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Preliminary communication

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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 HRu₃Au(μ_3 -S)(CO)₉(PPh₃), Ru₃Au₂(μ_3 -S)(CO)₉(PPh₃)₂ and Ru₃Au₃-(μ_3 -C₁₂H₁₅)(CO)₈(PPh₃)₃, none of which give metal-containing ions in conventional EI mass spectrometry. All the compounds give molecular (M^+) or quasimolecular ([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-

^{*}For Part XXVII, see ref. 11.

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 $HRu_3Au(\mu_3-S)(CO)_9(PPh_3)$, $Ru_3Au_2(\mu_3-S)(CO)_9(PPh_3)_2$ and $Ru_3Au_3(\mu_3-C_{12}H_{15})(CO)_9(PPh_3)_3$ were chosen as recent examples of mixedmetal 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 $HRu_3Au(\mu_3-S)(CO)_9(PPh_3)$ (1, m/z 1049), $Ru_3Au_2(\mu_3-S)(CO)_9(PPh_3)_2$ (2, m/z 1507) and $Ru_3Au_3(\mu_3-C_{12}H_{15})(CO)_8(PPh_3)_3$ (3, m/z 2065). We were not able to observe any ions other than those derived from PPh₃ 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) $HRu_{3}Au(\mu_{3}-S)(CO)_{9}(PPh_{3})$ (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) $Ru_3Au_2(\mu_3-S)(CO)_9(PPh_3)_2$ (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) $Ru_{3}Au_{3}(\mu_{3}-C_{12}H_{15})(CO)_{5}(PPh_{3})_{3}$ (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 $[M' - nCO]^+$ (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 $[M + 2H]^+$ (=M'). Quasi-molecular ions $[M + H]^+$ have been found previously, for example, in the spectra of co-enzyme B₁₂ (at m/z 1579) [3,4,9], several rhodium complexes, and the trinuclear complex Co₃(μ -PPh₂)₃-(CO)₆ [6,7]. Reactions of polynuclear metal carbonyl clusters with both H₂ 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 $\text{Ru}_3\text{Au}_3(\mu_3-\text{C}_{12}\text{H}_{15})(\text{CO})_8(\text{PPh}_3)_3$ (3) above m/z 2000, showing $[M + 2\text{H}]^+$, $[M + 2\text{H} - \text{CO}]^+$ and $[M + 2\text{H} - 2\text{CO}]^+$ ion.

TABLE 2

EXACT MASSES AND RELATIVE INTENSITIES OF IONS (m/z > 2000) IN FAB MASS SPECTRUM OF Ru₃Au₃(μ_3 -C₁₂H₁₅)(CO)₈(PPh₃)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)

