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Infrared and Raman Spectroscopy of the Dirhodium Tetraacetate Complexes $Rh_2(O_2CCH_3)_4$, $Rh_2(^{18}O_2CCH_3)_4$, $Rh_2(O_2CCD_3)_4$ and $Rh_2(O_2CCH_3)_4(H_2O)_2$

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The infrared (3500—50 cm^{-1}), and Raman (3550—30 cm^{-1}) spectra of the dirhodium tetraacetate species $Rh_2(O_2CCH_3)_4$, $Rh_2(^{18}O_2CCH_3)_4$, $Rh_2(O_2CCD_3)_4$, and $Rh_2(O_2CCH_3)_4(H_2O)_2$ have been recorded and the key bands assigned. The oxygen-18 and deuteration studies, in particular, assisted with making the important band assignments for the anhydrous complex, for which ν(RhRh) occurs at 355—351 cm^{-1}, and ν(RhO) at 389—319 cm^{-1} (Raman) and 398—341 cm^{-1} (infrared). The band attributed to ν(RhRh) is typically intense, sharp, and relatively insensitive to either ^{18}O- or CD_3-substitution. Thus ν(RhRh) shifts only 4 cm^{-1} on either ^{18}O or CD_3 substitution whereas ν(RhO) shifts 4—6 cm^{-1} in the Raman and 3—7 cm^{-1} in the infrared spectra on ^{18}O substitution but 12 cm^{-1} in the Raman and 11—18 cm^{-1} in the infrared spectra on CD_3 substitution. Some preliminary isotopic work for the complex $Rh_2(O_2CCH_3)_4(H_2O)_2$ is also presented.

INTRODUCTION

Recent electronic, infrared, Raman, resonance Raman and X-ray crystallographic studies have been aimed at resolving the long standing controversy regarding the assignment of the rhodium-rhodium stretching vibration, ν(RhRh), in dirhodium tetraacetate complexes of the sort $Rh_2(O_2CCH_3)_4 \cdot (MPh_3)_2$, M = P, As or Sb, *viz.* the controversy as to whether ν(RhRh) occurs near 170 or near 300 cm^{-1}, in favour of the latter assignment.[1-3] The present investigation is focussed upon anhydrous dirhodium tetraacetate, $Rh_2(O_2CCH_3)_4$ together with preliminary measurements on the di-axially substituted derivative $Rh_2(O_2CCH_3)_4(H_2O)_2$. In order to be able to assign the key modes of vibration of $Rh_2(O_2CCH_3)_4$, it proved to be essential, not only to study the oxygen-18 derivative, but also the deuterate $Rh_2(O_2CCD_3)_4$.

EXPERIMENTAL

Dirhodium tetraacetate was prepared as an emerald green powder by the method of Wilkinson *et al.*[4] Anal. Calcd. for $C_8H_{12}O_8Rh_2$ (M_r = 442.00): C 21.74, H 2.74%; found: C 21.7, H 2.66%. Slow evaporation of a solution of dirhodium tetraacetate in water afforded deep green crystals of the bis aquo complex.

Anal. Calcd. for $C_8H_{16}O_{10}Rh_2$ ($M_r = 478.04$): C 20.10, H. 3.37; found: C 20.2, H 3.25%. Samples of ^{18}O- and CD_3-substituted dirhodium tetraacetate were prepared as described previously.[2] Acetic acid D (99.6%) was obtained from the Aldrich Chemical Co. Inc. Acetic acid 78.5 atom % ^{18}O was obtained from Miles-Yeda Ltd.

Raman spectra of the complexes (as both pure solids and as KCl discs) were recorded using 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 514.5 nm excitation were also obtained in the triple monochromator mode for the region <400 cm^{-1}. Raman samples were held as pressed KCl discs at *ca.* 80 K using a liquid-nitrogen-cooled cell. The infrared spectra were recorded as KCl discs at *ca.* 80 K for the region above 700 cm^{-1} but as pressed wax discs at *ca.* 20 K for the region below 700 cm^{-1}. (Spectral resolution 1 cm^{-1}). The 700—500 cm^{-1} region was recorded with the samples in both forms. All infrared spectra were recorded using a Bruker 113V interferometer; for the region below 700 cm^{-1}, the samples were mounted inside a liquid-helium-cooled germanium bolometer with KRS5 (700—200 cm^{-1}) or TPX (400—50 cm^{-1}) windows. This detector was kindly lent by Dr. G. Gledhill (Royal Holloway and Bedford New College).

The electronic spectrum of $Rh_2(O_2CCH_3)_4$ was obtained as a KCl disc at *ca.* 20 K using an Air Products Displex system in conjunction with a Cary 14 spectrometer. Band maxima (in nm) were detected at 229 s, 246 sh, 268 s, 435 w, sh and 605 w.

RESULTS AND DISCUSSION

$Rh_2(O_2CCH_3)_4$, $Rh_2(^{18}O_2CCH_3)_4$ and $Rh_2(O_2CCD_3)_4$: Skeletal Modes

Despite the large amount of synthetic work which has been done on axially substituted complexes of dirhodium tetraacetate, no thorough vibrational or X-ray crystallographic study of the anhydrous complex has yet been carried out. However, it is imperative to do this in order to render the assignment of ν(RhRh) firm. Previous studies of axially substituted complexes $Rh_2(O_2CCH_3)_4 \cdot L_2$ have relied upon Raman studies[2] at resonance with the $\sigma \rightarrow \sigma^*$ transition in the near UV region, studies which have led to the assignment of ν(RhRh) to a band near 300 cm^{-1}; this band (and its overtones) are substantially enhanced near resonance via the so-called A-term mechanism of resonance Raman scattering.[5] However, for dirhodium tetraacetate itself the $\sigma \rightarrow \sigma^*$ transition (≤ 268 nm) is not accessible with available c. w. laser lines, and hence the assignment of ν(RhRh) via these means is not feasible.

TABLE I

Comparison Between the Raman Spectra of $Rh_2(O_2CCH_3)_4$, $Mo_2(O_2CCH_3)_4$ and $^{92}Mo_2(O_2CCH_3)_4$ in the Low Wavenumber Region

$Rh_2(O_2CCH_3)_4$[a]	$Mo_2(O_2CCH_3)_4$[b]	$^{92}Mo_2(O_2CCH_3)_4$[b]
176m	186m	186m
188m	200m	200m
331m	298m	299m
338m	311m,sh	314m
	321m	322m
355vs	404vs	413vs

[a] Recorded at *ca.* 80 K.

