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CLUSTER CHEMISTRY

XXVIII*. UTILITY OF FAST ATOM BOMBARDMENT MASS SPECTROMETRY FOR THE CHARACTERISATION OF HIGH MOLECULAR WEIGHT COMPLEXES CONTAINING METAL CLUSTERS

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Summary

Fast atom bombardment (FAB) mass spectrometry has been used to obtain spectra of $HRu_3Au(\mu_3\text{-}S)(CO)_9(PPh_3)$, $Ru_3Au_2(\mu_3\text{-}S)(CO)_9(PPh_3)_2$ and $Ru_3Au_3(\mu_3\text{-}C_{12}H_{15})(CO)_8(PPh_3)_3$, none of which give metal-containing ions in conventional EI mass spectrometry. All the compounds give molecular (M^+) or quasi-molecular ($[M + 2H]^+$) ions which fragment by conventional routes.

Fast atom bombardment (FAB) mass spectrometry is a relatively new technique which uses a stream of neutral atoms (argon or xenon) to sputter ions from solids or liquids [1]. The utility of the method is in its ability to generate ions from solutions in relatively non-volatile liquid matrices (glycerol, thioglycerol), allowing the recording of spectra (both of negative and positive ions) of polar molecules, ionic complexes, and particularly in the present context, of high molecular weight organometallic molecules, all of which are essentially involatile or thermally labile under "normal" electron impact source conditions.

Perhaps the most complex organometallic compounds to be studied, which understandably were hailed as an indicator of the use of this new technique, were vitamin B_{12} and its coenzyme [1—4]. Recent applications of FAB mass spectrometry to organometallics have been reviewed briefly [5], although an ob-

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vious use in the characterisation of high molecular weight metal cluster complexes of low volatility, has apparently received only two mentions to date [6,7]. In this note we draw attention to the relative ease with which spectra of polymetallic clusters, one with a molecular weight of over 2000, may be obtained and the wealth of fragmentation information contained in these spectra (a feature absent in other soft ionisation techniques).

Experimental

The complexes $HRu_3Au(\mu_3\text{-}S)(CO)_9(PPh_3)$, $Ru_3Au_2(\mu_3\text{-}S)(CO)_9(PPh_3)_2$ and $Ru_3Au_3(\mu_3\text{-}C_{12}H_{15})(CO)_9(PPh_3)_3$ were chosen as recent examples of mixed-metal clusters which have been prepared and crystallographically characterised by the Adelaide group [8].

Spectra were recorded, after FAB ionisation with Xe as the collision gas (ion gun conditions: 8 kV and 1 mA), using a VG MM ZAB2F(HF) mass spectrometer combined with a VG 11-250 data system, from solutions of the complexes in thioglycerol. Exact mass determinations were made after calibration of the instrument with suitable reference compounds.

Results

Molecular and fragment ions were measured for each of the three complexes $HRu_3Au(\mu_3\text{-}S)(CO)_9(PPh_3)$ (1, m/z 1049), $Ru_3Au_2(\mu_3\text{-}S)(CO)_9(PPh_3)_2$ (2, m/z 1507) and $Ru_3Au_3(\mu_3\text{-}C_{12}H_{15})(CO)_8(PPh_3)_3$ (3, m/z 2065). We were not able to observe any ions other than those derived from PPh_3 in a conventional EI mass spectrum. To avoid tedious repetition, Table 1 lists only the nominal masses and compositions of ions observed in the FAB spectrum, between m/z 700—1050 for 1, between m/z 1100—1500 for 2, and between m/z 1550—2100 for 3. The highest mass ions appear to be the commonly observed $[M + H]^+$ ions; the fragmentations are those which would be expected on the basis of conventional electron-impact induced fragmentations of similar complexes. In all cases, normalized values are given, corresponding to the most intense component of the isotopic cluster.

TABLE 1

IONS IN FAB MASS SPECTRA OF THREE RUTHENIUM-GOLD CLUSTER COMPLEXES

(a) $HRu_3Au(\mu_3\text{-}S)(CO)_9(PPh_3)$ (1)
1048, 21, $[M - H]^+$ (= M'); 1020, 5, $[M' - CO]^+$; 992, 8, $[M' - 2CO]^+$; 964, 5, $[M' - 3CO]^+$; 936, 13, $[M' - 4CO]^+$; 908, 11, $[M' - 5CO]^+$; 880, 5, $[M' - 6CO]^+$; 852, 12, $[M' - 7CO]^+$; 824, 100, $[M' - 8CO]^+$; 796, 23, $[M' - 9CO]^+$; 770, 16, $[M' - S - Ph - 6CO]^+$; 742, 85, $[M' - S - Ph - 7CO]$; 714, 38, $[M - S - Ph - 8CO]^+$.

(b) $Ru_3Au_2(\mu_3\text{-}S)(CO)_9(PPh_3)_2$ (2)
1504, 100, M^+; 1476, 36, $[M - CO]^+$; 1448, 60, $[M - 2CO]^+$; 1420, 55, $[M - 3CO]^+$; 1392, 63, $[M - 4CO]^+$; 1364, 96, $[M - 5CO]^+$; 1336, 44, $[M - 6CO]^+$; 1308, 98, $[M - 7CO]^+$; 1280, 98, $[M - 8CO]^+$; 1252, 95, $[M - 9CO]^+$; 1176, 67, $[M - 9CO - Ph]^+$.