| mass Calculated Observed Calculated Observed 2021 2021.80 5.5 2025 2024.91 0.3 4.5 2026 2025.99 2028.99 0.7 2028 2028.99 2028.95 2.5 11.0 2030 2028.99 2028.95 2.5 11.0 2031 2031.99 2031.86 7.7 5.0 2032 2033.99 2032.24 15.9 12.0 2034 2033.99 2033.92 2.8 17.5 2035 2034.99 2034.93 2.8 17.5 2036 2035.99 2035.92 7.2 32.7 2037 2036.99 2036.93 48.4 51.2 2038 2037.93 47.9 48.2 2038 2038 2038.99 2038.93 51.4 44.6 2041 2040.93 40.9 45.4 2041 2040.93 40.9 45.4 2041 <th rowspan="2">Nominal mass</th> <th colspan="2">Exact mass^a</th> <th colspan="3">Relative intensity^a</th> | Nominal mass | Exact mass ^a | | Relative intensity ^a | | |
|--|-----------------|-------------------------|----------|---------------------------------|----------|--|
| 20212021.000.320222021.885.520252025.992025.960.520262025.992025.960.720282027.901.77.520312028.992029.934.49.52031203.992031.961.61.62032203.992031.961.75.02033203.992031.961.81.62034203.992031.961.81.52035203.992033.922.81.7.520362035.992035.923.4.93.6.720372035.992035.934.93.720382037.992035.934.93.720372035.992035.934.94.620402039.992038.9351.44.4.62041204.99204.943.031.920422041.99204.943.031.920442042.992042.912.434.520442043.992045.9416.11.7.420452044.991.9204.942.42041204.991.92.434.520442043.992045.964.313.520472046.991.92.52054205205.993.320552054.993.45.020542055.993.34.720552056.993.34.720642065.9 | | Calculated | Observed | Calculated | Observed | |
| 20222021.885.520262025.992025.990.720272026.990.720282027.992027.9020302028.992028.9520312030.992031.9620322031.992031.9620332032.992031.9620342033.992031.9620352034.992034.9320362035.992034.9320372036.992034.9320382035.992035.9220372036.992036.9320382037.992037.9320382038.992038.9320382038.992038.9320342049.902049.9320412040.902049.9320422041.9920432042.91224344.520442043.9920452044.9320442045.9920452044.9320442045.9920452044.9320462045.9920472046.9920482044.902049204.9320590.520542051.9920552051.9920562051.9920582057.9920593.320572058.9820593.320572058.9920593.320572058.992058206.9420593.32059205.95 <td< td=""><td>2021</td><td>2021.00</td><td></td><td>0.3</td><td></td><td></td></td<> | 2021 | 2021.00 | | 0.3 | | |
| 2025 2024.99 2024.91 0.3 4.5 2026 2025.99 0.7 2028 2027.99 2028.95 2.5 2030 2028.99 2028.95 2.5 2031 2030.99 2028.95 2.5 2031 2030.99 2031.08 7.7 5.0 2033 2032.99 2031.96 1.6 10.5 2034 2033.99 2033.92 2.8 17.5 2035 2034.99 2034.93 2.8.0 18.0 2036 2035.99 2035.93 37.2 32.7 2037 2036.99 2036.93 43.9 38.7 2038 2037.99 2038.93 51.4 44.6 2040 203.99 2038.93 41.9 44.5 2041 204.99 204.93 44.9 5.0 2042 204.99 204.93 8.4 13.5 2045 2044.99 204.99 1.4 5.0 | 2022 | | 2021.88 | | 5.5 | |
| 2026 2025.99 2025.99 2027.90 0.7 2028 2027.99 2028.99 2028.95 2.5 11.0 2030 2029.99 2029.93 4.4 9.5 2031 2030.99 2031.96 1.7 7.5 2032 2031.99 2031.94 1.5 1.20 2034 2033.99 2033.92 2.8 1.7.5 2035 2034.99 2034.93 2.8 1.7.5 2036 2035.99 2035.93 3.7.2 3.2.7 2037 2036.99 2038.93 3.4.4 5.1.2 2038 2037.99 2038.93 3.4.4 5.1.2 2041 204.99 204.93 4.4.6 2.2 2042 204.99 204.93 4.4 5.1 2041 204.93 4.8 5.0 3.5 2042 204.99 204.93 3.8 3.5 2044 204.99 204.94 3.3 5.0 | 2025 | 2024.99 | 2024.91 | 0.3 | 4.5 | |
