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ON THE STRUCTURE OF $H_2Os_3(CO)_{12}$

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Summary

Infrared, far-infrared and Raman data are reported and discussed for $H_2Os_3(CO)_{12}$. ^{13}C NMR studies for $H_2Os_3(CO)_{12}$ are also reported. These data are consistent with a linear arrangement of the three osmium atoms with terminal hydrides occupying equatorial positions on the end osmium atoms.

Introduction

The significance of transition metal cluster complexes in catalysis is now well established [1,2]. One reaction that is currently of considerable importance is the reduction of carbon monoxide to alkanes and alcohols. It has been shown that the hydrogen reduction of carbon monoxide to give methane is catalyzed by $Os_3(CO)_{12}$ [3]. Thus, the interaction of hydrogen with $Os_3(CO)_{12}$ is of importance.

The reaction of hydrogen (1 atm, 120° C) with $Os_3(CO)_{12}$, has been reported to give $H_2Os_3(CO)_{10}$ [4], which on reaction with carbon monoxide gives $H_2Os_3(CO)_{11}$ [5,6], while the high pressure reaction of osmium tetraoxide with carbon monoxide and hydrogen (177 atm, 160° C) (i.e. conditions which are similar to those used in some Fischer-Tropsch syntheses) yields several products including the trinuclear species $Os_3(CO)_{12}$ and $H_2Os_3(CO)_{12}$ [7]. There are thus, three known trinuclear carbonyl hydrides of osmium which may be intermediates in hydrogenation reactions involving $Os_3(CO)_{12}$.

The structure of $H_2Os_3(CO)_{10}$ has been determined by several groups of workers using X-ray [8—10] and neutron [10,11] diffraction methods and shown to have a triangle of osmium atoms with the two hydrogen atoms bridging one edge. An X-ray structural analysis of $H_2Os_3(CO)_{11}$ has also been

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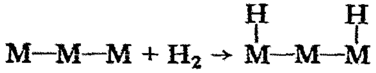
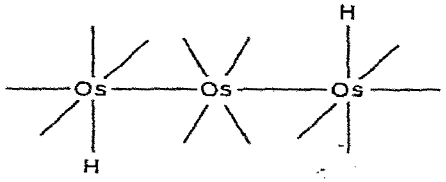
reported and shows a triangle of osmium atoms with one bridging and one terminal hydrogen [6,12]. Although $H_2Os_3(CO)_{12}$ was first reported in 1970 [13], the structure has not yet been determined by diffraction methods due to the difficulty in obtaining a suitable crystal *. We have previously suggested [7] that $H_2Os_3(CO)_{12}$ is a rare example of a polynuclear carbonyl hydride with terminal metal—hydrogen bonds. Polynuclear species with terminal metal—hydrogen bonds may be useful models for catalytic hydrogenation reactions which could involve processes of the type



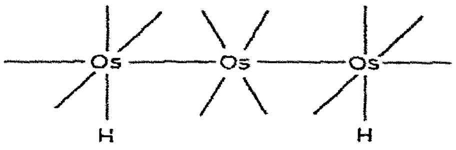
$$\mathrm{M{-}M{-}M} + \mathrm{H_2} \rightarrow \overset{\mathrm{H}}{\overset{|}{\mathrm{M}}}\mathrm{{-}M{-}}\overset{\mathrm{H}}{\overset{|}{\mathrm{M}}}$$

Also, a terminal M—H bond would be expected to be more reactive than a bridging M—H—M species and therefore of importance in catalytic reactions.

The following structures are considered possible for $H_2Os_3(CO)_{12}$ (carbonyl groups omitted for clarity):

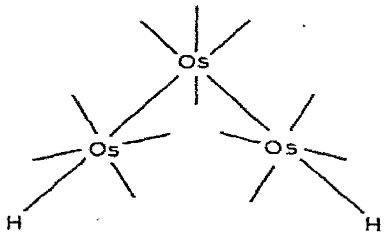


I (C_{2h})

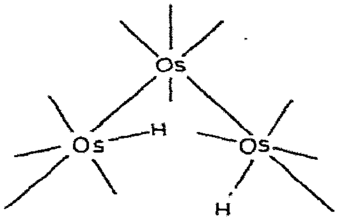


II (C_{2v})

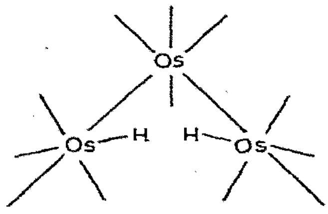
III (D_{4h})



IV (C_{2v})



V (C_2)



VI (C_s)

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* We are at present attempting to produce a crystal of $H_2Os_3(CO)_{12}$ suitable for diffraction studies.