[b] Data taken from reference 6, recorded at room temperature.

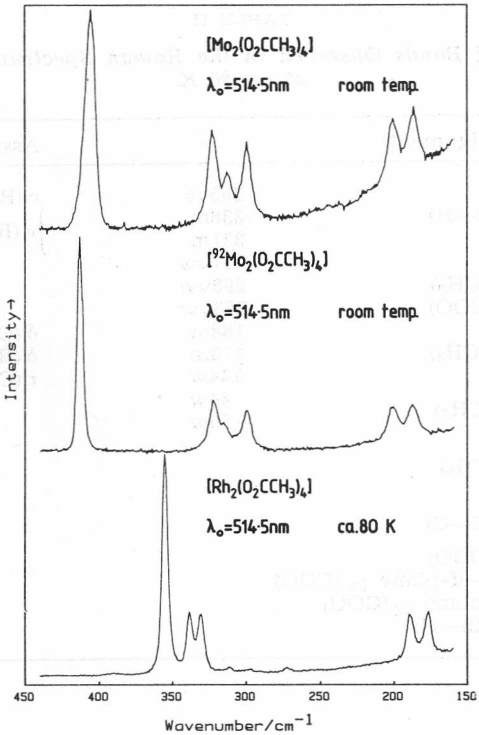

Figure 1. Comparison of the Raman spectrum (440—160 cm^{-1}) of $Rh_2(O_2CCH_3)_4$ at *ca.* 80 K with the room temperature Raman spectra of $Mo_2(O_2CCH_3)_4$ and $^{92}Mo_2(O_2CCH_3)_4$, as reproduced from reference 6. 514.5 nm excitation.

Our conviction that ν (RhRh) for $Rh_2(O_2CCH_3)_4$ is at 355 cm^{-1} lay with the close comparison (Table I, Figure 1) between the Raman spectra of $Rh_2(O_2CCH_3)_4$ and those[6] of $Mo_2(O_2CCH_3)_4$ and $^{92}Mo_2(O_2CCH_3)_4$. It appears that ν (MM) simply moves *ca.* 50 cm^{-1} to lower wavenumber on replacing molybdenum by rhodium (404 to 355 cm^{-1} — a consequence of the drop in metal-metal bond order from four to one), while all the ν (MO) bands remain relatively constant in the region 318 ± 18 cm^{-1} and the δ (OMO)/δ (MMO) bands likewise remain relatively constant in the region 188 ± 12 cm^{-1}. These conclusions are substantiated by the present detailed Raman studies (Table II), which include a study of the low wavenumber region using a triple monochromator (Figure 2). Subsequent, and much more detailed investigations[7] of the vibrational spectra of $Mo_2(O_2CCH_3)_4$ and $Mo_2(O_2CCD_3)_4$ have revealed an important difference between these and the spectra of $Rh_2(O_2CCH_3)_4$. In the Raman spectrum of $Rh_2(O_2CCH_3)_4$ there are no strong bands above 400 cm^{-1} while for $Mo_2(O_2CCH_3)_4$ many bands above 400 cm^{-1}, such as those arising from the acetate vibrations δ (OCO), ν (CC) and δ (CH_3) are intense. These differences do not appear to be related to resonance effects[5] since the Raman spectra of both $Mo_2(O_2CCH_3)_4$ and $Rh_2(O_2CCH_3)_4$ were obtained with 514.5 nm excitation; this wavelength is well removed from that of any electronic band of $Mo_2(O_2CCH_3)_4$, and falls between those of the two weak electronic bands responsible for the green colour of $Rh_2(O_2CCH_3)_4$.

TABLE II

Wavenumbers/cm⁻¹ of Bands Observed in the Raman Spectrum[a] *of* $[Rh_2(O_2CCH_3)_4]$ *at* ca. *80 K*

$\bar{\nu}$	Assignment	$\bar{\nu}$	Assignment
3012vw	ν (C—H)	355vs	ν (Rh—Rh)
2983vw		338m	ν (Rh—O)
2938vw		331m	
1500vw		311vw	
1460vw	δ_{as} (CH_3)	298vw	
1445vw	ν_s (COO)	273vw	
1436vw	δ_{as} (CH_3)	188m	δ (O—Rh—O) or
1425vw		176m	δ (Rh—Rh—O)
1400w		144w	τ (CH_3)
1368w	δ_s (CH_3)	84w	
1357vw		59w	
1058w	ϱ (CH_3)		
1050w			
1040vw			
962w	ν (C—C)		
954w			
734w	δ (OCO)		
629vw	out-of-plane ϱ_w (COO)		
591vw	in-plane ϱ_r (COO)		
389w	ν (Rh—O)		

[a] 514.5 nm excitation

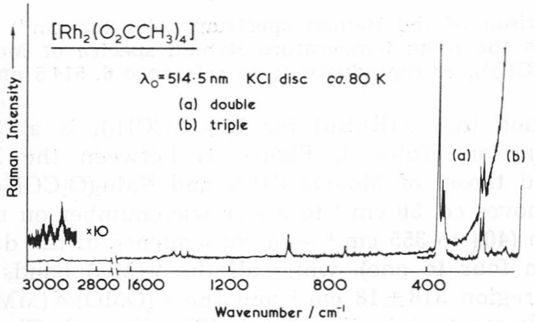

Figure 2. Raman spectrum (3100—2750 and 1650—20 cm⁻¹) of $Rh_2(O_2CCH_3)_4$ as a KCl disc at *ca.* 80 K with 514.5 nm excitation. Resolution *ca.* 3 cm⁻¹. The spectrometer was used in the (a) double and (b) triple mode.

