

MASS SPECTRA OF INORGANIC MOLECULES V. HYDRIDOMANGANESE TETRACARBONYL AND HYDRIDORHENIUM TETRACARBONYL TRIMERS

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In 1964 Kaesz and his co-workers¹ reported the preparation of hydrido-rheniumtetracarbonyl trimer. The presence of hydrogen in the molecule was supported by chemical analysis which indicated *about* one hydrogen per rhenium. The infrared spectra were compared for the hydride and deuteride but showed only minor differences and no evidence of a metal-hydrogen stretching frequency was found. More recently², the Raman spectrum of the hydride was measured when a very weak, very broad band at 1100 cm^{-1} , which appears at 787 cm^{-1} with the deuteride, was tentatively assigned to a metal-hydrogen-metal vibration $\nu(\text{Re-H-Re})$. It was also reported that a proton resonance has been observed on a broad-line spectrometer³ although further details are not yet available.

The corresponding manganese compound, $\text{H}_3\text{Mn}_3(\text{CO})_{12}$, has also been reported⁴, however, the formulation of this compound appears to rest upon the similarity of its infrared spectrum with that of the rhenium derivative*.

We wish to report the first conclusive evidence for the presence of three hydrogen atoms per trimeric molecule in both the manganese and rhenium compounds and also the preparation of $\text{H}_3\text{Mn}_3(\text{CO})_{12}$ in high yields. These results have been discussed briefly in a preliminary communication⁵.

Treatment of dimanganese decacarbonyl with strong base (*e.g.* KOH) followed by acidification (*e.g.* with H_2SO_4) produces the *red* $\text{H}_3\text{Mn}_3(\text{CO})_{12}$ in about 80% yield. This procedure has also been used with success on other carbonyl systems⁵. The hydride is stable in air for indefinite periods but decomposes slowly in a variety of organic solvents. It is volatile and may be sublimed ($60^\circ/0.01\text{ mm}$) without decomposition.

TABLE 1

INFRARED SPECTRA OF $\text{H}_3\text{Mn}_3(\text{CO})_{12}$ AND $\text{D}_3\text{Mn}_3(\text{CO})_{12}$ ^a

Compound	$\nu(\text{CO})$			
$\text{H}_3\text{Mn}_3(\text{CO})_{12}$	2080 (m),	2034 (s),	2008 (s),	1986 (s),
$\text{D}_3\text{Mn}_3(\text{CO})_{12}$	2075 (m),	2034 (s),	2008 (s),	1986 (s),

^a Spectra in cyclohexane.

* Note added in proof. After the submission of this paper, a preliminary report on the mass spectra of a series of hydride compounds was published. (J. M. SMITH, K. MEHNER AND H. D. KAESZ, *J. Am. Chem. Soc.*, 89 (1967) 1759) in which the formulation of the polynuclear manganese carbonyl hydride as $\text{H}_3\text{Mn}_3(\text{CO})_{12}$ was confirmed.

The infrared spectrum in the carbonyl stretching region (Table 1) is very similar to that of $\text{H}_3\text{Re}_3(\text{CO})_{12}$ as has been previously observed by Kaesz⁴. With the deuterio compound, $\text{D}_3\text{Mn}_3(\text{CO})_{12}$, the spectrum is virtually unchanged.

Attempts to obtain a proton NMR signal under conventional conditions have not been successful*. It is probable that the relaxation time of the hydride ligand is short and, as with $[\text{Cr}_2\text{H}(\text{CO})_{10}]^-$, not easily measured⁶.

Mass spectrometry has proved to be a particularly useful method for molecular weight determinations of inorganic compounds, especially with metal carbonyls and related systems⁷. To date, few transition metal hydrides have been studied by this method. Wilkinson and his co-workers⁸ have used mass spectral data as a method of detecting the presence of hydrogen in the ruthenium carbonyl hydride, $\text{H}_4\text{Ru}_4(\text{CO})_{12}$, but were only able to detect two of the four hydrogens in the complex. James

