Mass Spectra of Polynuclear Carbonyls: A New Polynuclear Carbonyl Oxide of Osmium

By B. F. G. JOHNSON, J. LEWIS, I. G. WILLIAMS, and J. WILSON
(*Department of Chemistry, University of Manchester*)

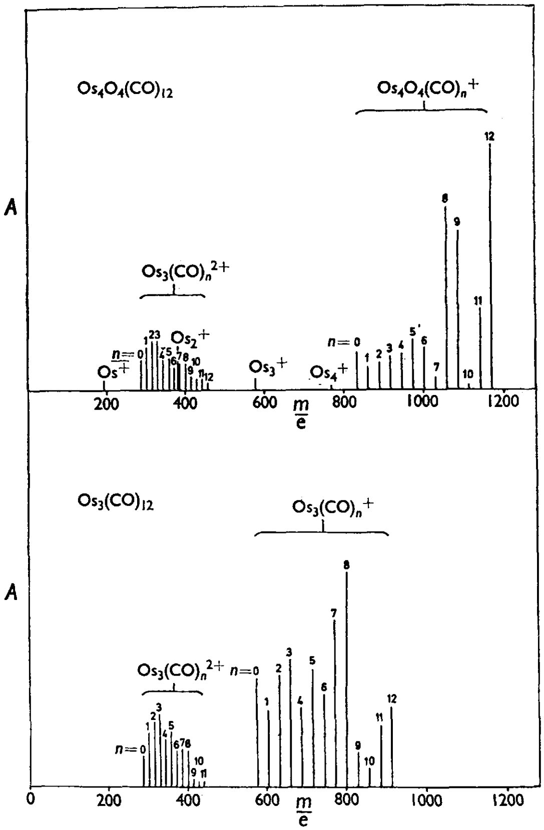
WE have studied the mass spectra of a number of polynuclear metal carbonyls to gain information on the relative probabilities of cleavage at the various types of bond and to correlate this with the various structural types.

During the course of this study we have prepared and characterised, on the basis of mass-spectral data, a novel polynuclear carbonyl of osmium, $Os_4O_4(CO)_{12}$. This compound is the product of the reaction between OsO_4 and CO under conditions (200 atm., 150°, 15 hrs.) less vigorous than those required for the preparation of $Os_3(CO)_{12}$ (300 atm., 150°, 15 hr.) and is obtained in small yields as a yellow–white solid. It is readily sublimed (170°/0·01 mm.) and soluble in a variety of organic solvents. The position of the CO stretching frequencies in the infrared spectra are significantly different from those of $Os_3(CO)_{12}$ (Table), but the number and intensity of the bands parallels those of the free carbonyl implying a similar basic carbonyl structural pattern to that occurring in the parent carbonyl. In addition two bands appearing at 1040 and 1060 cm.$^{-1}$ are tentatively attributed to an Os=O stretching vibration.

TABLE

Compound	CO frequency (cm.$^{-1}$)
$Os_3(CO)_{12}$ (C_6H_{12})	2068 (s), 2034 (s), 2014 (m), 2000 (m)[2]
$Os_4O_4(CO)_{12}$ ($CHCl_3$)	2100 (s), 2072 (m), 2016 (s), 2000 (m)

From our studies on $Ru_3(CO)_{12}$,[1] $Os_3(CO)_{12}$, and $Co_4(CO)_{12}$ we have established that under electron impact the *predominant* fragmentation scheme involves successive removal of CO groups without rupture of the metal cluster; only when all the CO groups have been removed does the fragmentation of the metal nucleus begin. Thus the most abundant singly-charged ions found in the fragmentation pattern of these carbonyls are of the types $Ru_3(CO)_n^+$, Ru_2^+, Ru^+; $Os_3(CO)_n^+$; $Co_4(CO)_n^+$, Co_3^+, Co_2^+, Co^+ (where n = 0—12). The mass spectrum of $Os_4O_4(CO)_{12}$ follows a similar pattern (Figure). Ions of the type $Os_4O_4(CO)_n^+$, (n = 0—12) occur in high abundance, whereas monopositive ions corresponding to the break up of the Os_4 nucleus are not observed until all the CO groups have been removed.



The molecular weight of the compound was derived from the group of ions for which $n = 12$; the relative isotopic abundances of this group were consistent with the presence of four Os atoms. A number of doubly-charged species of the type $Os_3(CO)_n^{2+}$ (n = 0—11) are also observed, being similar to the pattern obtained from the mass spectra of $Os_3(CO)_{12}$. However, the singly-charged species in the $Os_3(CO)_{12}$ system are absent for the spectrum, indicating that this is an integral part of the mass spectrum of the $Os_4O_4(CO)_{12}$ molecule. A plausible mechanism to explain this would be a disproportionation reaction of the type $Os_4O_4(CO)_{12}^+ \rightarrow OsO_4^- + Os_3(CO)_{12}^{2+}$. We are currently investigating the structure and reactivity of the complex and attempting the preparation of related complexes, as this compound is a member of a new series of carbonyl adducts, which possibly are formed as intermediates in the preparation of carbonyls from metal oxide.

(*Received, May 9th,* 1966; *Com.* 307.)

---

[1] J. Lewis, A. R. Manning, J. R. Miller, and J. Wilson, *J. Chem. Soc.* (*A*), 1966, in the press.
[2] D. K. Huggins, N. Flitcroft, and H. D. Kaesz, *Inorg. Chem.*, 1965, **4**, 166.