Note that I and II are equivalent and V and VI are equivalent if there is unrestricted rotation about the Os—Os bonds and that these pairs would represent extreme conformations for whole sets of rotamers. We have previously suggested that I and V are the most likely structures for $H_2Os_3(CO)_{12}$ [7].

We have already reported ^1H NMR data for $H_2Os_3(CO)_{12}$, infrared data, assigning $\nu(CO)$, $\nu(OsH)$ and $\nu(OsD)$, and mass spectra for $H_2Os_3(CO)_{12}$ and $D_2Os_3(CO)_{12}$ [7]. We now report some new data for these species with a view to obtaining more information concerning molecular structure.

Results and discussion

^{13}C NMR spectra

The ^{13}C NMR data for $H_2Os_3(CO)_{12}$ (see Table 1) are only consistent with the linear arrangement of osmium atoms with the hydrides occupying equatorial positions as in I, since four different ^{13}C environments are observed. If rotation about the Os—Os bonds in solution is fast on the NMR time scale, as expected, then it would not be possible to distinguish between rotamers of this structure. This type of structure has now been found from X-ray diffraction studies on $I_2Os_3(CO)_{12}$ [14] and $(CH_3)_2Os_3(CO)_{12}$ [15].

The following assignment of peaks in the ^{13}C NMR spectrum of $H_2Os_3(CO)_{12}$ can be made (see Figure 1). The peak at 188.0 ppm remains as a singlet in the proton coupled spectrum and can therefore be assigned to the four carbonyl groups (labelled CO^A in Figure 1) on the central osmium atom. The peak at 178.7 ppm appears as a doublet in the proton coupled spectrum and can be assigned to the four carbonyl groups, CO^B, on the terminal osmium atoms. The magnitude of this coupling constant is similar to that of 8 Hz found for $^2J(^{13}C—^1H_{cis})$ in *cis*-$[H_2Os(CO)_4]$ [17]. The peak at 174.1 ppm appears as a doublet with $^2J(^{13}C—^1H)$ of 18 Hz in the proton coupled spectrum and can be assigned to the two carbonyl groups, CO^C, trans to the hydride on the terminal osmium atoms. As might be expected, $^2J(^{13}C—^1H_{trans})$ is greater than $^2J(^{13}C—^1H_{cis})$. This is also found to be the case in *cis*-$[H_2Os(CO)_4]$ [17]. Also, the chemical shift for CO *trans* to hydrogen in $H_2Os(CO)_4$ (and other similar compounds) is at higher field than for CO *trans* to CO [17], as we observe for $H_2Os_3(CO)_{12}$. The peak at 166.1 ppm can be assigned to the two carbonyl groups, CO^D. In

TABLE 1

^{13}C NMR DATA FOR $H_2Os_3(CO)_{12}$

Chemical shift (ppm) (Downfield from $SiMe_4$)	$^2J(^1H—^{13}C)$ (Hz)	Relative intensity	Assignment [a]
188.0	0	2	A
178.7	6	2	B
174.1	18	1	C
166.1	ca. 9	1	D

[a] See Figure 1 for labelling of CO groups.