TABLE 2

MASS SPECTRUM OF $\text{H}_3\text{Mn}_3(\text{CO})_{12}$

Ion	A	Ion	A	Ion	A
$\text{H}_3\text{Mn}_3(\text{CO})_{12}^+$	2	$\text{Mn}_3(\text{CO})_2^+$	1	$\text{HMn}_2(\text{CO})^+$	14
$\text{H}_3\text{Mn}_3(\text{CO})_{10}^+$	1	$\text{H}_3\text{Mn}_2(\text{CO})_3^+$	3	$\text{Mn}(\text{CO})_3^+$	
$\text{HMn}_3(\text{CO})_{10}^+$	37	$\text{H}_2\text{Mn}(\text{CO})_5^+$		61	$\text{H}_2\text{Mn}(\text{CO})_2^+$
$\text{H}_3\text{Mn}_3(\text{CO})_9^+$	9	$\text{H}_3\text{Mn}_3(\text{CO})^+$	13		H_3Mn_2^+
$\text{HMn}_3(\text{CO})_9^+$	7	$\text{H}_2\text{Mn}_2(\text{CO})_3^+$		9	$\text{HMn}(\text{CO})_2^+$
$\text{H}_3\text{Mn}_3(\text{CO})_8^+$	6	$\text{H}_2\text{Mn}_3(\text{CO})^+$	47		H_2Mn_2^+
$\text{HMn}_3(\text{CO})_8^+$	2	$\text{HMn}_2(\text{CO})_3^+$		8	$\text{Mn}(\text{CO})_2^+$
$\text{H}_3\text{Mn}_3(\text{CO})_7^+$	4	$\text{HMn}_3(\text{CO})^+$	33		HMn_2^+
$\text{HMn}_3(\text{CO})_7^+$	5	$\text{Mn}_2(\text{CO})_3^+$		22	Mn_2^+
$\text{H}_3\text{Mn}_3(\text{CO})_6^+$	13	H_3Mn_3^+	19		$\text{HMn}(\text{CO})^+$
$\text{HMn}_3(\text{CO})_6^+$	4	$\text{HMn}(\text{CO})_4^+$		4	$\text{Mn}(\text{CO})^+$
$\text{H}_3\text{Mn}_3(\text{CO})_5^+$	27	$\text{H}_2\text{Mn}_2(\text{CO})_2^+$	3		MnC^+
$\text{HMn}_3(\text{CO})_5^+$	18	H_2Mn_3^+		8	MnH^+
$\text{H}_3\text{Mn}_3(\text{CO})_4^+$	100	$\text{Mn}(\text{CO})_4^+$	10		$\text{MnH}(\text{CO})_2^{2+}$
$\text{H}_2\text{Mn}_3(\text{CO})_4^+$	2	$\text{HMn}_2(\text{CO})_2^+$		3	Mn^+
$\text{HMn}_3(\text{CO})_4^+$	43	HMn_2^+	2		<i>Doubly-charged ions</i>
$\text{H}_3\text{Mn}_3(\text{CO})_3^+$	25	$\text{Mn}_2(\text{CO})_2^+$		19	$\text{Mn}(\text{CO})_3^{2+}$
$\text{H}_2\text{Mn}_3(\text{CO})_3^+$	6	Mn_3^+	8		$\text{Mn}_2\text{H}(\text{CO})_2^{2+}$
$\text{HMn}_3(\text{CO})_3^+$	51	$\text{H}_3\text{Mn}_2(\text{CO})^+$		12	$\text{Mn}(\text{CO})_2^{2+}$
$\text{Mn}_3(\text{CO})_3^+$	1	$\text{H}_2\text{Mn}(\text{CO})_3^+$	12		$\text{Mn}(\text{CO})^{2+}$
$\text{H}_3\text{Mn}_3(\text{CO})_2^+$	10	$\text{H}_2\text{Mn}_2(\text{CO})^+$			
$\text{H}_2\text{Mn}_3(\text{CO})_2^+$	2	$\text{HMn}(\text{CO})_3^+$			
$\text{HMn}_3(\text{CO})_2^+$	12				

*et al.*⁹ have established the presence of the hydrogen ligand in the molecule $(\text{C}_5\text{H}_5)_2\text{-Zr}(\text{H})\text{BH}_4$ from mass spectral measurements. In an earlier communication⁵ we emphasised the value of this method for the detection or confirmation of hydrogen in polynuclear carbonyl hydrides. Finally, the mass spectrum of $\text{HMn}(\text{CO})_5$ has recently been reported¹⁰.

In the mass spectra of $\text{H}_3\text{Mn}_3(\text{CO})_{12}$ and $\text{H}_3\text{Re}_3(\text{CO})_{12}$ (Tables 2 and 3), the parent molecular ion, $[\text{H}_3\text{M}_3(\text{CO})_{12}]^+$, is observed *confirming their formulation as*

* Note added in proof. A proton NMR signal in $\text{Fe}(\text{CO})_5$ at 24 ppm with respect to internal TMS has recently been reported (E. O. FISCHER AND R. AUMANN, *J. Organometal. Chem.*, 8 (1967) P1). The hydride was obtained in this case by the action of base on $\text{CH}_3\text{Mn}(\text{CO})_5$.

