Oxidation of Metals by Molybdenum and Tungsten Hexafluorides in Acetonitrile †

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The metals Ag, Tl, Pb, Zn, Cd, Hg, Mn, Co, Ni, and Cu are oxidised by molybdenum and tungsten hexafluorides in acetonitrile solution at ambient temperature. The products are solvated metal cations, the counter anions being hexafluoro-molybdate(V) or -tungstate(V). MoF_6 Oxidises Ag and Tl to Ag^{II} and Tl^{III} respectively whereas Ag^{I} and Tl^{I} are formed with WF_6. Thus MoF_6 is the stronger oxidising agent.

TUNGSTEN HEXAFLUORIDE is the weakest oxidising agent of the 5*d* series,[1] and is considered to be a weaker oxidising agent than molybdenum hexafluoride. For example MoF_6 oxidises both NO [2a] and $N_2H_6F_2$ [2b] and MoF_6 is reduced in many of its halogen-exchange reactions.[2c] Both hexafluorides are reduced to hexafluorometallates(V) by metal iodides in liquid SO_2,[3] and tetra-alkylammonium salts have been similarly obtained from MeCN or $MeNO_2$ solution.[4] Reaction in the absence of solvent is incomplete. The knowledge that such solvents are suitable reaction media for MoF_6 and WF_6 led to the present work, in which it has been shown that a variety of metals are oxidised by the hexafluorides and that under these conditions MoF_6 is the stronger oxidant. A preliminary account of some of this work has been given.[5]

† No reprints available.

[1] N. Bartlett, *Angew. Chem. Internat. Edn.*, 1968, **7**, 433; T. J. Richardson and N. Bartlett, *J.C.S. Chem. Comm.*, 1974, 427.

[2] (*a*) J. R. Geichman, E. A. Smith, S. S. Trond, and P. R. Ogle, *Inorg. Chem.*, 1962, **1**, 661; (*b*) B. Frlec, H. Selig, and H. H. Hyman, *Inorg. Chem.*, 1967, **6**, 1775; (*c*) T. A. O'Donnell and D. F. Stewart, *Inorg. Chem.*, 1966, **5**, 1434.

[3] G. B. Hargreaves and R. D. Peacock, *J. Chem. Soc.*, 1957, 4212; 1958, 3776.

[4] A. M. Noble, Ph.D. Thesis, University of Glasgow, 1970.

[5] A. Prescott, D. W. A. Sharp, and J. M. Winfield, *J.C.S. Chem. Comm.*, 1973, 667.

RESULTS AND DISCUSSION

The metals Cu, Ag, Zn, Cd, Hg, and Tl react rapidly with an excess of MoF_6 or WF_6 in MeCN at room temperature. The metals Mn, Co, Ni, and Pb react much more slowly and a slow reaction occurring between MoF_6 and MeCN prevented its reactions with Pb, Mn, and Ni from being studied in detail. The colour of the solutions obtained was, in general, characteristic of the solvated metal cations. The Raman spectra of the solutions contain a strongly polarised band at *ca.* 676 (Mo) or 695 (W) cm^{-1}. The spectra of caesium(I) hexafluorometallates(V) contain bands at similar frequencies, and hence the bands are assigned to the $\nu_1(a_{1g})$ mode of the $[MF_6]^-$ (M = Mo or W) anions. The ν_2 and ν_5 modes were not observed but this is not surprising as, by analogy with the spectra of MF_6 in MeCN, they would be very weak compared with ν_1. An additional polarised band at *ca.* 705 cm^{-1} in the WF_6 reaction solutions is assigned to $[WF_7]^-$,[6] and not to a tungsten(IV) species as originally suggested.[5]