TABLE 2

INFRARED AND RAMAN DATA FOR $H_2Os_3(CO)_{12}$ AND $D_2Os_3(CO)_{12}$

$H_2Os_3(CO)_{12}$		$D_2Os_3(CO)_{12}$		Regional assignement
IR [a]	Raman [b]	IR [a]	Raman [b]	
2134vvw	2135vs	2133vvw	2134vs	ν(CO)
2093s		2097s		
2070w		2068w		
	2066vs		2065vs	
2052s		2041vs		
2043m	2042w			
2037s		2037s	2038m(br)	
	2033sh(br)			
2030vs		2030s		
2021s		2014s		
	2011m		2004m(br)	
	1997w			
1993m(br)		1992m(br)		
1961vw(br)		1424vw(sh) [c]		ν(OsH) or ν(OsD)
1945(sh)		1407vw(br) [c]		
	1933w		1402w	
755(sh)				δ(COsH)
	749w			
740s				
623s		625w		δ(OsCO) and ν(OsC)
			621w	
595(sh)		595vs		
580m		575s		
	563w			
	552w	550w	550w	
547vs				
		535m		
	524w			
518w			515w	
	490s		490vs	ν(OsC) and δ(OsCO)
481w		480w		
	476(sh,br)		478(sh)	
	432w		432w	
429w		429w		
	415w		416m	
408m		408m		
392m		393m		
	360vw		381w	
	321vw			
159w		158w		ν(OsOs)
137m(br)		137m(br)		
	95vs		95vs	
105w		105w(br)		δ(OsOsOs) and δ(COsC) and δ(COsOs) and δ(HOsOs)
91m(br)				
87sh		86w		
70w(sh)	68(sh)	69w(sh)	68(sh)	
56w		57w		
	37s		37s	
29s				

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[a] Spectra measured in cyclohexane (2200—1400 cm^{-1}) and Nujol (1400—20 cm^{-1}). [b] Spectra measured in solid state. [c] Recorded in C_6D_6 (from ref. 7).
s = strong, m = medium, w = weak, br = broad, v = very, sh = shoulder.

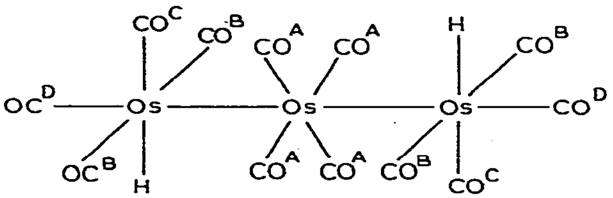

Fig. 1. Probable structure of $H_2Os_3(CO)_{12}$ showing the labelling of the CO groups.

the proton coupled spectrum, this peak appears as a broad singlet with width at half height of ca. 9 Hz. This broadening is presumably due to $^2J(^{13}C—^1H_{cis})$ and is of the expected order but not quite resolved. The chemical shift of CO *trans* to the Os—Os bond is thus at the highest field (c.f. in $Re_2(CO)_{10}$, CO *trans* to Re—Re is also at highest field [18]).

Vibrational Spectra

The infrared and Raman data for $H_2Os_3(CO)_{12}$ and $D_2Os_3(CO)_{12}$ between 4000 and 20 cm^{-1} are reported with regional assignments in Table 2. Structures V and VI (and intermediate conformations due to rotation about Os—Os bonds) can be eliminated since there is not complete coincidence between IR and Raman spectra. On the same basis, structures of C_{2v} symmetry, i.e. II or IV seem unlikely since all fundamental bands should be Raman active and there is not direct correlation between the bands observed in the IR and Raman. However, since II is a rotamer of I, it will be included in the ensuing discussion. More positive information, found on analysis of the spectra of $H_2Os_3(CO)_{12}$ and $D_2Os_3(CO)_{12}$ suggests that the structure is linear and of C_{2h} symmetry, i.e. I.

i) The ν(CO) region

Table 3 lists the number of ν(CO) bands expected for structures I to IV on group theoretical grounds. For $H_2Os_3(CO)_{12}$, we observe nine IR bands and six Raman bands with very little coincidence. This is already an indication that I is the most likely structure.

From electronic considerations, the character of the higher frequency peaks can be considered to be mostly stretching of pairs of *trans* carbonyls, whilst

TABLE 3

THE NUMBER OF ν(CO) BANDS EXPECTED, ON GROUP THEORETICAL GROUNDS, FOR SOME POSSIBLE STRUCTURES OF $H_2Os_3(CO)_{12}$

Structure	Symmetry	Number of ν(CO) bands in IR	Number of ν(CO) bands in Raman	Number of coincident IR and Raman bands
I	C_{2h}	6	6	0
II	C_{2v}	11	12	11
III	D_{4h}	3	5	0
IV	C_{2v}	10	12	10

lower frequency peaks are due more to carbonyls *trans* to H and axial carbonyls *trans* to Os [19—22].

