

It was suggested that C was formed by excitation of an electron from a metal-metal bonding orbital into a metal-metal antibonding orbital.

However, two other groups^{5,18,19} have found that the photo-generated species seems rather inert toward carbon tetrachloride, behavior unexpected of a diradical such as A, and have proposed carbonyl-bridged intermediates as alternatives. While we have little to offer in this continuing controversy,²⁰ we note that there appears to be a correlation between the relative amounts of I and IV that are formed and the initial concentration of III. Thus, IV is only obtained when the concentration of III is high, consistent with an oligomerization process. On this basis coupling of diradicals C would appear to be a reasonable route to a polymer or a cyclic oligomer containing repeating $[\text{Ru}_3(\text{CO})_{12}]$ units.

As mentioned above, a compound appearing to be IV has been previously prepared in THF but not characterized.⁴ We had initially assumed that the material reported and subsequently obtained by us was a THF adduct and hence was of little interest. It was only when we obtained it in hydrocarbon solvents as well that we suspected a new binary carbonyl compound. A similar material also appears to have been prepared by James et al.,²¹ who obtained an insoluble purple solid formulated as $[\text{HRu}(\text{CO})_3]_n$ from the carbonylation of aqueous solutions of ruthenium trichloride. We have repeated the synthesis of this material and found that it has an IR spectrum and an X-ray powder diffraction pattern similar to (but not identical with) the corresponding data for IV. We find that the purple solid reacts with iodine to form *cis*- $\text{Ru}(\text{CO})_4\text{I}_2$ quantitatively, and as the original evidence for the hydride ligand was indirect, we suggest that the material obtained from aqueous solution is an isomer of IV.

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Registry No. I, 16406-48-7; III, 15243-33-1; IV, 29718-13-6; $\text{H}_4\text{-Ru}_4(\text{CO})_{12}$, 34438-91-0; *cis*- $\text{Ru}(\text{CO})_4\text{I}_2$, 18475-75-7; *cis*- $\text{Ru}(\text{CO})_4\text{Br}_2$, 21439-16-7; $\text{Ru}_2(\text{CO})_6\text{Br}_4$, 22594-70-3; $\text{Ru}_2(\text{CO})_6\text{Cl}_4$, 22594-69-0; $\text{Ru}(\text{CO})_4(\text{PMe}_2\text{Ph})$, 31447-09-3; $\text{Ru}(\text{CO})_3(\text{PMe}_2\text{Ph})$, 31447-08-2; $\text{Ru}(\text{CO})_3(\text{PMe}_2)_2$, 75687-45-5; $\text{Ru}(\text{CO})_4(\text{PMe}_2)_3$, 93180-37-1.

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 (21) (a) James, B. R.; Rempel, G. L. *Chem. Ind. (London)* **1971**, 1036. (b) Rempel, G. L.; Teo, W. K.; James, B. R.; Plackett, D. V. *Adv. Chem. Ser.* **1974**, No. 132, 166. Interestingly, corroboration of the synthesis and spectroscopic properties of IV was also offered by a reviewer. We thank Dr. M. J. Mays, P. A. Loveday, and S. R. Drake for permission to mention unpublished results.

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Differentiation between Metal-Metal Stretching and Ligand-Sensitive Vibrations in Dimetal Tetraacetates by Ligand Deuteration

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The assignment of metal-metal stretching vibrations in some dimetal tetraacetates remains controversial.²⁻⁴ The main difficulty

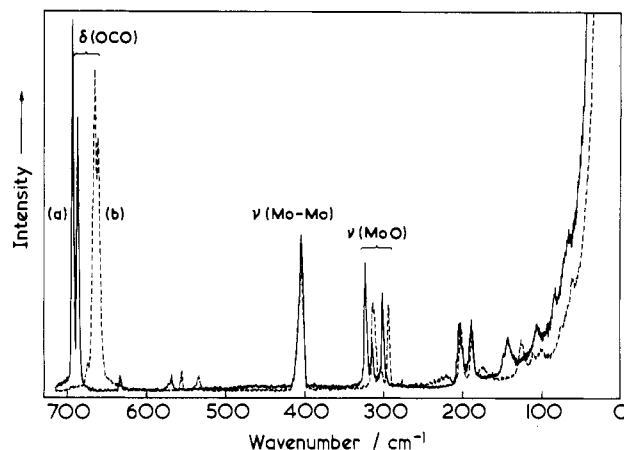


Figure 1. Raman spectra of (a) $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$ and (b) $\text{Mo}_2(\text{O}_2\text{CCD}_3)_4$.