TABLE 1

Analysis (%) of the solid products

Compound	Found (calc.) C	H	F	N
$Ag[MoF_6]_2\cdot 4MeCN$	14·7 (13·6)	1·5 (1·7)	34·2 (32·9)	8·3 (8·1)
$Ag[MoF_6]_2\cdot 4py$	29·5 (28·4)	2·7 (2·4)	29·6 (27·0)	6·3 (6·6)
$Ag[WF_6]\cdot 2MeCN$	9·6 (9·8)	1·3 (1·2)	23·0 (23·4)	5·7 (5·7)
$Tl[MoF_6]_3\cdot 6MeCN$	13·3 (13·3)	1·8 (1·7)	35·4 (31·7)	
$Tl[MoF_6]_3\cdot 6py$	27·7 (27·7)	2·9 (2·3)	24·3 (26·1)	7·1 (6·0)
$Tl^ITl^{III}[MoF_6]_4\cdot 2MeCN$	3·8 (3·6)	0·7 (0·5)	33·9 (34·1)	
$Tl[WF_6]$			23·6 (22·7)	
$Pb[WF_6]_2\cdot 2MeCN$	5·5 (5·4)	1·2 (0·7)	28·7 (25·8)	3·9 (3·2)
$Zn[MoF_6]_2\cdot 5MeCN$	17·4 (17·4)	2·4 (2·2)	27·3 (29·6)	11·2 (10·1)
$Zn[WF_6]_2\cdot 6MeCN$	15·8 (15·9)	2·0 (2·0)	27·7 (25·1)	8·2 (9·3)
$Cd[MoF_6]_2\cdot 5MeCN$	16·8 (16·3)	2·2 (2·1)	33·9 (31·0)	
$Cd[WF_6]_2\cdot 5MeCN$	12·9 (13·1)	2·0 (1·6)	25·4 (25·0)	7·3 (7·7)
$Hg[MoF_6]_2\cdot 4MeCN$	13·4 (12·3)	1·6 (1·5)	27·4 (29·0)	
$Mn[WF_6]_2\cdot 4MeCN$	12·4 (11·9)	2·0 (1·5)	26·9 (28·0)	
$Co[MoF_6]_2\cdot 5MeCN$	16·0 (17·6)	2·6 (2·2)	30·3 (33·4)	9·4 (10·2)
$Co[WF_6]_2\cdot 5MeCN$	14·1 (14·0)	2·2 (1·7)	26·9 (26·5)	8·5 (8·1)
$Ni[WF_6]_2\cdot 6MeCN$ [a]	16·7 (16·0)	2·0 (2·0)	25·6 (25·3)	7·8 (9·3)
$Cu[MoF_6]_2\cdot 5MeCN$	16·3 (17·4)	2·1 (2·2)	33·4 (33·2)	
$Cu[MoF_6]_2\cdot 4py$	33·4 (30·0)	3·4 (2·5)	27·5 (28·5)	8·7 (7·0)
$Cu[MoF_6]\cdot 4MeCN$	21·9 (21·9)	2·9 (2·2)	25·7 (26·0)	
$Cu[WF_6]_2\cdot 5MeCN$	13·9 (13·9)	2·0 (1·7)	28·7 (26·4)	7·9 (8·1)
$Cu[WF_6]\cdot 4MeCN$	18·4 (18·3)	2·2 (2·3)	21·9 (21·7)	10·5 (10·6)

[a] Ni 6·0 (6·5)%.

The involatile solids isolated from these reactions are moisture sensitive, the molybdenum-containing products being particularly reactive in this respect. Prolonged pumping usually leads to loss of MeCN and eventual decomposition. Although the characterisation of some products is incomplete, on the basis of their analysis (Table 1) and spectra (Table 2) the solids are formulated as solvated metal hexafluoromolybdates(V) and hexafluorotungstates(V). In many cases the Raman spectra of the latter indicate that the heptafluorotungstate(VI) anion is also present.

Co-ordination of MeCN to the metal cations, except for Tl^I, is suggested from the i.r. spectra of the solids. The colours and reflectance spectra of the Co^{II} and Ni^{II} salts are consistent with the presence of octahedrally co-ordinated metals; similarly Cu^{II} appears to have a pseudo-octahedral environment. The solid Mn^{II} compounds are colourless, but in solution they are yellow-green suggesting a tetrahedral environment for Mn^{II}.[7]

Except for nickel(II) hexafluorotungstate(V) the compounds are appreciably soluble in MeCN and silver(I) hexafluorotungstate(V) is also soluble in benzene. The Raman spectra of the redissolved solids are similar to those of the original solutions (Table 3) and addition of pyridine to some solutions results in the formation of metal–pyridine complexes (Table 1).