| 2027 2027.99 0.7 2028 2027.99 2028.95 2.5 11.0 2030 2029.99 2029.93 4.4 9.5 2031 2030.99 203.108 7.7 5.0 2032 2031.99 203.96 10.8 10.5 2033 2032.99 203.92 22.8 17.5 2034 2033.99 203.92 22.8 17.5 2035 2034.99 2034.93 28.0 18.0 2036 2035.99 2036.93 43.9 38.7 2037 2036.99 2037.93 47.9 48.2 2039 2038.99 2038.93 51.4 44.6 2040 2039.99 2038.93 51.4 44.6 2041 2041.99 204.93 40.9 45.4 2042 2041.99 2042.91 22.4 34.5 2044 2042.99 2042.91 22.4 34.5 2044 2042.99 2042.91 22.4 34.5 2044 2043.99 2042.91 204.93 8.4 2044 2043.99 2042.99 1.9 2044 2044.99 204.93 8.4 2045 2044.99 1.9 2044 2045.99 0.5 2055 2056.98 8.4 8.5 2055 2055.99 0.5 2056 2059.99 0.5 2056 2059.99 0.5 2056 205.99 0.5 </td <td>2026</td> <td>2025.99</td> <td>2025.96</td> <td>0.5</td> <td>8.0</td> <td></td> | 2026 | 2025.99 | 2025.96 | 0.5 | 8.0 | |
| 2028 2027.99 2028.99 2028.99 2028.99 2030 2029.99 2029.93 4.4 9.5 2031 2030.99 2031.96 7.7 5.0 2032 2031.99 2032.94 15.9 12.0 2034 2033.99 2032.94 15.9 12.0 2035 2034.99 2034.93 28.0 18.0 2036 2036.99 2036.92 37.2 32.7 2037 2036.99 2036.93 44.4 61.2 2040 2038.99 2039.93 48.4 61.2 2041 204.99 204.93 40.9 46.4 2042 2041.99 204.93 8.4 13.5 2043 2044.99 2044.93 8.4 13.5 2044 2044.99 2044.93 8.4 13.5 2044 2045.99 2045.96 4.3 15.5 2044 2045.99 0.5 205 205 205.99 3.3 2055 2054.99 1.4 205 205.99 3.3 <td>2027</td> <td>2026.99</td> <td></td> <td>0.7</td> <td></td> <td></td> | 2027 | 2026.99 | | 0.7 | | |
| 2029 2028.99 2028.95 2.5 11.0 2030 2029.99 2029.93 4.4 9.5 2031 2030.99 2029.93 4.4 9.5 2032 2031.99 2031.96 10.8 10.5 2034 2032.99 2032.92 22.8 17.5 2035 2034.99 203.92 27.2 32.7 2037 2035.99 203.93 43.9 38.7 2038 2037.93 203.93 51.4 44.6 2040 2039.99 203.93 48.4 61.2 2041 2040.99 204.93 44.4 51.2 2042 2041.99 2042.91 22.4 34.5 2043 2042.99 204.93 8.4 13.5 2044 2043.99 2042.91 22.4 34.5 2045 2044.99 204.93 8.4 13.5 2044 2045.99 0.5 205 205.9 2054 2053.99 0.5 205 205.99 2055 205.99 | 2028 | 2027.99 | 2027.90 | 1.7 | 7.5 | |
| 2030 2029.99 2029.33 4.4 9.5 2031 2030.99 2031.06 7.7 5.0 2032 2031.99 2032.94 15.9 12.0 2035 2034.99 2032.94 15.9 12.0 2036 2035.99 2034.93 28.0 18.0 2037 2036.99 2036.93 43.9 38.7 2038 2037.99 2037.93 47.9 48.2 2040 2038.99 2038.93 51.4 44.6 2041 2040.99 204.93 40.9 45.4 2042 2041.99 2042.91 22.4 34.5 2043 2042.90 2042.91 22.4 34.5 2044 2043.99 2043.94 16.1 17.4 2045 2044.90 0.6 2045.99 2045.91 2.4 2044 2045.99 204.93 8.4 13.5 2047 2044 2043.99 2043.94 16.1 17.4 2046 2045.99 205 2047 2046.99 0 | 2029 | 2028.99 | 2028.95 | 2.5 | 11.0 | |
