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1 Raman Studies of Hydrido- and Deutero- Rhenium Tetracarbonyl Trimer¹

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4 In a previous study the trimer of rhenium tetracarbonyl was found to be diamagnetic, suggesting the presence of hydrogen in the compound.⁴ This was supported by chemical analysis, which indicated about one hydrogen per rhenium, and the compound was formulated⁴ as $[\text{Re}(\text{CO})_4\text{H}]_3$. Subsequently a proton resonance was observed on a broad line spectrometer.⁵ In the original work⁴ the infrared spectra were compared for the hydride and deuteride; cyclohexane solutions were used for the CO stretching region and KBr discs were used for the rest of the spectrum. Surprisingly, the spectra of the hydride and deuteride showed only minor differences, insufficient to confirm the presence of hydrogen. No evidence of a hydrogen stretching frequency was found.

5 In the present work, the previously unobserved Raman spectra were measured for the hydride and deuteride. In the solid state rather striking shifts were observed in the CO stretching region. Also there is some evidence

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for a metal-hydrogen stretching band at the rather low frequency of 1100 cm^{-1} . In an attempt to support the interpretation of the Raman spectra more detailed infrared studies of the solid in KBr discs were made. The hope was to observe a metal-hydrogen stretching frequency and to explain the shifts in the CO stretching frequencies.

Experimental

Preparation. — The trimeric tetracarbonyl hydride and deuteride of rhenium were prepared by the method of Huggins, et al.⁴ Completeness of deuteration in the deuteride was checked on one small sample by using NaBD_4 in the reduction step as well as D_3PO_4 in the acidification step. The infrared spectrum of this sample is identical to that found for deuterated samples obtained using NaBH_4 and D_3PO_4 .

Recording of Raman Spectra. — Raman spectra were obtained on a Cary Model 81 Raman spectrometer, using the standard 5 ml sample tubes for solution spectra and a conical vessel based on a design supplied by R. H. Busey and O. L. Keller⁶ for spectra of the solids. Saturated solutions of the hydride and deuteride in cyclohexane gave very weak spectra, due to the low solubility of the compounds (about $1.5 \times 10^{-3}\text{ M}$). However, we were able to observe the strong Raman shifts and these are listed in Table 1. Spectra of the solid samples were quite intense. The CO stretching region is shown in Fig. 1. Tabulated values are given in Table 2.

Table 1

Raman Spectra of Cyclohexane Solutions^(a)

<u>[Re(CO)₄H]₃</u>	<u>[Re(CO)₄D]₃</u>
2125 cm ⁻¹	2125
2023	2023
1983	1982

(a) Concentration is about 1.5×10^{-3} M. Raman peaks
are all weak due to low concentration.

Fig. 1. — Raman Spectra of Solid $[\text{Re}(\text{CO})_4\text{H}]_3$ (upper curve) and Solid $[\text{Re}(\text{CO})_4\text{D}]_3$ (lower curve).

Table 2

Raman Spectra of $[\text{Re}(\text{CO})_4\text{H}]_3$ and $[\text{Re}(\text{CO})_4\text{D}]_3$

H		D	
$\nu \text{ cm}^{-1}$	Int ^(a)	$\nu \text{ cm}^{-1}$	Int ^(a)
2127	31	2124	53
2095	1	2093	1.5
2058	2	2047	6
2025	4	2023	35
2012	27	2015	10 sh?
(2007 Shoulder?)		2000	4 ?
1979	7.5	1979	12
1965	19	1962	43
1954	19	1956	5-10 Sh?
1928	0.5	1946	2- 4 ?
1100	Very broad and very weak	787	13 Broad
622	5	621	10
560	2.5	563	2.5
491	100	487	100
		478	63 Sh
452	18 Sh	452	25
420	2.5	421	5
371	7.5	372	10
170	--	169	5
147	--	145	5
		104	7
91	--	91	5
81	5	77	9

(a) The intensities are normalized to 100 for the most intense band for each molecule.