In order to be able to assign ν (RhRh) for $Rh_2(O_2CCH_3)_4$, in a similar manner to that for $Rh_2(O_2CCH_3)_4(PPh_3)_2$, ^{18}O and CD_3 samples were synthesised. The Raman spectra obtained for $Rh_2(O_2CCH_3)_4$ and its ^{18}O and CD_3 isotopomers (Tables II—IV) in the range 450—160 cm⁻¹ are shown in Figure 3. All bands in the 400—300 cm⁻¹ region show some sensitivity to both ^{18}O and CD_3 substitution. The strong band occurring at 355 cm⁻¹ for $Rh_2(O_2CCH_3)_4$ is assigned to ν (RhRh) for the following reasons. First, the close similarity between the Raman spectra of $Rh_2(O_2CCH_3)_4$ and $Mo_2(O_2CCH_3)_4$ in the low wavenumber region, *vide supra*. Second, the 355 cm⁻¹ band is the strongest in the Raman spectrum, this observation being consistent with those made using 514.5 nm excitation for the complexes $Rh_2(O_2CCH_3)_4L_2$, where L = PPh_3, $AsPh_3$, $SbPh_3$ or $S(CH_2Ph)_2$.[1,3] Third, the shifts of this band upon either ^{18}O or CD_3 substitution are the same as each other, *viz.* 4 cm^{-1}. This is in contrast to the behaviour of the two bands of medium intensity at 338 and 331 cm^{-1} for $Rh_2(O_2CCH_3)_4$ which shift by 5 and 4 cm^{-1}, respectively, upon ^{18}O substitution but by 12 cm^{-1} upon CD_3 substitution. These last two bands are assigned to ν(RhO) vibrations because their shifts upon ^{18}O and CD_3 substitution are similar to those observed for the Raman-active ν(RhO) bands of $Rh_2(O_2CCH_3)_4(PPh_3)_2$, namely 6 and 13 cm^{-1}, respectively.[2] In addition the Raman band observed at 389 cm^{-1} for $Rh_2(O_2CCH_3)_4$ which shifts upon ^{18}O and CD_3 substitution to 385 and 377 cm^{-1}, respectively, is tentatively also assigned to ν(RhO).

TABLE III

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

$\bar{\nu}$	Assignment	$\bar{\nu}$	Assignment
2939vw	ν (C—H)	708vw,br	δ (OCO)
1533vw		623vw	ϱ_w (COO)
1497vw		569vw	ϱ_r (COO)
1483vw		385w	ν (Rh—O)
1451vw	δ_{as} (CH_3)	351vs	ν (Rh—Rh)
1433vw		333m	ν (Rh—O)
1413vw	ν_s (COO)	325m	
1396vw	δ_{as} (CH_3)	307vw	
1358vw	δ_s (CH_3)	297vw	
1047vw,br	ϱ (CH_3)	263vw,br	
936vw	ν (C—C)	180m	δ (O—Rh—O) or δ (Rh—Rh—O)
922vw		172m	

[a] 514.5 nm excitation

TABLE IV

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

$\bar{\nu}$	Assignment	$\bar{\nu}$	Assignment
2259vw	ν (C—D)	920w	ν (C—C) & ϱ (CD_3)
2234vw		913vw	
2203vw		909w	
2114vw		897vw	ϱ (CD_3)
1498vw		855vw	
1485vw		703w	δ (OCO)
1466vw	913 + 550	550vw	out-of-plane ϱ_w (COO)
1434vw	ν_s (COO)	377w	ν (Rh—O)
1419vw	1099 + 319	351vs	ν (Rh—Rh)
1403vw	2 × 703	326m	ν (Rh—O)
1099vw	δ_s (CD_3)	319m	
1045vw	δ_{as} (CD_3)	295vw	
1037vw		284vw	
		264vw	
		185m	δ (O—Rh—O) or δ (Rh—Rh—O)
		176m	

[a] 514.5 nm excitation

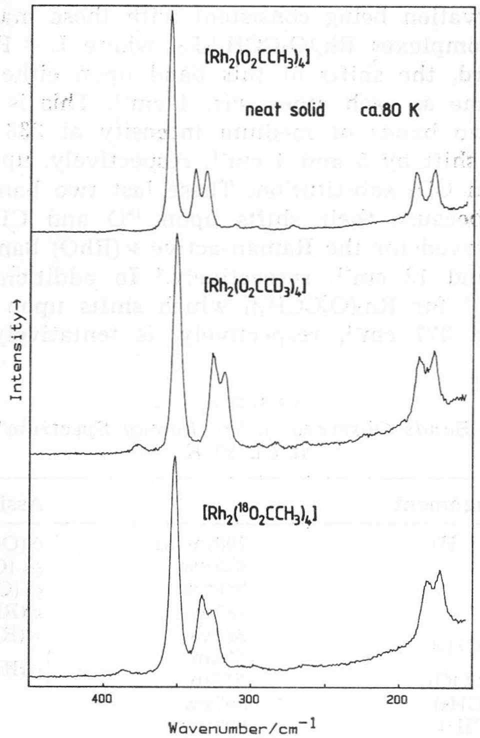

Figure 3. Raman spectra (450—160 cm^{-1}) of $Rh_2(O_2CCH_3)_4$, $Rh_2(O_2CCD_3)_4$ and $Rh_2(^{18}O_2CCH_3)_4$ as pure solids at *ca.* 80 K with 514.5 nm excitation. Resolution *ca.* 3 cm^{-1}.

The slight sensitivity of ν(RhRh) to both ^{18}O and CD_3 substitution is thought to arise from coupling between the ν(RhRh) and ν(RhO) symmetry coordinates. The reason for the dependence being more pronounced for $Rh_2(O_2CCH_3)_4$ than for $Rh_2(O_2CCH_3)_4(PPh_3)_2$ is thought to be due to the lesser wavenumber separation of these bands for the former case. Thus for $Rh_2(O_2CCH_3)_4(PPh_3)_2$ ν_2, ν(RhO) is 49 cm^{-1} higher than ν(RhRh) whereas it is only 43 cm^{-1} higher for the ^{18}O derivative, 38 cm^{-1} higher for the CD_3-derivative, and 17 cm^{-1} higher for $Rh_2(O_2CCH_3)_4$ itself.

The two bands at 188 and 176 cm^{-1} in the Raman spectrum of $Rh_2(O_2CCH_3)_4$ show little sensitivity to deuteration; however they shift to lower wavenumber by 8 and 4 cm^{-1}, respectively, upon ^{18}O substitution and are assigned to skeletal deformation modes of the type δ(ORhO) or δ(RhRhO). For $Mo_2(O_2CCH_3)_4$ two bands occurring at 204 and 190 cm^{-1} also been assigned to similar vibrations. They show no sensitivity to ^{92}Mo substitution[6] and shift by only 3 cm^{-1} upon deuteration.[7]

The infrared spectra of $Rh_2(O_2CCH_3)_4$ in the range 660—200 cm^{-1} and of its ^{18}O and CD_3 isotopomers are shown in Figure 4. Just as for $Mo_2(O_2CCH_3)_4$,[7] $Os_2(O_2CCH_3)_4Cl_2$,[8] and $Rh_2(O_2CCH_3)_4(PPh_3)_2$,[3] a triplet of bands of medium intensity is observed in the 400—300 cm^{-1} region which, by comparison, is assigned to ν(RhO) vibrations. For $Rh_2(O_2CCH_3)_4$ they occur at 398, 383 and

359 cm^{-1}, shifting to 394, 380 and 352 cm^{-1} and to 384, 372 and 341 cm^{-1} upon ^{18}O and CD_3 substitution, respectively. For the ^{18}O and CD_3 complexes there is a fourth band occurring as a shoulder at 387 and 379 cm^{-1}, respectively, which is also assigned to ν (RhO).