| 2031 203.0.99 2031.08 7.7 5.0 2032 2031.99 2031.96 10.8 10.5 2034 2032.99 2032.92 22.8 17.5 2035 2036.99 2035.92 22.8 17.5 2036 2036.99 2035.92 37.2 32.7 2037 2036.99 2035.92 37.2 32.7 2038 2037.99 2035.93 51.4 44.6 2040 2039.99 2038.93 51.4 44.6 2041 2040.99 2040.93 40.9 46.4 2042 2041.99 2042.91 22.4 34.5 2043 2042.99 2043.94 16.1 17.4 2045 2044.99 2043.94 16.1 17.4 2045 2044.99 2043.94 16.1 17.4 2045 2044.99 2043.94 16.1 17.4 2046 2045.99 0.5 205 205 2054 2051.99 0.5 205 205 2055 2056.99< | 2030 | 2029.99 | 2029.93 | 4.4 | 9.5 | |
| 2032 2031.99 2032.99 2032.94 15.9 12.0 2034 2033.99 2032.94 15.9 12.0 2035 2034.99 2034.93 28.0 18.0 2036 2035.99 2036.93 43.9 38.7 2037 2036.99 2036.93 43.9 38.7 2038 2037.99 2037.93 47.9 48.2 2040 2039.99 2039.93 48.4 51.2 2041 2040.90 2040.93 40.9 46.4 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 0.5 15 15 2055 2054.99 1.4 205 2055.9 205 2056 2057.99 205.5 9.0 205 205 2057 2056.99 205.9 9.0 1.4 | 2031 | 2030.99 | 2031.08 | 7.7 | 5.0 | |
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| 2034 2033.99 2034.99 2034.93 22.8 17.5 2035 2034.99 2034.93 28.0 18.0 2037 2036.99 2036.92 37.2 32.7 2038 2037.99 2038.93 48.4 51.2 2040 2039.99 2039.93 48.4 51.2 2041 2040.99 2049.93 48.4 51.2 2042 2041.99 2042.91 22.4 34.5 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 2047 2046.99 1.9 1.9 2048 2048.00 0.6 2055 2054.99 1.4 2056 2055.99 3.3 2057 2056.99 2057 2058 2059 2059 2058 2057.99 2059 1.6 11.2 2060 2059.98 2059 205 2061 2061.98 2065.93 72.2 57.7 <td>2033</td> <td>2032.99</td> <td>2032.94</td> <td>15.9</td> <td>12.0</td> <td></td> | 2033 | 2032.99 | 2032.94 | 15.9 | 12.0 | |
| 2035 2034.99 2034.93 28.0 18.0 2036 2035.99 2035.92 37.2 32.7 2038 2037.93 2037.93 47.9 48.2 2039 2038.99 2038.93 51.4 44.6 2040 2039.99 2038.93 51.4 44.6 2041 2040.99 2040.93 40.9 45.4 2042 2041.99 2042.91 22.4 34.5 2044 2043.99 2043.94 16.1 17.4 2045 2044.93 8.4 13.5 2044 2045.99 1.9 2048 2044.93 2045 2045.99 0.6 2053 2054.99 1.4 2056 2054.99 1.4 2056 2058 2059 205 2057 2056.99 205.99 3.3 2059 205 205 205 205 205 205 205 205 205 205 205 205 206 205 205 205 205 205 205 205 205 | 2034 | 2033.99 | 2033.92 | 22.8 | 17.5 | |
| 2036 2035.99 2036.99 2036.93 43.9 38.7 2037 2036.99 2036.93 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 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 2044.93 8.4 13.5 2046 2045.99 1.9 2048 2044.93 2047 2046.99 1.9 2048 2044.90 0.2 2053 2052.99 0.5 2054 2054.99 1.4 2056 2054.99 1.4 2056 2055.99 3.3 2057 2056.99 2059.98 2058.98 2059.93 205 2058 2059.98 2059.95 21.0 13.5 2061 2060.94 30.9 22.5 2061 2060.98 2065.95 21.0 13.5 <td< td=""><td>2035</td><td>2034.99</td><td>2034,93</td><td>28.0</td><td>18.0</td><td></td></td<> | 2035 | 2034.99 | 2034,93 | 28.0 | 18.0 | |
