Oxidising Behaviour of Molybdenum and Tungsten Hexafluorides

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Summary Silver metal reacts with Mo_6F or WF_6 in acetonitrile to give $[Ag^{II}(NCMe)_4][Mo^{V}F_6]_2$ or $[Ag^{I}(NCMe)_2][W^{V}F_6]$ respectively; the results clearly show the greater oxidising power of MoF_6 as compared with WF_6.

It has been suggested previously[1] that molybdenum hexafluoride is a stronger oxidising agent than tungsten hexafluoride, but definitive evidence is lacking. Silver metal is oxidised by the hexafluorides in acetonitrile at room temperature to give soluble silver(II) hexafluoromolybdate(V) and silver(I) hexafluorotungstate(V) demonstrating unambiguously that MoF_6 is the stronger oxidising agent. The difference in behaviour is consistent with recent estimates of the hexafluorides' electron affinities.[2] The solvent properties of MeCN are crucial, for example in solvating Ag^+ (ref. 3) and Ag^{2+}. The oxidation of metals by this method is quite general; for example thallium and lead react with WF_6 in MeCN to give thallium(I) and lead(II) hexafluorotungstates(V) respectively.

The white, moisture-sensitive solids isolated from the Ag reactions have been characterised as $[Ag^{II}(NCMe)_4][Mo^{V}F_6]_2$ and $[Ag^{I}(NCMe)_2][W^{V}F_6]$ by elemental (C, H, F, and N) analysis, their i.r. spectra which show the presence of co-ordinated MeCN and bands assigned to MF_6^- anions by analogy with AMF_6 ($A = K$ or Cs, $M = Mo$ or W) compounds,[4] and the room temperature e.s.r. spectrum of the Ag^{II} compound, $g = 2{\cdot}3300$. Co-ordinated MeCN is readily replaced by pyridine, but its attempted removal by prolonged pumping leads to decomposition.

TABLE

Totally symmetric M–F stretching frequencies (cm^{-1})

MoF_6 in MeCN	740
$CsMoF_6$ (s)	676
$[Ag^{II}(NCMe)_4][Mo^{V}F_6]_2$ (s)	676
MoF_6^- in MeCN[a]	676
WF_6 in MeCN[b]	773
$CsWF_6$ (s)	695
$[Ag^{I}(NCMe)_2][W^{V}F_6]$ (s)	695
WF_6^- in MeCN[c]	770[d], 705, 695

[a] Ag^{II} and Cs compounds. [b] H. J. Clase, A. M. Noble, and J. M. Winfield, *Spectrochim. Acta*, 1969, **25A**, 293. [c] Ag^{I} and Cs compounds. [d] Not always observed.

Bands in the Raman spectra of MF_6 and MF_6^- compounds assigned to totally symmetric M–F stretching modes on the basis of solution polarisation measurements are given in the Table. Solutions containing the WF_6^- anion contain two completely polarised bands, and a third band at 770 cm^{-1} which is assigned to WF_6 is often observed in freshly prepared solutions. Tungsten pentafluoride disproportionates readily to give the tetra- and hexa-fluorides,[5] and a similar disproportionation has been noted for quinolin-8-ol derivatives of W^{V} in basic solution.[6] It is possible that the additional band near 700 cm^{-1} is due to formation of WF_6^{2-} by disproportionation.

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