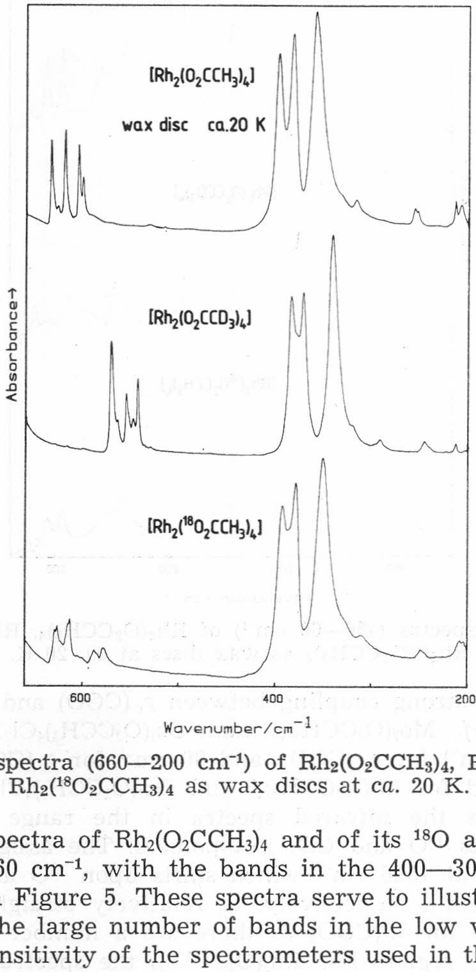

Figure 4. FTIR spectra (660—200 cm^{-1}) of $Rh_2(O_2CCH_3)_4$, $Rh_2(O_2CCD_3)_4$ and $Rh_2(^{18}O_2CCH_3)_4$ as wax discs at *ca.* 20 K.

The infrared spectra of $Rh_2(O_2CCH_3)_4$ and of its ^{18}O and CD_3 isotopomers in the range 450—60 cm^{-1}, with the bands in the 400—300 cm^{-1} region truncated, are shown in Figure 5. These spectra serve to illustrate several important points. First, the large number of bands in the low wavenumber region. Second, the high sensitivity of the spectrometers used in the study. Third, the strong dependence of many bands on CD_3 substitution. The only band which shows no sensitivity to deuteration is that at 214 cm^{-1}; this is assigned to the infrared counterpart of the Raman-active δ (ORhO) or δ (RhRhO) vibrations, shifting by 6 cm^{-1} to 208 cm^{-1} upon ^{18}O substitution.

Acetate Modes

The in-plane, ρ_r (COO), and out of plane, ρ_ω (COO), bands of $Rh_2(O_2CCH_3)_4$ are easily assigned from the infrared spectrum. The wavenumber of ρ_ω (COO) is virtually identical with that observed for $Rh_2(O_2CCH_3)_4(PPh_3)_2$;[3] however ρ_r (COO) is 15 cm^{-1} higher for the former. In view of the fact that ν (RhO) is higher for $Rh_2(O_2CCH_3)_4$ than $Rh_2(O_2CCH_3)_4(PPh_3)_2$ this result is further

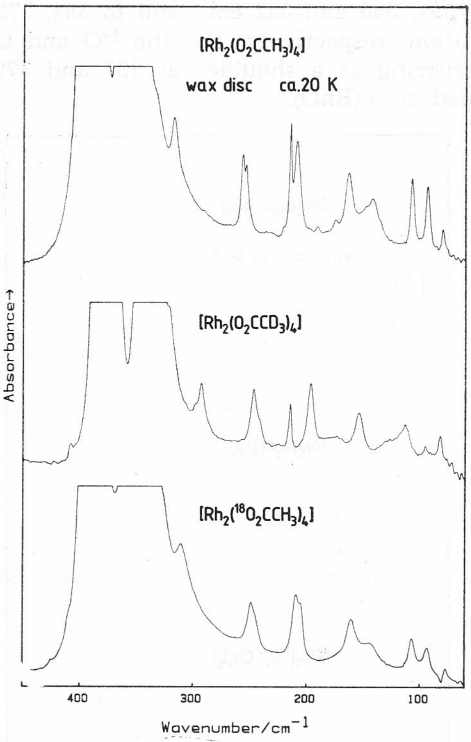

Figure 5. FTIR spectra (450—60 cm^{-1}) of $Rh_2(O_2CCH_3)_4$, $Rh_2(O_2CCD_3)_4$ and $Rh_2(^{18}O_2CCH_3)_4$ as wax discs at *ca.* 20 K.

confirmation of the strong coupling between ρ_r (COO) and ν (MO) for dimeric tetracarboxylates, *cf.* $Mo_2(O_2CCH_3)_4$[7] and $Os_2(O_2CCH_3)_4Cl_2$.[8] The shifts upon deuteration of 80 cm^{-1} for ρ_ω (COO), and 30 cm^{-1} for ρ_r (COO) are comparable with those observed for $M_2(O_2CCH_3)_4$[7] and $Os_2(O_2CCH_3)_4Cl_2$.[8]

Figure 6 shows the infrared spectra in the range 1600—600 cm^{-1} of $Rh_2(O_2CCH_3)_4$ and its ^{18}O and CD_3 isotopomers. The assignment of ν_{as} (COO) to the strong band at 1586 cm^{-1} which shifts upon ^{18}O and CD_3 substitution to 1571 and 1577 cm^{-1}, respectively, is relatively straightforward; however this is not the case for ν_s (COO) as there are a number of strong bands in the 1500—1400 cm^{-1} region. For $Rh_2(O_2CCD_3)_4$ the spectrum is much simpler in this region and ν_{as} (COO) is clearly assigned to the strong band at 1425 cm^{-1} which means that, for $Rh_2(O_2CCH_3)_4$, ν_s (COO) must lie above this; consequently it is assigned to a shoulder, at 1438 cm^{-1}, on the strong band at 1446 cm^{-1}. On the basis that ν_{as} (COO) shifts more upon ^{18}O substitution than it does upon CD_3 substitution, ν_s (COO) for $Rh_2(^{18}O_2CCH_3)_4$ is assigned to a band at 1410 cm^{-1}, although the shift upon ^{18}O substitution (28 cm^{-1}) is much larger than that observed (15 cm^{-1}) for ν_{as} (COO). Unfortunately, no ^{18}O substitution data are available for NaO_2CCH_3 or for any dimeric tetracarboxylates with which to enable proper comparisons to be made.