(c) $Ru_3Au_3(\mu_3\text{-}C_{12}H_{15})(CO)_8(PPh_3)_3$ (3)
2067, 88, $[M + 2H]^+$ (= M'); 2040, 38, $[M' - CO]^+$; 2012, 58, $[M' - 2CO]^+$; 1980, 27, $[M' - 3CO]^+$; 1960, 14, $[M' - CO - Ph]^+$; 1952, 51, $[M' - 4CO]^+$; 1924, 54, $[M' - 5CO]^+$; 1896, 28, $[M' - 6CO]^+$; 1880, 12, $[M' - PPh_2]^+$; 1868, 39, $[M' - 7CO]^+$; 1840, 11, $[M' - 8CO]^+$; 1791, 16, $[M - 7CO - Ph]^+$; 1760, 17, $[M - 7CO - PPh]^+$; 1732, 10, $[M - 8CO - PPh]^+$; 1686, 33, $[M - AuPPh_2]^+$; 1658, 27, $[M - CO - AuPPh_2]^+$; 1630, 60, $[M - 2CO - AuPPh_2]^+$; 1602, 100, $[M' - AuPPh_3]^+$; 1574, 74, $[M - CO - AuPPh_3]^+$.

Figure 1 illustrates a portion of the FAB spectrum of 3 above m/z 2000, containing the ion clusters $[M' - n\mathrm{CO}]^+$ (n = 0, 1 and 2). From Table 2, which lists the corresponding exact masses of the observed ions compared with the calculated values, together with relative intensities, it can be seen that the highest ion appears to be $[M + 2\mathrm{H}]^+$ ($= M'$). Quasi-molecular ions $[M + \mathrm{H}]^+$ have been found previously, for example, in the spectra of co-enzyme B_{12} (at m/z 1579) [3,4,9], several rhodium complexes, and the trinuclear complex $Co_3(\mu\text{-}PPh_2)_3(CO)_6$ [6,7]. Reactions of polynuclear metal carbonyl clusters with both H_2 and H^+ are well-documented [10], the former occurring with either loss of CO or opening of a metal—metal bond, and we suggest that similar processes may be oc-

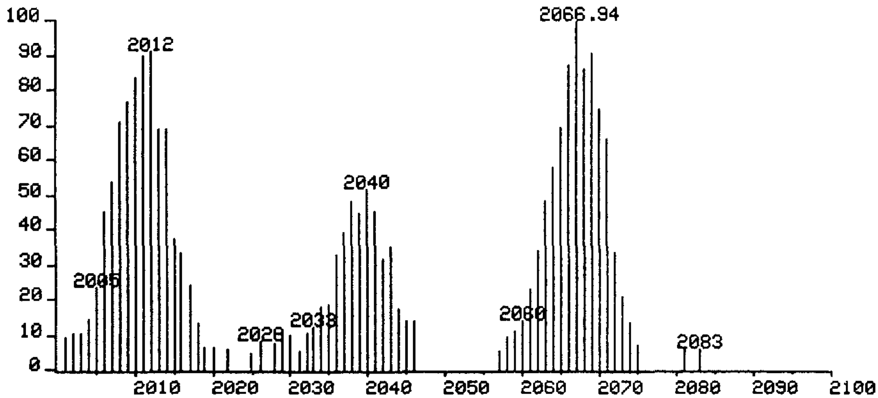

Fig. 1. Portion of FAB mass spectrum of $Ru_3Au_3(\mu_3\text{-}C_{12}H_{15})(CO)_8(PPh_3)_3$ (3) above m/z 2000, showing $[M + 2\mathrm{H}]^+$, $[M + 2\mathrm{H} - \mathrm{CO}]^+$ and $[M + 2\mathrm{H} - 2\mathrm{CO}]^+$ ion.

TABLE 2

EXACT MASSES AND RELATIVE INTENSITIES OF IONS (m/z > 2000) IN FAB MASS SPECTRUM OF $Ru_3Au_3(\mu_3\text{-}C_{12}H_{15})(CO)_8(PPh_3)_3$ (3)

Nominal mass	Exact mass [a]		Relative intensity [a]	
	Calculated	Observed	Calculated	Observed
2000	2000.00	1999.89	3.1	5.5
2001	2001.00	2000.90	4.5	9.3
2002	2002.00	2001.93	7.8	10.0
2003	2002.99	2002.91	13.7	10.5
2004	2003.99	2003.89	19.2	14.4
2005	2004.99	2004.91	28.3	23.7
2006	2005.99	2005.91	40.6	45.4
2007	2006.99	2006.90	49.6	53.7
2008	2007.99	2007.90	66.0	70.6
2009	2008.99	2008.90	77.9	76.2
2010	2009.99	2009.90	84.7	83.1
2011	2010.99	2010.92	91.0	89.7
2012	2011.99	2011.91	85.5	91.0
2013	2012.99	2012.92	72.1	69.0
2014	2013.99	2013.92	61.8	68.2
2015	2014.99	2014.93	39.1	37.4
2016	2015.99	2015.92	28.3	33.0
2017	2017.00	2016.92	14.6	24.4
2018	2018.00	2017.95	7.5	13.3
2019	2019.00	2018.92	3.2	6.5
2020	2020.00	2019.96	1.1	6.0