Effects of deuteration: ν(CO) modes which are coupled to ν(OsH) will become decoupled on deuteration and are expected to undergo a lowering in frequency of 5—10 cm^{-1} [23]. This coupling can only occur between modes of the same symmetry. Further, it is known that the coupling at one metal centre is restricted to the carbonyls *trans* to H [23,24] and it may be expected that inter-metal-unit coupling would only be significant for *cis* equatorial groups on adjacent metal atoms [25]. Thus, since considerable change in the ν(CO) region occurs on deuteration (see Table 2 and Figure 1 ref. 7), we would expect the hydrogen atoms to occupy equatorial positions *cis* to the Os—Os bonds, rather than axial positions where their coupling to all ν(CO) modes is likely to be small. On this basis, we may preclude a linear structure III and a bent structure IV.

For structure I, there are two Os—H stretching modes of symmetry B_u and A_g. Coupling should therefore give two significant ν(CO) shifts in the IR (2 B_u) and two significant shifts in the Raman (2 A_g), corresponding to vibrations of carbonyls *trans* to H and to those of carbonyls on the central osmium atom. For structure II, there will be two Os—H stretching modes of symmetry A_1 and B_1 and these will couple to two corresponding ν(CO) of carbonyls *trans* to H and to one (A_1) ν(CO) of *cis* equatorial carbonyls on the central osmium. This should give three band shifts, identical in the IR and in the Raman (2 A_1 + B_1).

In the IR: two ν(CO) band shifts are observed on deuteration of $H_2Os_3(CO)_{12}$. In the lower frequency region, there is a band at 2021 cm^{-1} in $H_2Os_3(CO)_{12}$ which is shifted to 2014 cm^{-1} in $D_2Os_3(CO)_{12}$. This is assigned primarily to ν(CO) of carbonyls *trans* to H. In the higher frequency, there is a band at 2052 cm^{-1} in $H_2Os_3(CO)_{12}$ which is shifted to 2041 cm^{-1} on deuteration *. This band may thus be assigned chiefly to ν(CO) of carbonyls on the central osmium atom.

In the Raman: the bands are broad and so determination of band shifts between $H_2Os_3(CO)_{12}$ and $D_2Os_3(CO)_{12}$ is difficult. Tentatively, a band at 2042 cm^{-1} which shifts to 2038 cm^{-1} on deuteration could be assigned to ν(CO) of carbonyls on the central osmium atom and a band at 2011 cm^{-1} which drops to 2004 cm^{-1} to ν(CO) of carbonyls *trans* to H. The coincidence required between IR and Raman modes for structure II is not observed. The effects of deuteration thus suggest the likelihood of structure I.

ii) The ν(OsH) and ν(OsD) regions

Os—H stretching frequencies are unambiguously assigned by deuteration. ν(OsH) in the IR is very broad and may be interpreted as either one or two bands. One (B_u) is expected for structure I and two (A_1 + B_1) for structure II. Similarly, in the Raman, Os—H stretching modes expected are one (A_g) for I and two (A_1 + B_1) for II.

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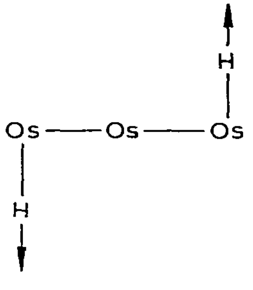
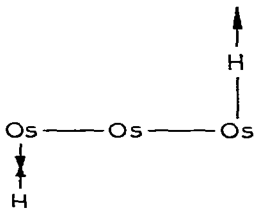
[*] There is a very weak shoulder at 2051 cm^{-1} in the IR spectrum of $D_2Os_3(CO)_{12}$. The "band-shift" from 2052—2041 cm^{-1} can thus alternatively be interpreted as a drastic intensity transference between bands at ca. 2052 cm^{-1} and ca. 2042 cm^{-1}. Since we know of no precedent for such behaviour, it is presumed not to be the case.