In some cases the products isolated depend on the ratio of metal : hexafluoride used in the reaction. With a large excess of MoF_6, the product isolated from the oxidation of Tl is $Tl[MoF_6]_3\cdot 6MeCN$, but with the mole ratio Tl : MoF_6 *ca.* 1 : 2 the yellow salt isolated is formulated as $Tl^ITl^{III}[MoF_6]_4\cdot 2MeCN$ by analogy with 'thallium dibromide.'[8] It hydrolyses more slowly than the Tl^{III} compound. Solutions containing Cu^{II} are rapidly reduced by copper metal to give copper(I) hexafluorometallates(V). Equilibria between Hg^I and Hg^{II} species are possibly important in the Hg oxidation reactions. There is evidence for the presence of Hg_2^{2+} in the Raman spectrum of the Hg–WF_6 solutions, although decomposition occurred to give metallic Hg and a cream solid when the solvent was removed. The product from the corresponding reaction with MoF_6 appears to be a Hg^{II} compound. It is noteworthy that oxidation of Hg by the hexafluorides in the absence of solvent produces $Hg[WF_6]_2$ or $Hg_2[MoF_6]_2$ respectively,[9] and by AsF_5 in

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[6] A. Prescott, D. W. A. Sharp, and J. W. Winfield, preceding paper.

[7] F. A. Cotton, D. M. L. Goodgame, and M. Goodgame, *J. Amer. Chem. Soc.*, 1962, **84**, 167.

[8] A. C. Hazell, *J. Chem. Soc.*, 1963, 3459.

[9] I. D. MacLeod, Ph.D. Thesis, University of Melbourne, 1974.

TABLE 2

Spectra of the solid products

Compound	Colour	Raman and i.r. spectra (in cm^{-1}) and assignments [a,b] $\nu_1(MF_6^-)$	$\nu_3(MF_6^-)$	$\nu(WF_7^-)$	Electronic spectra (in cm^{-1}) and tentative assignments [c]	E.p.r. spectra
$Ag[MoF_6]_2 \cdot 4MeCN$	White	676	620			$\langle g \rangle = 2{\cdot}330$
$Ag[WF_6] \cdot 2MeCN$	White	695	590			
$Tl^ITl^{III}[MoF_6]_4 \cdot 2MeCN$	Yellow	Decomp.	620			
$Tl[WF_6]$	White	695	590			
$Pb[WF_6]_2 \cdot 2MeCN$	Cream	698m	570	710m		
$Zn[MoF_6]_2 \cdot 5MeCN$	White	678	625			
$Zn[WF_6]_2 \cdot 6MeCN$	Cream	695m		709m		
$Cd[MoF_6]_2 \cdot 5MeCN$	White	679	625			
$Cd[WF_6]_2 \cdot 5MeCN$	Cream	695s		707m		
$Hg[MoF_6]_2 \cdot 4MeCN$	Cream	678	620			
$Mn[WF_6]_2 \cdot 4MeCN$	White	697m		705s		
$Co[MoF_6]_2 \cdot 5MeCN$	Pink	677			21 800, ${}^4T_{1g}(F) \longrightarrow {}^4T_{1g}(P)$	
$Co[WF_6]_2 \cdot 5MeCN$	Salmon	694			21 800	
$Ni[WF_6]_2 \cdot 6MeCN$	Blue-pink	695m		709m	11 000, ${}^3A_{2g} \longrightarrow {}^3T_{2g}$ 17 700, ${}^3A_{2g} \longrightarrow {}^3T_{1g}(F)$ 28 200, ${}^3A_{2g} \longrightarrow {}^3T_{1g}(P)$	
$Cu[MoF_6]_2 \cdot 5MeCN$	Blue	677	625		13 350	$\langle g \rangle = 2{\cdot}129$
$Cu[MoF_6] \cdot 4MeCN$	Yellow	676	625			
$Cu[WF_6] \cdot 4MeCN$	Yellow	695	595			