It is noteworthy that, in the infrared spectrum of $Rh_2(O_2CCD_3)_4$, the band assigned to ν_s (COO) is stronger than that assigned to ν_{as} (COO), a situation which is the reverse of that for $Rh_2(O_2CCH_3)_4$.

TABLE V

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

$\bar{\nu}$	Assignment	$\bar{\nu}$	Assignment
3014vw	ν (C—H)	1260vw	
2979vw,br		1252vw	
2930vw,br		1051w	ϱ (CH_3)
2714vw	2 × 1357	1046w,sh	
2708vw	1357 + 1352	1037w	
2479vw,br	1429 + 1051	945vw	ν (C—C)
2462vw,br	1415 + 1046	941vw	
2441vw,br	1405 + 1037	722w	
2409vw,br	1357 + 1051	709m	δ (OCO)
2394vw,br	1357 + 1037	704m	
2364vw,br	1423 + 941	700m	
2081vw	1446 + 635	635w	out-of-plane ϱ_w (COO)
2067vw	1446 + 621	628vw	
2056vw	1429 + 628	621w	
2051vw	1429 + 621	606w	in-plane ϱ_r (COO)
1586vs	ν_{as} (COO)	602w	
1555w	2979—1423?	398m	ν (Rh—O)
1547w	2979—1429?	383m	
1534w	2979—1446?	359m	
1527w	2930—1405?	333vw,sh	
1503w,br	2930—1429?	318vw	
1446s	δ_{as} (CH_3)	257vw	
1438m,sh	ν_s (COO)	254vw	
1429m,sh	δ_{as} (CH_3)	214vw	δ (O—Rh—O)/δ (Rh—Rh—O)
1423s,sh		209vw	τ (CH_3)
1415s	δ_{as} (CH_3)	163vw	
1405m,sh		142vw	
1372vw		106vw	
1357m	δ_s (CH_3)	93vw	
1352w,sh			

[a] Bands below 700 cm^{-1} recorded at *ca.* 20 K

Upon deuteration these bands shift to lower wavenumber and appear as much weaker features; this in turn simplifies the 1600—1400 cm^{-1} region. The spectrum in this region is much simpler for $Rh_2(O_2CCH_3)_4$ than for $Mo_2(O_2CCH_3)_4$ due to the much higher wavenumber of ν_{as} (COO), 1586 cm^{-1}, for $Rh_2(O_2CCH_3)_4$, compared to that, 1500 cm^{-1}, for $Mo_2(O_2CCH_3)_4$,[7] which places ν_{as} (COO) higher than bands arising from δ_{as} (CH_3) and from combination tones.

Many of the remaining infrared and Raman band assignments for $Rh_2(O_2CCH_3)_4$ and $Rh_2(O_2CCD_3)_4$ are made by comparison with the spectra of the corresponding molybdenum compounds.[7] The sensitivity of many of the methyl group bands appears to be small.

$Rh_2(O_2CCH_3)_4(H_2O)_2$: *Skeletal Modes*

The Raman spectrum of $Rh_2(O_2CCH_3)_4(H_2O)_2$ at 80 K with 514.5 nm excitation (Figure 7) is similar to that of the anhydrous material in the sense that the strongest bands lie below 400 cm^{-1}. The band assignments are given in Table VIII. The spectrum is dominated by a band at 347 cm^{-1} and its side

TABLE VI

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

$\bar{\nu}$	Assignment	$\bar{\nu}$	Assignment
3012vw	ν (C—H)	629w	out-of-plane ϱ_w (COO)
2977vw,br		626w	
2928vw,br		623w,sh	
2701vw	2 × 1352	615w	
2320vw		613w	
1571vs	ν_{as} (COO)	588vw	in-plane ϱ_r (COO)
1518w	2928—1410?	584vw	
1511w		578vw	
1496vw		394m	ν (Rh—O)
1444m,sh	δ_{as} (CH_3)	387m,sh	
1425m,sh		380m	
1410vs	ν_s (COO)	352m	
1352m	δ_s (CH_3)	327w,sh	
1245vw		311vw,br	
1050w	ϱ (CH_3)	248vw	
1034w		244vw	
721w		208vw	τ (CH_3)
709w		204vw	δ (O—Rh—O)/δ (Rh—Rh—O)
692m,sh	δ (OCO)	159vw	
680m		143vw,br	
676m		106vw	
		92vw	

[a] Bands below 700 cm^{-1} recorded at *ca.* 20 K

TABLE VII

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

$\bar{\nu}$	Assignment	$\bar{\nu}$	Assignment
2913vw	2230 + 681	696w,sh	δ (OCO)
2255vw	ν (C—D)	681m	
2230vw		674m	
2111vw		571w	in-plane ϱ_r (COO)
1577s	ν_{as} (COO)	565vw	
1514w		556w	out-of-plane ϱ_w (COO)
1496vw		549vw	
1468w	898 + 571	544w	
1456w	914 + 544	384m	ν (Rh—O)
1425vs	ν_s (COO)	379m,sh	
1379w		372m	
1364w,sh	2 × 681	341m	
1103vw,sh	δ_s (CD_3)	322vw	
1092vw		298vw	
1048vw,sh	δ_{as} (CD_3)	292vw	
1030w		246vw	
920w		241vw	
914w,sh	ϱ (CD_3)	214vw	δ (O—Rh—O)/δ (Rh—Rh—O)
898vw		196vw	τ (CD_3)
893vw	ν (C—C)	153vw	
889vw,sh		112vw	
853w	ϱ (CD_3)	94vw	