It is interesting to note that there exist pairs of IR and Raman modes which differ only in the phase relationship between vibrations of the end osmium units. For pure modes therefore, the difference in the corresponding Raman and IR frequencies is a reflection of the extent of interaction between the end osmium units [26]. The only vibration which can be considered to be entirely pure is ν(OsD), which is far removed in frequency from all other vibrations.



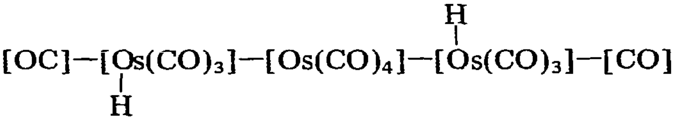
A_g (Raman active)



B_u (IR active)

Note that the difference between these IR and Raman frequencies is only 5 cm^{-1}, an indication that interaction between the end osmium units is small.

An approximate Os—H stretching force constant has been calculated to be 2.32 mdyn Å^{-1} [27]. This was calculated on a seven-centre model



$$[\mathrm{OC}]-[\underset{\displaystyle \mathrm{H}}{\underset{|}{\mathrm{Os}}}(\mathrm{CO})_3]-[\mathrm{Os}(\mathrm{CO})_4]-[\overset{\displaystyle \mathrm{H}}{\overset{|}{\mathrm{Os}}}(\mathrm{CO})_3]-[\mathrm{CO}]$$

from the Os—D stretching frequency. ν(OsH) is coupled to ν(CO) and shifted to lower frequency than a pure ν(OsH). In fact, frequency calculation for ν(OsH) using a force constant of 2.32 mdyn Å^{-1} gives a value of 1982 cm^{-1}, i.e. 21 cm^{-1} higher than the observed frequency.

iii) The δ(COsH) and δ(COsD) regions

The C—Os—H bending modes are assigned by comparison of the spectra of $H_2Os_3(CO)_{12}$ and $D_2Os_3(CO)_{12}$. In the IR, two bands are expected for structure I ($A_u + B_u$) and three for II ($A_1 + B_1 + B_2$). One peak and a shoulder are observed for δ(COsH). No δ(COsD) bands are assigned; calculation [27] shows that they occur at about 540 cm^{-1} and therefore overlap with δ(OsCO).

iv) The δ(OsCO) and ν(OsC) regions

Considerable coupling between these two vibrations probably occurs since they are so close in frequency, although the higher frequency region is considered to be mostly Os—C—O bending in character and the lower frequency region, Os—C stretching [20,26]. The IR spectrum of $H_2Os_3(CO)_{12}$ in this region is identical in both solution (cyclohexane) and semicrystalline (Nujol) states. This is a good indication that the skeletal structure of $H_2Os_3(CO)_{12}$ does not change with change of state or concentration, that site symmetry effects are small and that the vibrational spectra being studied are a good