TABLE 3

MASS SPECTRUM OF $H_3Re_3(CO)_{12}$

<i>Ion</i>	<i>A</i>	<i>Ion</i>	<i>A</i>	<i>Ion</i>	<i>A</i>
$H_3Re_3(CO)_{12}^+$	82	$H_2Re_3(CO)_3^+$	6	Re_3CH^+	7
$HRe_3(CO)_{12}^+$	20	$HRe_3(CO)_3^+$	67	Re_3C^+	15
$H_3Re_3(CO)_{11}^+$	37	$Re_3(CO)_3^+$	17	$H_2Re_2(CO)_6^+$	} 7
$HRe_3(CO)_{11}^+$	9	$H_3Re_3(CO)_2^+$	1	$HRe_2(CO)_6^+$	
$H_3Re_3(CO)_{10}^+$	27	$H_2Re_3(CO)_2^+$	4	$Re_2(CO)_6^+$	} 3
$HRe_3(CO)_{10}^+$	16	$HRe_3(CO)_2^+$	43	$HRe_2(CO)_5^+$	
$H_3Re_3(CO)_9^+$	52	$Re_3(CO)_2^+$	22	$Re_2(CO)_5^+$	} 2
$HRe_3(CO)_9^+$	100	$H_3Re_3(CO)^+$	1	$HRe_2(CO)_4^+$	
$H_3Re_3(CO)_8^+$	27	$H_2Re_3(CO)^+$	2	$Re_2(CO)_4^+$	} 2
$H_2Re_3(CO)_8^+$	5	$HRe_3(CO)^+$	26	$HRe_2(CO)_3^+$	
$HRe_3(CO)_8^+$	45	$Re_3(CO)^+$	17	$Re_2(CO)_3^+$	} 2
$H_3Re_3(CO)_7^+$	85	$H_3Re_3^+$	1	$HRe_2(CO)_2^+$	
$H_2Re_3(CO)_7^+$	4	$H_2Re_3^+$	4	$Re_2(CO)_2^+$	} 8
$HRe_3(CO)_7^+$	57	HRe_3^+	24	Re_2^+	
$H_3Re_3(CO)_6^+$	12	Re_3^+	26		
$H_2Re_3(CO)_6^+$	5	$Re_3(CO)_5CH^+$	} 1	<i>Doubly-charged ions</i>	
$HRe_3(CO)_6^+$	54	$Re_3(CO)_5C^+$			$HxRe_3(CO)_8^{2+}$
$H_3Re_3(CO)_5^+$	4	$Re_3(CO)_4CH^+$	} 1	$HxRe_3(CO)_7^{2+}$	7
$H_2Re_3(CO)_5^+$	3	$Re_3(CO)_4C^+$			$HxRe_3(CO)_6^{2+}$
$HRe_3(CO)_5^+$	64	$Re_3(CO)_3CH^+$	} 2	$HxRe_3(CO)_5^{2+}$	44
$Re_3(CO)_5^+$	4	$Re_3(CO)_3C^+$			$HxRe_3(CO)_4^{2+}$
$H_3Re_3(CO)_4^+$	9	$Re_3(CO)_2CH^+$	} 3	$HxRe_3(CO)_3^{2+}$	55
$H_2Re_3(CO)_4^+$	9	$Re_3(CO)_2C^+$			$HxRe_3(CO)_2^{2+}$
$HRe_3(CO)_4^+$	54	$Re_3(CO)CH^+$	} 6	$HxRe_3(CO)^{2+}$	27
$Re_3(CO)_4^+$	9	$Re_3(CO)C^+$			$HxRe_3^{2+}$
$H_3Re_3(CO)_3^+$	1				

trimeric hydrides. Furthermore, the isotopic pattern obtained for the rhenium compound is consistent with the presence of three rhenium atoms per molecular ion. With $H_3Mn_3(CO)_{12}$ the parent ion is observed in low abundance (2%); however, the related trimeric ions $[H_3Mn_3(CO)_4]^+$ and $[H_3Mn_3(CO)]^+$ occur in appreciable amounts (18% and 90% respectively). Monomeric ions $[HMn(CO)]^+$ and $[Mn(CO)]^+$ are also present in high abundances but the only dimeric ions observed are $[Mn_2(CO)]^+$ and $[Mn_2]^+$. In contrast, with $H_3Re_3(CO)_{12}$ the parent molecular ion, $[H_3Re_3(CO)_{12}]^+$, is present in high abundance (82%) as are other trimeric ions, $[H_mRe_3(CO)_n]^+$; dimeric and monomeric ions are not observed in significant amounts. The stability of the Re_3 cluster towards fragmentation follows the trend established for related systems⁷. Monomeric ions with more than four carbonyl groups per metal atom are not observed in either case. This observation is consistent with a trinuclear (M_3) structure involving four terminal CO groups per metal atom and may be compared with the results of mass spectral studies carried out on $Fe_3(CO)_{12}$ ^{7a}, $Ru_3(CO)_{12}$ ^{7a}, and $Os_3(CO)_{12}$ ^{7b}.