[a] Bands below 700 cm^{-1} recorded at *ca.* 20 K

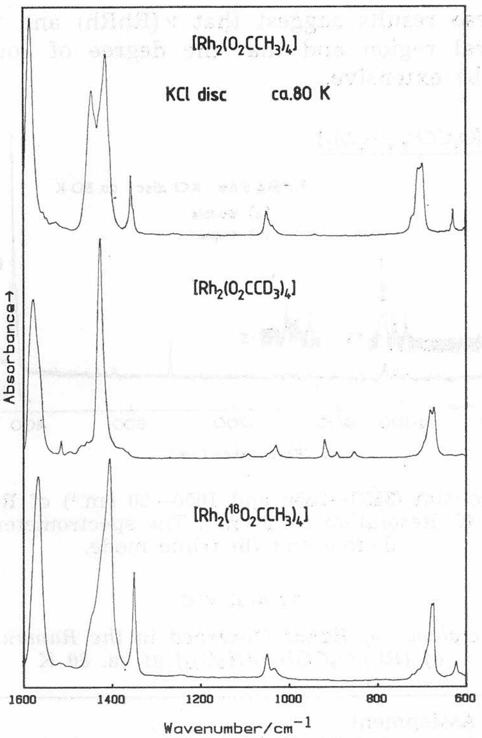

Figure 6. FTIR spectra (1600—600 cm^{-1}) of $Rh_2(O_2CCH_3)_4$, $Rh_2(O_2CCD_3)_4$ and $Rh_2(^{18}O_2CCH_3)_4$ as KCl discs at *ca.* 80 K.

bands at higher and lower wavenumbers; on intensity grounds the 347 cm^{-1} band might have been expected to be attributable to ν(RhRh), and hence, in order to probe this question, some isotopic work was attempted. Upon CD_3 substitution, the 360, 347 and 322 cm^{-1} triplet of bands move down by 2, 13 and 12 cm, respectively. This preliminary result suggests that the 347 and 332 cm^{-1} bands are correctly assigned to ν(RhO) modes, leaving the 360 cm^{-1} band as the ν(RhRh) mode. However, consideration of bond length/bond stretching frequency relationships suggests that such a value would be unacceptably high. Thus a ν(RhRh) value of 360 cm^{-1} for $Rh_2(O_2CCH_3)_4(H_2O)_2$ would place it well above ν(RuRu) of $[Ru_2(O_2CCH_3)_4(H_2O)_2]BF_4$ (326 cm^{-1}),[9] despite the fact that the RhRh bond length (2.3855 Å)[10] of the former is considerably longer than the RuRu bond length (2.248 Å)[11] of the latter. Thus, ν(RhRh) would be comparable with the ν(MoMo) value[12,13] of 367 cm^{-1} for $Mo_2(O_2CCF_3)_4(py)_2$, py = pyridine, for which the MoMo distance is only 2.129 Å.[13] Moreover, it would be greater than that of anhydrous $Rh_2(O_2CCH_3)_4$, a result which would not be expected since axial coordination is understood to weaken the RhRh bond. For the very closely related complexes $Rh_2(O_2CCH_3)_4L_2$, L = PPh_3, $AsPh_3$ $SbPh_3$, $S(CH_2Ph)_2$, and H_2O, the RhRh bond lengths are 2.4505,[14] 2.427,[1] 2.421,[1] 2.406,[1] 2.3855 Å,[10] respectively; on the basis of the known ν(RhRh) values for the first four complexes, 289, 297, 307 and 314 cm^{-1}, the corresponding value for the diaquo complex would be expected near 330 cm^{-1}. These results suggest that ν (RhRh) and ν (RhO) must occur in the same spectral region and that the degree of coupling between the modes is likely to be extensive.

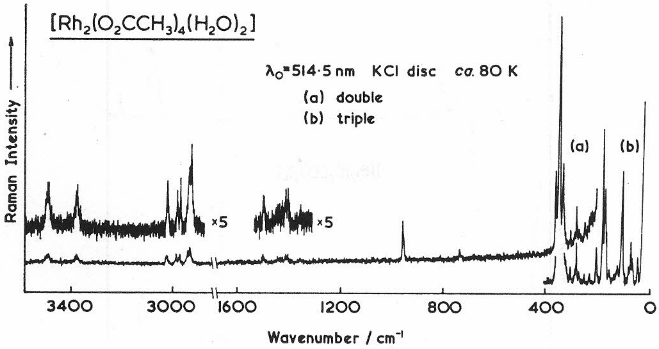

Figure 7. Raman spectrum (3550—2850 and 1650—20 cm^{-1}) of $Rh_2(O_2CCH_3)_4(H_2O)_2$ as a KCl disc at *ca.* 80 K. Resolution ca. 3 cm^{-1}. The spectrometer was used in the (a) double and (b) triple mode.

TABLE VIII

Wavenumbers/cm^{-1} of Bands Observed in the Raman Spectrum[a] *of [$Rh_2(O_2CCH_3)_4(H_2O)_2$] at* ca. *80 K*

$\bar{\nu}$	Assignment	$\bar{\nu}$	Assignment
3490vw	ν (O—H)	303w	
3378vw		286vw	
3024vw	ν (C—H)	280w	
2986vw		269vw	
2972vw		247vw	
2940w,sh		228vw	
2931w		201w	
1503vw		177s	δ (O—Rh—O) or δ (Rh—Rh—O)
1456vw	δ_{as} (CH_3)	168m	
1447vw	ν_s (COO)	163m	
1430vw	δ_{as} (CH_3)	151vw	
1416vw		119vw	
1408vw		102m	
1358vw	δ_s (CH_3)	74w,sh	
957w	ν (C—C)	66w	
953w,sh		60w	
735vw	δ (OCO)	40w	
360m			
347vs	ν (Rh—O)		
332m			
321m,sh			

[a] 514.5 nm excitation

One other possible assignment for the 360 cm^{-1} band is to ν (Rh—O_w), where O_w is an oxygen atom of the axial water molecules. Mathey *et al.*[15] have tentatively assigned the band at 302 cm^{-1} in the spectrum of $Cu_2(O_2CCH_3)_4(H_2O)_2$ to ν (Cu—O_w); it is insensitive to ^{65}Cu substitution, and shifts 2 cm^{-1}

lower upon $H_2{}^{18}O$ substitution and 3 cm^{-1} lower on CD_3 substitution; but its shift on D_2O substitution was not reported. On the assumption that this assignment is correct, the corresponding one for $Rh_2(O_2CCH_3)_4(H_2O)_2$ would be expected to lie at lower wavenumber, probably in the 200—250 cm^{-1} region since the Rh—O distance (2.310 Å)[10] is much larger than the Cu—O distance (2.156 Å) of $Cu_2(O_2CCH_3)_4(H_2O)_2$.[16] Thus it seems improbable that the 360 cm^{-1} band could be assigned to ν(RhO$_w$). Clearly it is not possible to make a firm assignment for the 360 cm^{-1} band in the absence of not only CD_3 data but also ^{18}O and D_2O data and (probably) force field calculations. Possibly also ν(RhRh) is very weak in the Raman spectrum of the diaquo species, and thus difficult to identify in the absence of laser lines which might induce resonance effects, *i. e.* $\lambda_0 \leq 270$ nm.