lies in the distinction between the metal-metal vibrations and the metal-oxygen vibrations since both may occur in similar spectral regions.⁵ The most satisfactory method of assignment is to make use of the small shifts that occur on isotopic substitution of the metal atoms.^{6,7} This method is, however, not generally applicable since suitable isotopes of some metals are not readily available and, in other cases, the cost may be prohibitive. The alternative procedure of ^{18}O substitution of the acetate grouping is also expensive.⁵

In the course of our studies of the Raman, resonance Raman, and electronic spectra of dirhodium tetracarboxylates,^{8,9} we observed that the wavenumber shifts in the metal-carboxylate modes induced by deuteration of the carboxylate ligand are larger than those caused by oxygen isotopic substitution. We were unable to confirm our assignments by metal isotope substitution since there are no stable isotopes of rhodium other than naturally occurring ^{103}Rh . It seemed possible that acetate deuteration would provide a low-cost, readily available, and generally applicable method for differentiation of predominantly metal-metal and metal-carboxylate stretching vibrations. In order to test this hypothesis, we have applied the method to the well-established case of $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$ where $\nu(\text{Mo-Mo})$ has been shown to occur at 404 cm^{-1} by metal isotope substitution.⁶

Experimental Section

$\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$ and its deuterated analogue were prepared by the method of Holste et al.¹⁰ Acetic-*d*₃ acid-*d* (99.96%) was obtained from Aldrich Chemical Co., Inc. The samples for Raman spectroscopy were mounted as pressed disks side by side in the cryostat and measured under identical conditions (sample temperature 20 K with <3 mW of 5145-Å excitation at a spectral slit width of 2 cm^{-1}) to ensure equal temperatures. Infrared spectra were measured at 80 K as pressed wax disks at a spectral resolution of 1 cm^{-1} with a Bruker 113 V interferometer.

Results

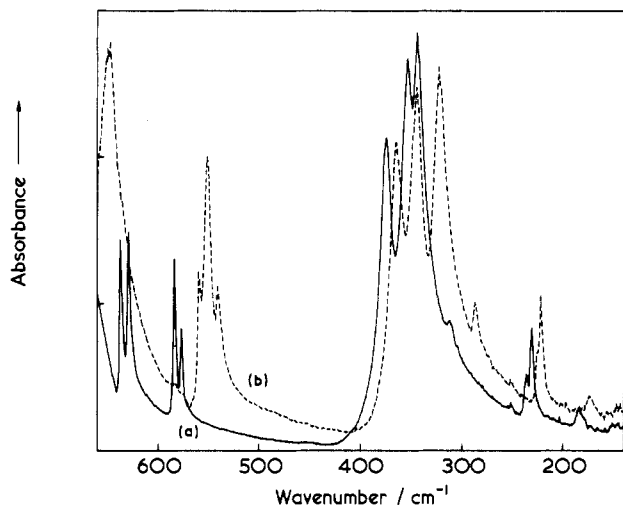
The 20 K Raman spectra of $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$ and $\text{Mo}_2(\text{O}_2\text{CCD}_3)_4$ are shown in Figure 1, and the wavenumbers of the prominent features below 450 cm^{-1} are given in Table I. It is immediately clear that the band at 404 cm^{-1} is essentially unshifted on deuteration whereas the group of three bands in the $323\text{--}301\text{ cm}^{-1}$

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Table I. Vibrational Data for Isotopomers of $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$ in the Range 450–150 cm^{-1} ^a

Raman				infrared	
^{NA} Mo ₂	^{NA} Mo ₂ ^b	⁹² Mo ₂ ^b	^{NA} Mo ₂ -d ₁₂	^{NA} Mo ₂	^{NA} Mo ₂ -d ₁₂
404	404	413	403		
				373	363
				353	343
				342	321
323	321	322	313, 310		
315	311	314	302		
301	298	299	293		
				311	285
				235	224
				230	220
204	200	200	201		
189	186	186	187		
				183	172

^aNA = natural abundance. ^bValues were taken from ref 6. The excitation wavelength was 5145 Å, with the samples held at room temperature.