| 2037 2036.99 2037.93 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 2038.93 48.4 51.2 2041 2040.99 2041.94 35.0 31.9 2042 2043.99 2042.91 22.4 34.5 2044 2043.99 2044.93 8.4 13.5 2045 2044.99 2044.93 8.4 13.5 2046 2045.99 1.9 1.9 2048 2048.00 0.6 2049 2049.00 0.2 2053 2052.99 0.5 2054 2055.99 3.3 2055 2054.99 1.4 2056 2059.99 2057 2055 2058.98 2058.93 15.0 11.2 2060 2059.95 21.0 13.5 2061 2060.98 2061.94 44.3 33.9 2064 2063.98 2062.93 54.3 47.7 2064 | 2036 | 2035.99 | 2035.92 | 37.2 | 32.7 | |
| 2038 2037.99 2037.93 47.9 48.2 2039 2038.99 2038.93 51.4 44.6 2040 2039.99 204.93 40.9 45.4 2041 2040.99 204.93 40.9 45.4 2042 2041.99 204.94 35.0 31.9 2043 2042.99 2043.94 16.1 17.4 2045 2044.99 2045.96 4.3 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 2054.99 0.5 2055 2054.99 1.4 2056 2055.99 3.3 2057 2056.98 2056.98 4.8 5.0 2058 2057.99 2057.99 8.5 9.0 2059 2058.98 2058.93 15.0 11.2 2061 2062.98 2065.94 33.1 86.6 2062 2061.94 44.3 33.9 | 2037 | 2036.99 | 2036.93 | 43.9 | 38.7 | |
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| 2058 2057.99 2057.99 8.5 9.0 2059 2058.98 2058.93 15.0 11.2 2060 2059.98 2069.95 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 2065.94 85.4 69.1 2066 2065.98 2066.94 100 100 2068 2067.98 2066.94 100 100 2068 2067.98 2067.93 94.4 86.6 2069 2068.98 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 2074.87 3.7 7.0 2076 2075.99 1.3 2074.87 3.7 | 2057 | 2056.99 | 2056.98 | 4.8 | 5.0 | |
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| 2067 2066.98 2066.94 100 100 2068 2067.98 2067.93 94.4 86.0 2069 2068.98 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 0.3 0.3 | 2066 | 2065.98 | 2065.94 | 93.1 | 86.6 | |
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| 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 0.3 0.3 | 2069 | 2068.98 | 2068 94 | 79.9 | 90.5 | |
| 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 2074.87 3.7 7.0 2076 2075.99 0.3 | 2070 | 2069 98 | 2069 94 | 68.4 | 74.9 | |
| 2071 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 2075.99 0.3 | 2071 | 2070 98 | 2070 95 | 43.9 | 65.6 | |
| 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 2075.99 0.3 | 2072 | 2071.99 | 2071 94 | 31.6 | 33.3 | |
| 2074 2073.99 2073.96 8.5 13.0 2075 2074.99 2074.87 3.7 7.0 2076 2075.99 1.3 0.3 | 2073 | 2072 99 | 2072 97 | 166 | 20.5 | |
| 2015 2076 2074.99 2074.87 3.7 7.0 2076 2075.99 1.3 0.3 0.3 0.3 0.3 | 2074 | 2073 99 | 2073 96 | 8.5 | 19.0 | |
| 2076 2075.99 1.3 2077 2076.99 0.3 | 2075 | 2010.00 | 2074.87 | 3.7 | 7.0 | |
| 2077 2076.99 0.3 | 2076 | 2075 99 | 2014.01 | 1.9 | 1.0 | |
| | 2077 | 2076.99 | | 0.3 | | |

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

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 $[PMePh_3][Os_{11}C(CO)_{27} \{Cu(NCMe)\}] (m/z 2880) [D. Braga, K. Henrick, B.F.G. Johnson, J. Lewis, M. McPartlin, W.J.H. Nelson, A. Sironi and M.D. Vargas, J. Chem. Commun., (1983) 1131] have been described, further emphasising the utility of the method to characterise high molecular weight neutral and ionic cluster complexes.$

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