Doubly-charged ions, $[H_mRe_3(CO)_n]^{2+}$, are also observed in the spectrum of the rhenium compound reflecting the stability of the trimeric unit towards oxidation.

The intermediate anionic species produced during the preparation of H_3Mn_3-

(CO)₁₂ are of interest. The green solution initially produced by the treatment of Mn₂(CO)₁₀ with aqueous potassium hydroxide (*ca.* 15 M) is stable only in the presence of excess base and all attempts to isolate the complex present have failed. Neutralization of this green solution produces a purple solution from which purple salts may be isolated by the addition of large cations such as Et₄N⁺ or Ph₄As⁺. This reaction is reversible and on addition of strong base the purple solution or complexes revert to the initial green coloration suggesting that the green and purple derivative have some simple relationship, possibly involving an OH group. The purple complexes are electrolytes in a number of solvents but are too unstable for molecular-weight studies. The infrared spectra in the carbonyl stretching region

TABLE 4

INFRARED SPECTRA OF PURPLE IONIC COMPOUNDS IN THE CARBONYL STRETCHING REGION

Cation	$\nu(\text{CO})$ (cm ⁻¹)						
K ⁺ ^a	2060 (w)	2045 (m)		2000 (s)	1980 (m)	1940 (m)	1897 (w)
	^b 2060 (w)	2043 (m)		2000 (s)	1975 (m)	1943 (m)	1900 (w)
Et ₄ N ⁺ ^a	2075 (w)	2043 (m)	2035 (m)	2015 (m)	1982 (s)	1930 (s)	1900 (m)
	^c	2040 (m)		2020 (s)	1975 (s)	1923 (s)	
Ph ₄ As ⁺ ^d	2095 (w)	2047 (m)	2028 (m)	2015 (s)	1982 (s)	1935 (s)	

^a Spectrum in nujol. ^b Spectrum in acetone. ^c Spectrum in dichloromethane. ^d Spectrum in chloroform.

are complex (Table 4) consistent with a polymeric species of low symmetry. The exact nature of these complexes is not known and is currently under investigation. Addition of three moles of acid (titration) to the purple solution produces the trimeric hydride, H₃Mn₃(CO)₁₂, in high yields (~80%).

On a number of occasions a green hydride was also isolated from these reactions although it has not been possible to determine the exact conditions required for its formation. In solution or on heating (*e.g.* in mass spectrometer) decomposition occurs to give H₃Mn₃(CO)₁₂ and HMn(CO)₅. The exact nature and reactivity of this complex must await the result of further studies although the above evidence might suggest that it is a hydride derivative of some Mn₄-carbonyl system.

We also confirm the observations of Hieber and his co-workers¹¹ that treatment of dimanganese decacarbonyl with dilute alkali gives a yellow solution which on acidification yields Mn₂(CO)₁₀ and HMn(CO)₅.

The analogous rhenium derivative, H₃Re₃(CO)₁₂, could not be obtained by this method. In this case the known anionic species¹², [Re₂(CO)₈O₂H]⁻, was produced.

Treatment of H₃Mn₃(CO)₁₂ with triphenylphosphine, -arsine or -stibine in refluxing cyclohexane yields the dimeric derivatives [Ph₃M·Mn(CO)₄]₂. In the cold, it would appear from the infrared spectra of the reaction solutions that some intermediate trimeric species are formed. With alkyl phosphines, *e.g.* Et₃P although addition occurs initially cleavage rapidly follows to give [Et₃P·Mn(CO)₄]₂.

EXPERIMENTAL

All solvents were degassed before use and all reactions and manipulations

were carried out under nitrogen unless otherwise stated. We thank the Ethyl Corporation for their generous gift of dimanganese decacarbonyl.

Reaction of dimanganese decacarbonyl with alkali

A solution of potassium hydroxide in water (15 M; 8 ml) was added to manganese carbonyl (0.5 g) contained in a flask and the system evacuated. The reaction mixture was then heated to 60° and shaken vigorously for ~1 h. On cooling the resultant emerald green solution, dark green crystals precipitated. These crystals were separated by filtration and quickly redissolved in dilute base.

Preparation of $H_3Mn_3(CO)_{12}$

The green solution was acidified with 85% phosphoric acid when the product separated as an orange-red solid. It was separated by filtration, washed with water until the washings were neutral and dried *in vacuo*. Sublimation under reduced pressure (60°/0.01 mm) gave the pure compound as dark red crystals; yield ~80%.

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SUMMARY

The mass spectra of $H_3Mn_3(CO)_{12}$ and $H_3Re_3(CO)_{12}$ have been recorded. Parent molecular-ions are observed with both compounds and provide the first conclusive evidence for their formulation as trimeric hydrides. A convenient synthesis of $H_3Mn_3(CO)_{12}$ is also described together with some of its reactions with triphenylphosphine, arsine and stibine.

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