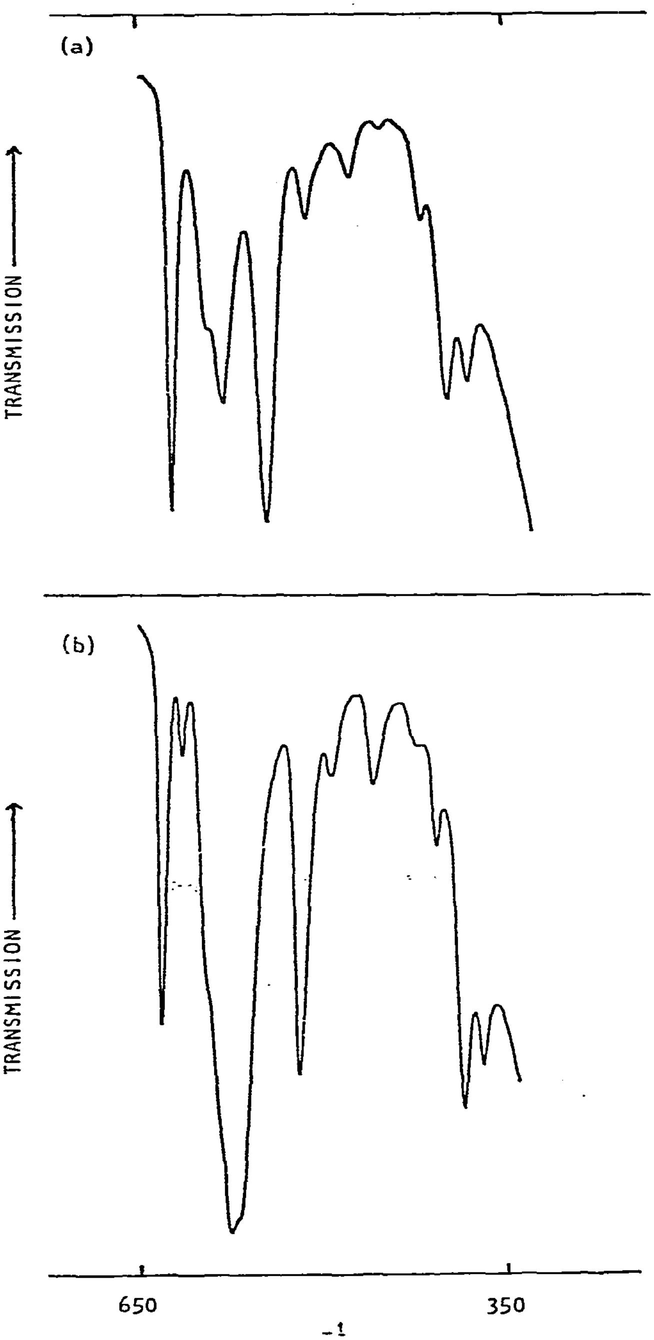


Fig. 2. IR spectra in Nujol mulls of (a) $H_2Os_3(CO)_{12}$ and (b) $Br_2Os_3(CO)_{12}$ in the region 650—350 cm^{-1}.

representation of an independent molecule.

There is considerable similarity in the band structures of $H_2Os_3(CO)_{12}$ and $Br_2Os_3(CO)_{12}$, especially in the lower frequency ν(OsC) region of the IR spectra

TABLE 4

CALCULATED FORCE CONSTANTS FOR ν(OsOs) [a] USING TWO VALUES OF $\nu(\mathrm{OsOs})_{\mathrm{asym}}$

	$\nu(\mathrm{OsOs})_{\mathrm{asym}} = 137\ \mathrm{cm}^{-1}$	$\nu(\mathrm{OsOs})_{\mathrm{asym}} = 158\ \mathrm{cm}^{-1}$
k_{OsOs} [b]	1.34	1.54
$k'_{\mathrm{OsOs,OsOs}}$ [c]	0.26	0.06
k_θ [d]	0.35	0.35

[a] Assuming $\nu(\mathrm{OsOs})_{\mathrm{sym}} = 95\ \mathrm{cm}^{-1}$ and δ(OsOsOs) = 37 cm^{-1}. [b] k_{OsOs} = Os—Os stretching force constant. [c] $k'_{\mathrm{OsOs,OsOs}}$ = Os—Os stretch interaction force constant. [d] k_θ = Os—Os—Os bending force constant.

(see Figure 2) *. This is an indication that the two molecules probably have the same skeletal structure.

v) The ν(OsOs) and δ(OsOsOs) regions

Structure I would give one Raman symmetric ν(OsOs), one IR asymmetric ν(OsOs) and two IR δ(OsOsOs). For structure II, all metal stretching and bending vibrations should occur in both the IR and Raman; these are two ν(OsOs) ($A_1 + B_1$) and two δ(OsOsOs) ($A_1 + B_2$). The spectra of $H_2Os_3(CO)_{12}$ and $D_2Os_3(CO)_{12}$ in the low frequency region are suggestive of I.

We observe no coincidence of IR and Raman bands. There is only one Raman band, at 95 cm^{-1}, which may be assigned to ν(OsOs). Its very high intensity suggests that the mode is symmetric, A_g. Similar Raman bands have been assigned to ν(OsOs) in the compounds $X_2Os_3(CO)_{12}$ (X = Cl, Br or I) [28].

Assignment of ν(OsOs) in the IR is less certain because of the large number of low intensity peaks that occur in this region. ν(OsOs) may tentatively be assigned to a band at 137 cm^{-1} which is of medium intensity. It is known that ν(MM) is often weak in the IR [29,30a]. Alternatively, a weak band at ca. 158 cm^{-1} may be ν(OsOs) by analogy to assignments made for $X_2Os_3(CO)_{12}$ (X = Cl, Br or I) [28].