It should be noted that, in an earlier study of this species in aqueous solution, Miskowski *et al.*[17] assigned a polarised band at 343 cm^{-1} to ν(RhO) (a_{1g} species in the D_{4h} point group). However, some aspects of the discussion in this paper are invalid owing to their dependence on an incorrect argument to do with the depolarisation ratio of this Raman band.[18]

The far-infrared spectrum of $Rh_2(O_2CCH_3)_4(H_2O)_2$ in the range 660—200 cm^{-1} is shown in Figure 8. The main difference between this spectrum and that of anhydrous $Rh_2(O_2CCH_3)_4$ lies in the 600—400 cm^{-1} region where several broad bands are observed and are assigned to rotational or librational modes of the axial water molecules. The five bands at 392, 389, 377, 352, and 345 cm^{-1} are assigned to ν(RhO) modes. Miskowski *et al.*[17] observed only three bands at 386, 374 and 342 cm^{-1} in the infrared spectrum of $Rh_2(O_2CCH_3)_4(H_2O)_2$ and, whilst they assigned them to ν(RhO) modes, they also suggested that the upper two bands arise from an e_u mode which is split by the crystal field. This may be the case as a similar band splitting, 8 cm^{-1}, is observed for the upper two ν(RhO) bands of $Rh_2(O_2CCH_3)_4(PPh_3)_2$ for which there is only one molecule per unit cell;[14] however for $Rh_2(O_2CCH_3)_4(H_2O)_2$ there are four

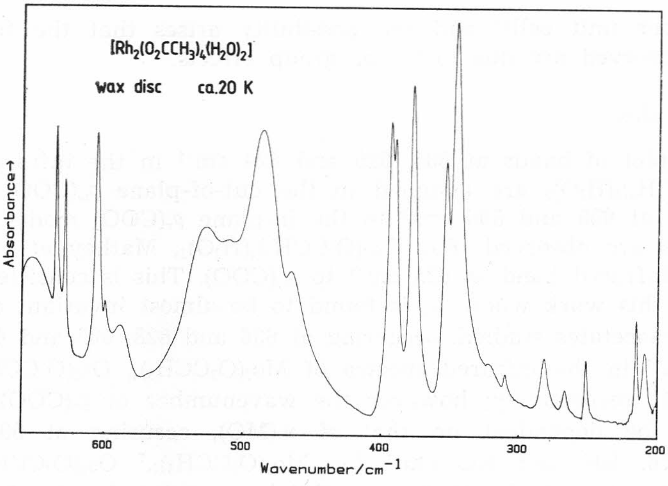

Figure 8. FTIR spectrum (660—200 cm^{-1}) of $Rh_2(O_2CCH_3)_4(H_2O)_2$ as a wax disc at *ca.* 20 K.

TABLE IX

Wavenumbers/cm^{-1} of Bands Observed in the Infrared Spectrum of [$Rh_2(O_2CCH_3)_4(H_2O)_2$] at ca. *80 K*[a]

$\bar{\nu}$	Assignment	$\bar{\nu}$	Assignment
3495m	ν (O—H)	718m	δ (OCO)
3380m		710m	
3266m		702m	
3024vw	ν (C—H)	653w,br	ϱ (H_2O)
2984vw		635w	ϱ_w (COO)
2974vw		629w	
2942vw		624vw	
2931vw		605w	ϱ_r (COO)
1661vw	δ (O—H)	599vw	
1644vw		588vw,br	ϱ (H_2O)
1587vs	ν_{as} (COO)	527w,br	
1556w	2974—1416?	510w	
1548w	2984—1438?	486w,br	
1528w	2942—1416?	465w,br	
1513vw	2931—1416?	392w	ν (Rh—O)
1455m,sh		389w	
1446s	δ_{as} (CH_3)	377w	
1438m	ν_s (COO)	352w	
1431m	δ_{as} (CH_3)	345w	
1416vs		322vw	
1405m,sh		310vw	
1357m	δ_{as} (CH_3)	281vw	
1355m		266vw	
1055m	ϱ (CH_3)	251vw	
1051m		215vw	δ (O—Rh—O)/δ (Rh—Rh—O)
1046m		209vw	τ (CH_3)
1037w		197vw	
1030w		187vw	
941vw	ν (C—C)		

[a] Bands below 700 cm^{-1} recorded at *ca.* 20 K

molecules per unit cell[10] and the possibility arises that the further band splittings observed are due to factor group effects.

Acetate Modes

The triplet of bands at 635, 629 and 624 cm^{-1} in the infrared spectrum of $Rh_2(O_2CCH_3)_4(H_2O)_2$ are assigned to the out-of-plane ρ_ω(COO) modes and the doublet at 605 and 599 cm^{-1} to the in-plane ρ_r(COO) modes. No Raman counterparts are observed. For $Cu_2(O_2CCH_3)_4(H_2O)_2$, Mathey *et al.*[9] have assigned the infrared band at 625 cm^{-1} to ρ_ω(COO). This is consistent with the findings of this work where ρ_ω is found to be almost invariant over several dimeric tetraacetates studied, occurring at 636 and 628, 635 and 630, 635, 628 and 621 cm^{-1} in the infrared spectra of $Mo_2(O_2CCH_3)_4$, $Os_2(O_2CCH_3)_4Cl_2$,[8] and $Rh_2(O_2CCH_3)_4$, respectively; however the wavenumber of ρ_r(COO) varies and appears to be dependent on that of ν (MO), occuring at 583 and 575, 618 and 616, 606 and 602 cm^{-1} for $Mo_2(O_2CCH_3)_4$,[7] $Os_2(O_2CCH_3)_4Cl_2$,[8] and $Rh_2(O_2CCH_3)_4$, respectively. Mathey *et al.*[15] have assigned a band at 460 cm^{-1} for $Cu_2(O_2CCH_3)_4(H_2O)_2$ to ρ_r (COO); this band wavenumber is identical to that observed for NaO_2CCH_3,[19] although for $Cu_2(O_2CCD_3)_4(H_2O)_2$ it has risen by 18 cm^{-1} to 478 cm^{-1}. This assignment must be incorrect as, for the molybdenum, osmium and rhodium tetraacetates, ρ_r(COO) typically shifts 30 cm^{-1} lower upon CD_3 substitution. Alternatively a band at 560 cm^{-1} in the spectrum of $Cu_2(O_2CCH_3)_4(H_2O)_2$ may be assigned to ρ_r(COO),[15] although there is some difficulty in making the assignment due to the close proximity of librational modes of the axial water molecules.