**Figure 2.** Far-infrared spectra of (a) $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$ and (b) $\text{Mo}_2(\text{O}_2\text{CCD}_3)_4$.

region shift by about 10 cm^{-1} to low wavenumbers. This is entirely consistent with the assignment of the 404- cm^{-1} band to the metal-metal stretch and the lower group of bands to the three Raman-active Mo–O stretching modes expected on a Mo_2O_8 vibrational model.¹¹ These Mo–O stretching modes shift by about 2 cm^{-1} to lower wavenumber on ⁹²Mo substitution of the natural molybdenum. The relative insensitivity of the two bands at 204 and 189 cm^{-1} to both ⁹²Mo⁶ and deuterium substitutions suggests that they involve bending modes of the Mo_2O_8 skeleton. We also note that the insensitivity of the main progression-forming mode in the lowest energy electronic transition to deuteration¹² confirms that this progression is in the excited-state $\nu(\text{Mo-Mo})$ mode, which has a wavenumber ca. 370 cm^{-1} .

The 80 K infrared spectrum (Figure 2) is consistent with these assignments. The three bands in the 373–342- cm^{-1} region shift 10–21 cm^{-1} to low wavenumber on deuteration. The shift of the member of this group with lowest wavenumber is much larger than would be expected on the basis of a pure Mo–acetate stretching mode in a Mo_2O_8 model (8 cm^{-1}), which suggests that some methyl rocking motion is also involved in this mode. This is not unexpected. Most of the higher wavenumber bands in the infrared and Raman spectra show appreciable shifts on deuteration, the smallest shifts being shown by the symmetric and asymmetric CO_2 stretching vibrations. There is no evidence in the infrared spectrum

for a band at 404 cm^{-1} . This is consistent with the assignment of the Raman band at this wavenumber to $\nu(\text{Mo-Mo})$, a fundamental that would be Raman- but not infrared-active in the D_{4h} point group to which the molecule belongs.

The effects of solid-state interactions on the number of Mo–O stretching modes active in the infrared spectra, on the appearance of new bands around 200 cm^{-1} , and on the substantial changes on deuteration in the 500–650- cm^{-1} region will be detailed in a separate study.¹³

Conclusion

The results of this study indicate that deuteration of the carboxylate group may provide a useful, low-cost alternative to ¹⁸O- and metal-isotope-substitution experiments for the assignment of metal-metal stretching vibrations in dimeric tetracarboxylates.

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Registry No. $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$, 14221-06-8; $\text{Mo}_2(\text{O}_2\text{CCD}_3)_4$, 61483-82-7; D₂, 7782-39-0.

(13) Hempleman, A. J.; Clark, R. J. H.; Flint, C. D., to be submitted for publication.

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Synthesis and Molecular Structure of $\text{Os}_2(\mu\text{-PPh}_2)(\mu\text{-I})(\text{CO})_6$. High-Yield Syntheses of $\text{Os}_2(\mu\text{-I})_2(\text{CO})_6$ and $\text{Os}_2\text{I}_2(\text{CO})_8$

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The binuclear phosphido-bridged osmium complexes $\text{Os}_2(\text{CO})_6(\mu\text{-X})(\mu\text{-PPh}_2)$ (**1**) and $\text{Os}_2(\text{CO})_6(\mu\text{-PPh}_2)_2$ (**2**) are interesting compounds because the μ -halide functionality of **1** should allow the preparation of derivatives with organic ligands and **2** is analogous to the well-studied complex $\text{Fe}_2(\mu\text{-PPh}_2)_2(\text{CO})_6$.^{1,2} The relative chemical inertness of Os in **2**, as compared to Fe, should permit the preparation of intermediates that have escaped detection or isolation in the Fe system.^{1,2}

The logical approach to the synthesis of phosphido-bridged compounds containing halide ligands is the metathesis reaction between LiPPh_2 and binuclear metal halide complex.^{3,4} For the preparation of the desired Os_2 complexes **1** and **2**, potentially useful synthetic reagents are the halide complexes $\text{Os}_2\text{I}_2(\text{CO})_8$ (**3**) and $\text{Os}_2(\mu\text{-I})_2(\text{CO})_6$ (**4**).^{5,6} Herein we describe the synthesis of **1** (X = I) from **4** and its structural characterization as well as some aspects of its reactivity. Also described are attempts to prepare the bis(phosphido)-bridged complex **2**. During the course of these studies we optimized the syntheses of **3** and **4**, and those details are also reported.

Results

The reactions successfully carried out in this work are summarized in Schemes I and II.

High-Yield Syntheses of $\text{Os}_2\text{I}_2(\text{CO})_8$ (3**) and $\text{Os}_2(\mu\text{-I})_2(\text{CO})_6$ (**4**).** The title complexes can be prepared by the thermal reaction of $\text{Os}_3(\text{CO})_{12}$ with I_2 in toluene.⁵ We have found that the temperature at which the reaction is conducted is critical in deter-

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