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Preliminary communication

OBSERVATION AND INTERPRETATION OF H—H COUPLING IN ^{1}H—^{187}Os SATELLITE NMR SPECTRA

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Summary

The single hydride resonance observed for each of the compounds $H_3Os_3(CO)_9CX$ (X = OMe, Br, H) has one set of ^{187}Os satellites which are further split into doublets by H—H coupling. The implications of this observation for structural assignments based on ^{187}Os satellites are discussed.

Lewis and coworkers [1] have shown how ^{187}Os satellites seen in the ^{1}H NMR spectra of osmium cluster hydrides can be used for the assignment of molecular structure and dynamics. Recently, Koridze et al. [2] have employed the same approach in an attempt to probe the dynamics of the $H_3Os_3(CO)_9(CCR_2)^+$ system. We wish to show that H—H couplings, which can become visible when symmetry is reduced by ^{187}Os substitution, are an important and useful aspect of these satellite spectra.

The compounds $H_3Os_3(CO)_9CX$ (X = OMe [3], Br [4], H [5]) each show just one hydride resonance, implying equivalent sites. Though they have not

TABLE 1

^{1}H NMR DATA [a]

Complex	Chemical shift (δ, ppm)	$J(^{187}Os$—H) (Hz)	J(H—H) (Hz)
$H_3Os_3(CO)_9COMe$	—18.58	28.4	1.6
$H_3Os_3(CO)_9CBr$	—18.90	28.9	1.5
$H_3Os_3(CO)_9CH$	—19.58	27.5	1.5

[a] At 360 MHz in $CDCl_3$ solutions at 17°C.

been the subject of crystallographic studies, the structures of the compounds can be safely assigned as analogous to that of $H_3Ru_3(CO)_9(\mu_3\text{-}CCH_3)$ [6] (I). Recording the hydride region of the ^1H NMR spectrum at high signal to noise and restricted sweep shows in each case a pair of ^{187}Os satellites (see Fig. 1), which we assign as due to H—H coupling (Table 1).

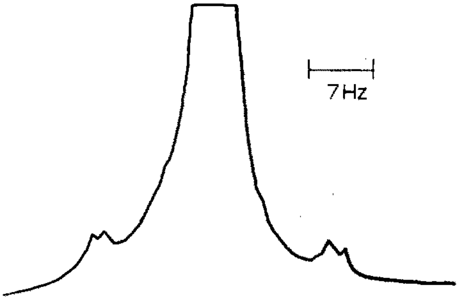
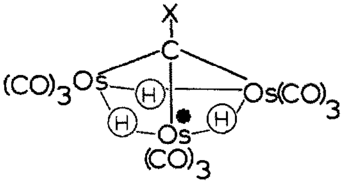


Fig. 1. ^1H NMR spectrum (360 MHz) of $H_3Os_3(CO)_9CBr$ in $CDCl_3$ at 17°C. Number of pulses: 1000, sweep width: ± 155 Hz, acquisition time: 13.21 sec.

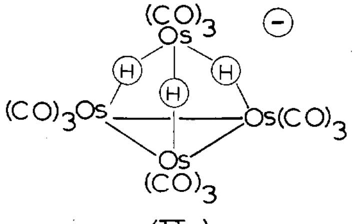
The spectral features are readily explained by considering isotopomers containing just one ^{187}Os, since at 1.64% natural abundance doubly and triply labelled molecules cannot be observed. Introduction of a ^{187}Os nucleus into cluster I lowers the symmetry such that the two hydrides adjacent to the labelled osmium are equivalent to each other but inequivalent to the third hydride. Recognition of these "extra" splittings is necessary for proper interpretation of the ^{187}Os satellite spectrum.



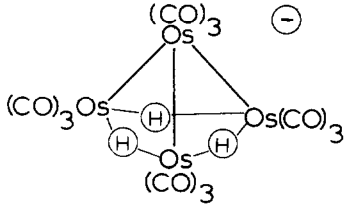
(I)

The labelled osmium is coupled to the two adjacent hydrides with $J \approx 30$ Hz and these hydrides are in turn coupled to the third hydride with $J \approx 1.5$ Hz. The resultant spectrum shows ^{187}Os satellites placed at $\frac{1}{2}J(^{187}Os\text{—}H)$ around the hydride signal and each satellite is further split into a doublet by $J(H\text{—}H)$. This is an approximate analysis of the complete A_2BX spin system which is valid since $[J(Os\text{—}H_A)-J(Os\text{—}H_B)] \gg J(H_A\text{—}H_B)$; similar approaches are well known for ^1H-^{13}C satellite spectra [7].