The bands assigned to the O—H stretching modes of the axial water ligands are clearly observed, occurring at 3495, 3380 and 3266 cm^{-1} in the infrared spectrum and a 3490 and 3378 cm^{-1} in the Raman spectrum, whereas the HOH bend gives rise in the infrared spectrum to a doublet at 1661 and 1644 cm^{-1}. The remaining infrared and Raman band assignments are based upon those presented for $Rh_2(O_2CCH_3)_4$.

Clearly this complex requires further investigation along with both ^{18}O and CD_3 isotopomers as well as $Rh_2(O_2CCH_3)_4(D_2O)_2$. This would be a project of some length as the Raman spectra of such complexes would be difficult to obtain owing to the weakness of the scattering.

CONCLUSION

ν(RhRh) has been found to occur over the range 355—289 cm^{-1} for all of the dirhodium complexes recently studied.[1-3,20] Its high value for $Rh_2(O_2CCH_3)_4$ (355 cm^{-1}) implies that the RhRh bond length must be short for this complex, possibly of the order of 2.38 Å. Earlier difficulties over such assignments in dirhodium complexes have largely arisen through the expectation that, based upon a consideration of ν(MM) values for other singly metal-metal bonded complexes, ν(RhRh) should lie below 200 cm^{-1}. Such a consideration ignores the substantial additional restoring force along the RhRh bond to be associated with the four acetate bridges. This has been further compounded by the inadequacy of earlier experimental data in the low wavenumber region. The high quality of the spectrometers used in this study has allowed accurate measurements to be made on bands of low wavenumber. Spectra have been collected several times for each complex in order to ensure consistency and infrared samples have been made at different concentrations to allow the observation of weak features. For the Raman spectra the use of holographic diffraction gratings excludes the possibility of grating ghosts, and the recording of spectra using several different excitation lines allows the identification of bands due to plasma radiation. Further studies using single crystal electronic, infrared and Raman spectroscopy are required in order to further the understanding of the nature of the absorption bands in the visible.

The identification of many other bands of the tetracarboxylate cage has also been carried out during the course of this study. Isotopically substituted molecules have been shown to be a necessity in order to make firm bands assignments. In particular the use of readily available, low cost and high purity (99+ % atom D) substituted acetic acid makes possible the identification of those bands attributable to ν(RhO).

The present results clearly indicate that the band at 184 cm^{-1} in the Raman spectrum of $Rh_2(mhp)_4$, Hmhp = 6-methyl-2-hydroxypyridine, cannot be attributed to ν(RhRh) as indicated by Garner *et al.*[21] the very short RhRh distance in this complex (2.359 Å)[22] is suggestive of a ν(RhRh) of significantly above 300 cm^{-1}. Likewise the recent molecular mechanics calculation[23] on $M_2(O_2CCH_3)_4L_2$ and related complexes, which favoured the *ca.* 170 cm^{-1} region for ν(RhRh), must need reexamination.

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18. Depolarisation ratios (ϱ) of totally symmetric modes take limiting values of 1/3 or 1/8 in resonance Raman spectra, but only if the resonant electronic transition is either z or xy polarised; off resonance, the only stricture on ϱ is that $0 < \varrho < 3/4$. Moreover, the limiting ϱ-values provide information on the polarisation of the resonant electronic transition, not on the vibrational modes, as implied in ref. 17. Thus, since the spectra were taken off resonance, even with the weak ($\varepsilon_{\max} < 250$ dm^3 mol^{-1} cm^{-1}) bands in the visible, and since in no case were resonance effects observed, no special significance (*i. e.* to do with the polarisation of the »resonant« electronic transition) can be attached to the observed ϱ value (0.1) of the 343 cm^{-1} band other than that it pertains to a totally symmetric mode.
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SAŽETAK

Infracrvena i Ramanova spektroskopija dirodij-tetraacetatnih kompleksa $Rh_2(O_2CCH_3)_4$, $Rh_2(^{18}O_2CCH_3)_4$ $Rh_2(O_2CCD_3)_4$ i $Rh_2(O_2CCH_3)_4(H_2O)_2$

Robin J. H. Clark i Andrew J. Hempleman

Snimljeni su infracrveni (3500—50 cm^{-1}) i Ramanovi (3550—30 cm^{-1}) spektri dirodij-tetraacetatnih spojeva $Rh_2(O_2CCH_3)_4$, $Rh_2(^{18}O_2CCH_3)_4$, $Rh_2(O_2CCD_3)_4$ i $Rh_2(O_2CCH_3)_4(H_2O)_2$, te asignirane ključne vrpce. Vrste s kisikom-18 i deuterijem osobito su pomogle u važnoj asignaciji vrpci za bezvodni kompleks, za koji se ν (RhRh) nalazi na 355—351 cm^{-1}, a ν (RhO) na 389—319 (Raman) i 398—341 cm^{-1} (IR). Vrpca koja se pripisuje ν (RhRh) tipično je intezivna, oštra i relativno neosjetljiva na ^{18}O- i CD_3-supstituciju. Tako se ν (RhRh) pomiče za samo 4 cm^{-1} bilo ^{18}O, bilo CD_3 supstitucijom, dok se ν (RhO) pomiče za 4—6 cm^{-1} u Ramanovim i 3—7 cm^{-1} u infracrvenim spektrima supstitucijom s ^{18}O ali za 12 cm^{-1} u Ramanovim i 11—18 cm^{-1} u infracrvenim spektrima s CD_3 supstitucijom. Prikazani su i prethodni rezultati za kompleks $Rh_2(O_2CCH_3)_4 \cdot (H_2O)_2$.