TABLE 2 (*continued*)

Nominal mass	Exact mass [a]		Relative intensity [a]	
	Calculated	Observed	Calculated	Observed
2021	2021.00		0.3	
2022		2021.88		5.5
2025	2024.99	2024.91	0.3	4.5
2026	2025.99	2025.96	0.5	8.0
2027	2026.99		0.7	
2028	2027.99	2027.90	1.7	7.5
2029	2028.99	2028.95	2.5	11.0
2030	2029.99	2029.93	4.4	9.5
2031	2030.99	2031.08	7.7	5.0
2032	2031.99	2031.96	10.8	10.5
2033	2032.99	2032.94	15.9	12.0
2034	2033.99	2033.92	22.8	17.5
2035	2034.99	2034.93	28.0	18.0
2036	2035.99	2035.92	37.2	32.7
2037	2036.99	2036.93	43.9	38.7
2038	2037.99	2037.93	47.9	48.2
2039	2038.99	2038.93	51.4	44.6
2040	2039.99	2039.93	48.4	51.2
2041	2040.99	2040.93	40.9	45.4
2042	2041.99	2041.94	35.0	31.9
2043	2042.99	2042.91	22.4	34.5
2044	2043.99	2043.94	16.1	17.4
2045	2044.99	2044.93	8.4	13.5
2046	2045.99	2045.96	4.3	13.5
2047	2046.99		1.9	
2048	2048.00		0.6	
2049	2049.00		0.2	
2053	2052.99		0.5	
2054	2053.99		0.8	
2055	2054.99		1.4	
2056	2055.99		3.3	
2057	2056.99	2056.98	4.8	5.0
2058	2057.99	2057.99	8.5	9.0
2059	2058.98	2058.93	15.0	11.2
2060	2059.98	2059.95	21.0	13.5
2061	2060.98	2060.94	30.9	22.5
2062	2061.98	2061.94	44.3	33.9
2063	2062.98	2062.93	54.3	47.7
2064	2063.98	2063.93	72.2	57.7
2065	2064.98	2064.94	85.4	69.1
2066	2065.98	2065.94	93.1	86.6
2067	2066.98	2066.94	100	100
2068	2067.98	2067.93	94.4	86.0
2069	2068.98	2068.94	79.9	90.5
2070	2069.98	2069.94	68.4	74.2
2071	2070.98	2070.95	43.9	65.6
2072	2071.98	2071.94	31.6	33.3
2073	2072.99	2072.97	16.6	20.5
2074	2073.99	2073.96	8.5	13.0
2075	2074.99	2074.87	3.7	7.0
2076	2075.99		1.3	
2077	2076.99		0.3	

[a] Exact masses and relative intensities calculated for the ions $[C_{72}H_{62}Au_3O_6P_3Ru_3]^+$ ($[M + 2H - 2CO]^+$), $[C_{73}H_{62}Au_3O_7P_3Ru_3]^+$ ($[M + 2H - CO]^+$), and $[C_{74}H_{62}Au_3O_8P_3Ru_3]^+$ ($[M + 2H]^+$).

curring with complex **3**. The solvent thioglycerol is known to have mild reducing properties.

Conclusion

It has not been the purpose of this note to examine in detail the spectra of t these three complexes. The type of information given in Table 2 is available in principle for all ions in the spectrum, and would enable a full analysis of the fragmentations to be undertaken. The lower m/z reaches of FAB mass spectra may be complicated by the presence of 'cluster ions' originating from the liquid matrix, but these should be readily identified by exact-mass measurements. While this powerful technique will not give stereochemical information about cluster complexes, which may only be forthcoming from single-crystal X-ray diffraction studies, nevertheless the examples presented above provide an impressive indication of the utility of this new development in the characterisation of large polynuclear metal cluster complexes.

Note added in proof. More recently, the identification of the $[N(PPh_3)_2]^+$ salts of the anions $[Os_9(CO)_{21}(CHCRCH)]^-$ (m/z 2907 (R = Me), 2921 (R = Et)) (B.F.G. Johnson, J. Lewis, M. McPartlin, W.J.H. Nelson, P.R. Raithby, A. Sironi and M.D. Vargas, J. Chem. Soc., Chem. Commun., (1983) 1476) and of $[PMePh_3][Os_{11}C(CO)_{27}\{Cu(NCMe)\}]$ (m/z 2880) [D. Braga, K. Henrick, B.F.G. Johnson, J. Lewis, M. McPartlin, W.J.H. Nelson, A. Sironi and M.D. Vargas, J. Chem. Soc., Chem. Commun., (1983) 1131] have been described, further emphasising the utility of the method to characterise high molecular weight neutral and ionic cluster complexes.

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