Lewis and coworkers [1] studied the ^1H NMR spectrum of the more symmetrical form of $H_3Os_4(CO)_{12}^-$ and observed a singlet at δ −16.7 ppm with ^{187}Os satellite at ±15.5 and ±14.4 Hz. These satellites were assigned to two different sets of ^{187}Os—^1H couplings (J 30.9, 28.8 Hz), due to the hydrides bridging inequivalent osmium atoms. They therefore concluded that the solution structure for C_{3v} $[H_3Os_4(CO)_{12}]^-$ has three hydrides bridging apical to basal edges of the osmium tetrahedron (IIa). However we suggest that the satellite spectrum is better interpreted as consisting of two doublets with $J(^{187}Os{-}^{1}H)$ 29.9 Hz and $J(^{1}H{-}^{1}H)$ 2.1 Hz. This is consistent with structure IIb for C_{3v} $[H_3Os_4(CO)_{12}]^-$, which is also the structure found for the analogous ruthenium compound [8].

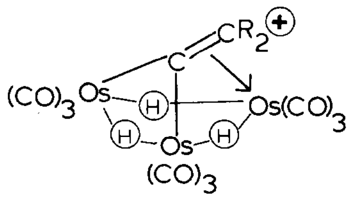


(IIa)

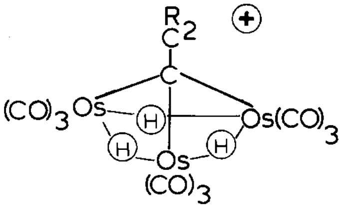


(IIb)

The compound $[H_3Os_3(CO)_9(C{=}CH_2)]^+$ shows ^1H NMR inequivalent hydrides at —10°C, which has been taken to indicate a tilted structure (see III, R = H). At higher temperatures the protons become equilibrated by a dynamic process [9]. Koridze and coworkers [2] in the process of investigating the mechanism of this fluxional process, studied the ^1H NMR spectrum of $[H_3Os_3(CO)_9(C{=}CC_3H_6)]^+$ and found it to consist of a singlet at δ —19.63 ppm with ^{187}Os satellites at ±16.0, 14.4 Hz [2]. These were assigned as two sets of osmium satellites with $J(^{187}Os{-}^{1}H)$ 32.0, 28.8 Hz resulting from the inequivalent osmium atoms in III, and their observation under conditions of rapid equilibration was taken to preclude the three-fold symmetric species IV as an intermediate in this process. We believe that the satellite spectrum is better interpreted as consisting of two doublets with $J(^{187}Os{-}^{1}H)$ 30.4 Hz and $J(^{1}H{-}^{1}H)$ 3.2 Hz. This immediately rules out H—H exchange in III, as Koridze et al., also concluded. However, rapid movement of the $CR_2{}^+$ group over all three osmium atoms in III cannot be distinguished from the intermediacy of IV on the basis of these observations.



(III)



(IV)

We conclude that the interpretation of structural data from ^{187}Os satellites can be more complex than was previously considered, i.e., when more than one set of satellites is observed. Our work indicates that H—H coupling should be in the range of 1—3 Hz [10], whereas previous examples which unequivocally involve two inequivalent osmiums show that the coupling constants may differ by up to 15 Hz [1,2].

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10 These vales are in good agreement with *J*(HH) values found for closely related osmium clusters, e.g., $H_2Os_3(CO)_9(CCH_2)$, *J*(HH) 1.4 Hz (A.J. Deeming, S. Hasso and M. Underhill, J. Chem. Soc. Dalton, (1975) 1614) or *J*(HH) 1.6 Hz (J.B. Keister and J.R. Shapley, J. Organomet. Chem., 85 (1975) C29).