Certainly, it appears that $\nu(\mathrm{OsOs})_{\mathrm{sym}} < \nu(\mathrm{OsOs})_{\mathrm{asym}}$, as expected for a linear structure. It is interesting to note that the difference in frequency between $\nu(\mathrm{OsOs})_{\mathrm{sym}}$ and $\nu(\mathrm{OsOs})_{\mathrm{asym}}$ is fairly large, suggesting that the structure is linear rather than bent. For bent triatomic species, symmetric and asymmetric stretches are often close in frequency (refs. 30b, 31 and computer calculation using ref. 27).

δ(OsOsOs) should occur at very low frequency. There is an intense band at 37 cm^{-1} in the Raman which could be assigned to an Os—Os—Os bending mode. According to symmetry predictions for I, it should not occur. It is considered to arise because of distortion of the molecule from ideal geometry [31]. The high intensity of this band makes it unlikely that it is due to δ(COsC), which would be expected to be weak [32]. Approximate force constants were calculated [27] for the osmium skeleton, using a linear triatomic model $[HOs(CO)_4]$—$[Os(CO)_4]$—$[Os(CO)_4H]$, which is a reasonable approximation for a linear structure [29,32]. Force constants are given in Table 4

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* Band positions (in the region 650—350 cm^{-1}) for $Br_2Os_3(CO)_{12}$ in the IR spectrum are: 627s, 612w, 590(sh), 570vs, 561(sh), 520s, 498w, 465w, 431vw, 415w, 392m, 375 m cm^{-1}.

for two values of $\nu(OsOs)_{asym}$. Note, from Table 4, that the size of the interaction constant has a marked effect on the frequency difference between $\nu(OsOs)_{sym}$ and $\nu(OsOs)_{asym}$.

Conclusion

From ^{13}C NMR and vibrational spectra, we conclude that $H_2Os_3(CO)_{12}$ has the linear structure I. If there is unrestricted rotation about the Os—Os bonds, then several conformations could exist in solution. Because of the short time scale of IR, all of these conformations would be observed with intensities proportional to their relative abundances [33]. This situation is not likely to extend to the solid state, yet IR spectra in solution and semi-solid state are identical in a sample region 600—300 cm^{-1}. Thus, although rotation about the Os—Os bonds almost certainly does occur, I would appear to be the most stable rotamer. The flexibility of the osmium skeleton could be an important factor in bringing groups on the end osmium atoms close enough to react in intramolecular elimination reactions involving such species.

It has already been pointed out that the IR spectra in the $\nu(CO)$ region of $H_2Os_3(CO)_{12}$ and $(CH_3)_2Os_3(CO)_{12}$ are similar [34] and $(CH_3)_2Os_3(CO)_{12}$ has been shown to adopt a structure analogous to I [15]. Also, it has been found from a survey of structures of trinuclear chain compounds containing transition metals [35] that those compounds with the transition metal as central atom are often linear whereas those with a main group metal as central atom are bent. This may be correlated with the involvement of *d*-orbital hybrids on the central transition metal in the formation of metal—metal bonds whereas the central main group metal uses *p*-orbital hybrids.

Experimental

The compounds $H_2Os_3(CO)_{12}$ and $D_2Os_3(CO)_{12}$ were prepared from $Br_2Os_3(CO)_{12}$ as described previously [7].

^{13}C NMR spectra were measured on a JEOL PFT-100 spectrometer at 25.15 MHz; chemical shifts are relative to $SiMe_4$ as external reference. The spectra were measured at room temperature using saturated solutions of $H_2Os_3(CO)_{12}$ in C_6D_6 with added $Cr(acac)_3$.

Infrared spectra (4000—400 cm^{-1}) were measured on a Perkin-Elmer 180 spectrophotometer using samples as Nujol mulls between KBr plates. Far infrared spectra (400—20 cm^{-1}) were measured on a Digilab FTS 16B/D Vacuum Interferometer with samples as Nujol mulls between polyethylene windows. Raman spectra were measured, using solid samples, on a Codberg model T800 triple monochromator using excitation at 647.1 nm as described previously [36].

Acknowledgements

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