Hempleman, A. J. *Croat. Chem. Acta*, in press.
(14) Mazo, G. Ya.; Baranovskii, I. B.; Shchelokov, R. N. *Russ. J. Inorg. Chem. (Engl. Transl.)* **1979**, *24*, 1855.
(15) Sowa, T.; Kawamura, T.; Shida, T.; Yonezawa, T. *Inorg. Chem.* **1983**, *22*, 56.
(16) Clark, R. J. H.; Stewart, B. *Struct. Bonding (Berlin)* **1979**, *36*, 1.
(17) Clark, R. J. H.; Dines, T. J. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 131.
(18) Miskowski, V. M.; Dallinger, R. F., Christoph, G. G.; Morris, D. E.; Spies, G. H.; Woodruff, W. H., *Inorg. Chem.* **1987**, *26*, 2127.