The Vibrational Spectra and Structures of Some Derivatives of Triosmium Dodecacarbonyl

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INTENSE fundamentals lying between 100 and 200 cm.$^{-1}$ in the Raman spectra of compounds containing metal–metal (M–M) bonds may be identified[1] with approximately-localised vibrations of the M–M skeleton, provided that the masses and bond force constants of substituent ligands are not such as to mix extensively[2] the symmetry co-ordinate representations of the normal modes. These criteria are quite well satisfied in polynuclear metal carbonyls; Quicksall and Spiro[3] have recently reported the Raman spectrum of $Ir_4(CO)_{12}$ in the low frequency region and find it consistent with the known[4] molecular geometry (point group T_d). To exploit the diagnostic use of M–M vibrations, we have studied the Raman and i.r. spectra of $Os_3(CO)_{12}$ and certain of its derivatives[5,6] in the solid state, in order to determine the geometry of the M–M skeletons in the latter.

An *X*-ray study[7] has located the osmium atoms in the parent carbonyl at the corners of an equilateral triangle; the molecular point group is thus D_{3h}, for which group theory predicts two M–M stretching modes: $\Gamma_{M-M} = a'_1(R) + e'(R,i.r.)$. The observed spectra in the low frequency region (see Table) are consistent with these selection rules, and the ratio $\nu_{a'_1}/\nu_{e'}$ (1·34) is close to that predicted (1·41) by a SVFF calculation. The isomorphous $Ru_3(CO)_{12}$ gives similar results, with the expected shift in ν(M–M). Approximate force constants, based on a pseudotriatomic $[Os(CO)_4]_3$ system, are listed in the Table, and are comparable with the values found[1] for related M–M compounds.

Derivatives of $Os_3(CO)_{12}$ of the types $Os_3(CO)_{12}X_2$ (X = Cl, Br, I)[5] and $Os_3(CO)_{10}Y_2$ (Y = OMe,H)[6] have recently been prepared by Johnson, Lewis, and Kilty. In these species the geometry of the Os_3 skeleton is of particular

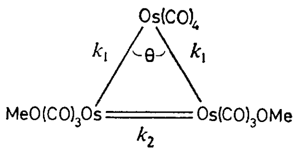
Vibrational spectra [ν(M–M) and ν(M–X)] *of* Os_3 *compounds*

Compound	Point group	ν(M–M)		ν(M–X)		Force constants (m dyne/Å)			
		Raman	i.r.	Raman	i.r.	k_M	k'	k_X	k''
$Os_3(CO)_{12}$	D_{3h}	161 a'_1	—	—	—	1·6	−0·1	—	—
		120 e'	121 e'						
$Ru_3(CO)_{12}$		186 a'_1	n.i.	—	—	1·7	−0·2	—	—
		152 e'							
$Os_3(CO)_{12}Cl_2$	D_{4h}	116 a_{1g}	163 a_{2u}	313 a_{1g}	304 a_{2u}	1·6	0·2	2·0	0·1
$Os_3(CO)_{12}Br_2$		100 a_{1g}	157 a_{2u}	212 a_{1g}	203 a_{2u}	1·6	0·2	1·8	0·3
$Os_3(CO)_{12}I_2$		97 a_{1g}	153 a_{2u}	170 a_{1g}	169 a_{2u}	1·7	0·2	1·7	0·5
$Os_3(CO)_{10}(OCH_3)_2$	C_{2v}	172 a_1	n.o.	—	—	k_1	k'	k_2	θ
		136 a_1	132 a_1			1·7	−0·1	2·2	50°
		119 b_2	121 b_2						

k_M force constant of metal–metal bond; k_X force constant of metal-halogen bond; k' interaction constant between adjacent metal–metal bonds; k'' interaction constant between adjacent metal–metal and metal–halogen bonds; n.i. not investigated; n.o. not observed.

interest, since it can no longer be an exact equilateral triangle like the parent carbonyl. Johnson, Lewis, and Kilty have found mass spectral evidence to suggest that the Os atoms are noncyclic in the former, but cyclic in the latter derivatives. The vibrational spectra of the dihalides in the ν(M–M) and ν(M–X) regions provide strong evidence for a linear XOs_3X molecular skeleton. The appropriate point group is $D_{\infty h}$, or D_{4h} if we recognise the presence of the carbonyl ligands. Both point groups predict the same selection rules for the stretching modes of the heavy-atom skeleton: two Raman lines (species a_{1g}) and two nonco-incident i.r. bands (species a_{2u}) are expected, and observed, as shown in the Table. The two high frequency fundamentals are most sensitive to the nature of the halogen, which permits them to be formally labelled as ν(M–X), although a normal co-ordinate analysis shows that they entail considerable mixing of M–M and M–X motions, particularly in the heavier halides. The force constants in the Table are calculated on the basis of a linear 'pentatomic' molecule X–[$Os(CO)_4$]–[$Os(CO)_4$]–[$Os(CO)_4$]–X.

$Os_3(CO)_{10}(OMe)_2$, which is typical of the second class of derivative, has vibrational spectra fitting neither the linear Os_3 structure nor the equiangular arrangement of the parent carbonyl. The appearance of *three* very strong Raman lines attributable to ν(M–M), two of which are coincident with features in the far infrared, suggests a molecule of lower symmetry, having three Os–Os bonds. For any such cyclic structure all three ν(M–M) modes should appear as fundamentals in the infrared; evidently one has escaped observation. The most probable arrangement of Os atoms is at the apices of an isosceles triangle (point group C_{2v}) as shown in the Figure. One Os–Os bond (force constant k_2) differs from the other two (force constant k_1) owing to the presence of the two methoxide groups. For a range of assumed values of the angle θ, sets of force constants k_1, k_2, and k' have been calculated from the three frequencies. Physically reasonable solutions are only obtained for values of θ less than 60°. In the Table we quote the figures obtained when θ is assumed to be 50°; k_1 is similar to k_M in $Os_3(CO)_{12}$, but k_2 is significantly higher. This is in keeping with the formal Os=Os double bond which has been proposed[6] in order to satisfy the effective atomic number rule.



The vibrational spectra of all compounds in the characteristic ν(CO) region are also consistent with the proposed structures, and have been assigned on the basis of a Cotton–Kraihanzel force field. Complete vibrational spectra of these and related compounds, in which the Os_3 unit is shown to adopt three different geometrical configurations, will be published.

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