Recording of Infrared Spectra. — Infrared spectra were obtained on a Perkin Elmer Model 521 infrared grating spectrometer, using the KBr pellet technique. Pellet concentrations of about 0.1 to 0.3 mg/100 mg of KBr were used for the carbonyl stretching region, and about 10 to 20 mg/100 mg for the region 700 to 1200 cm^{-1} . We were prompted to re-examine the infrared spectra after observing what might possibly be assigned as metal-hydrogen and metal-deuterium absorptions at 1100 and 787 cm^{-1} , respectively, in the Raman spectra. Also, it was desirable to obtain infrared spectra of the carbonyl stretching region for the solids for comparison with the excellent Raman spectra of these samples. The carbonyl stretching frequencies are shown in Fig. 2 and tabulated in Table 3.

Discussion

The search for a metal-hydrogen stretching frequency was only partially successful. A very weak and very broad band was observed at 1100 cm^{-1} in the Raman spectrum of $[\text{Re}(\text{CO})_4\text{H}]_3$. This was not present for the deuteride for which a new Raman band appeared at 787 cm^{-1} . The shift from 1100 to 787 cm^{-1} is quite reasonable for a Re-H $\rightarrow$ Re-D vibration. The disturbing feature is that the hydride band is much broader than the deuteride band. No explanation is offered at the present time for the difference in band shape; however, it is reasonable to assign 1100 cm^{-1} as an Re-H stretching frequency.⁷

In the Raman spectra of the solids, rather striking differences appear in the CO stretching region. For example, peaks at 2012 and 1954 for the hydride are shifted to 2023 and 1962, respectively, for the deuteride. There are other

Fig. 2. — Infrared Spectra of KBr Discs of $[\text{Re}(\text{CO})_4\text{H}]_3$ (solid line) and $[\text{Re}(\text{CO})_4\text{D}]_3$ (dashed line).

TRANSMISSION

Table 3

Infrared Spectra of Solid $[\text{Re}(\text{CO})_4\text{H}]_3$ and $[\text{Re}(\text{CO})_4\text{D}]_3$ in CO Stretching Region

$[\text{Re}(\text{CO})_4\text{H}]_3$		$[\text{Re}(\text{CO})_4\text{D}]_3$	
$\nu \text{ cm}^{-1}$	Int. (a)	$\nu \text{ cm}^{-1}$	Int. (a)
2095	m	2093	m
		2045	w
2030	m, Sh	2030	m
		2018	m
2005	S	2000	S
1985	w, Sh	1982	m
		1970	w
1962	m	1958	S

(a) Intensities are rough estimates. S = strong, m = medium, w = weak, and Sh = Shoulder.

less dramatic changes also. In the infrared spectrum the shifts are somewhat less pronounced and more difficult to assign because of the number of peaks. The shifts specified above for the CO stretching region are too small, and in the wrong direction, for a hydrogen vibration. However, we can certainly conclude that the substitution of deuterium for hydrogen has led to definite changes in the CO stretching frequencies. Thus the hydrogen (or deuterium) is part of the molecular entity.

A reasonable explanation of the shifts in CO stretching frequencies can be offered. The Re-H stretching vibration at 1100 cm^{-1} may have an overtone, or combination, with another Re-H frequency, in the $2000 - 2100\text{ cm}^{-1}$ region. This overtone or combination could then interact through Fermi resonance, with nearby CO stretching vibrations of proper symmetry, depressing their frequencies. For the deuteride the analogous overtone, or combination, would be out of the CO stretching region and thus would not interact.

It is surprising that the Raman solution spectra of the hydride and deuteride do not show the differences brought out in the spectra of the solids. Thus from the three peaks reported in Table 1 it would be impossible to distinguish hydride from deuteride. In the infrared⁴ the differences are very slight for solutions of the hydride and deuteride. Apparently the hydrogen stretching frequency interacts with the CO stretching frequencies only weakly in solution but quite strongly in the solid. This may be because the symmetry is lower in the solid than in solution, giving increased possibility of Fermi resonance.

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- (7) Unfortunately the infrared spectra showed only very weak and ill-defined absorptions in this region and thus offered no further support to such an assignment.