[a] Assignments by comparison with the spectra of $Cs[MoF_6]$ ν_1 677, ν_3 623; $Cs[WF_6]$ ν_1 695, ν_3 594; $Tl[WF_7]$ $\nu(WF)$ 705 cm^{-1}. [b] Except for $Tl[WF_7]$ bands at *ca.* 2 300 and 940 cm^{-1}, assigned to co-ordinated MeCN (R. J. H. Clark, J. Lewis, D. J. Machin, and R. S. Nyholm, *J. Chem. Soc.*, 1963, 379; J. Reedijk, A. P. Zuur, and W. L. Groeneveld, *Rec. Trav. chim.*, 1967, **86**, 1127) were observed. [c] Assignments by comparison with $[M(NCMe)_6]^{2+}$; M = Co 20 400; M = Ni 10 600, 17 500, 28 100; M = Cu 13 450 cm^{-1} (B. J. Hathaway, D. G. Holah, and A. E. Underhill, *J. Chem. Soc.*, 1962, 2444; A. E. Wickenden and R. A. Krause, *Inorg. Chem.*, 1965, **4**, 404; J. Reedijk and W. L. Groeneveld, *Rec. Trav. chim.*, 1967, **86**, 1103.)

SO_2 gives $Hg_{2.86}AsF_6$, Hg_4^{2+}, Hg_3^{2+}, or Hg_2^{2+} depending on the reaction stoicheiometry.[10]

Evidence that $[WF_6]^-$ reacts with WF_6 in MeCN to give $[WF_7]^-$ has been given elsewhere,[6] and the experimental conditions under which the oxidation reactions are carried out are likely to be the major influence on the relative proportions of $[WF_6]^-$ and $[WF_7]^-$ ions present in the solid products. For example both Zn and Cd react with WF_6 more slowly than does Ag. The products are less soluble in MeCN than is silver(I) hexafluorotungstate(V). Consequently the ratio of $[WF_6]^-$ to $[WF_7]^-$ may be disturbed either by co-precipitation of $[WF_7]^-$ with $[WF_6]^-$ during the oxidation or by some irreversible change in the equilibrium between WF_5 and its disproportionation products.[11]

TABLE 3

Raman spectra (M–F stretching region) of the reaction mixtures

Reactants [a]	Colour	Raman bands (cm^{-1}) and assignments [b] $\nu_1(MF_6^-)$	$\nu(WF_7^-)$	$\nu_1(MF_6)$
$Ag + MoF_6$	Colourless	676		740
$Ag + WF_6$	Pale yellow	695s	705m	770m
$Tl + MoF_6$	Colourless	677		
$Tl + WF_6$	Colourless	695s	705w	
$Pb + MoF_6$	Colourless	677		
$Pb + WF_6$	Yellow	695m	707m	
$Zn + MoF_6$	Colourless	676		
$Zn + WF_6$	Yellow [c]	695	705	
$Cd + MoF_6$	Colourless	676		
$Cd + WF_6$	Colourless	695s	705w	
$Hg + MoF_6$	Pale yellow	677		
$Hg + WF_6$	Yellow [c,d]	695	705	770
$Mn + MoF_6$	Yellow-green	677		
$Mn + WF_6$	Yellow-green [c]	696	705	
$Co + MoF_6$	Pink	678		
$Co + WF_6$	Pink [c]	695	710	
$Ni + WF_6$	Green	Sparingly soluble		
$Cu + MoF_6$	Blue	676		
$Cu(excess) + MoF_6$	Yellow	678		
$Cu + WF_6$	Blue		705	
$Cu(excess) + WF_6$	Yellow	695		

[a] In MeCN solution. [b] Strongly polarised. Assignments by comparison with the spectra of $Cs[MoF]_6$ ν_1 677, $Cs(Et_4N)[WF_6]$ ν_1 694, $Tl[WF_7]$ $\nu(WF)$ 705 (ref. 16), MoF_6 ν_1 740, WF_6 ν_1 773 cm^{-1} (H. J. Clase, A. M. Noble, and J. M. Winfield, *Spectrochim. Acta*, 1969, **25A**, 293). [c] Relative peak heights depend on the reaction stoicheiometry. [d] Band at 167 cm^{-1} assigned to Hg_2^{2+} (L. A. Woodward, *Phil. Mag.*, 1934, **18**, 323; H. Stammreich and T. Teixeira Sans, *J. Mol. Structure*, 1967–68, **1**, 55).

An analogous reaction between $[MoF_6]^-$ and MoF_6 might be assumed to occur in solution, particularly as complexes between MoF_5 and MeCN are known.[12] No reaction between $[MoF_6]^-$ and MoF_6 was detected in solution (*cf.* ref. 13) although there is some evidence of an interaction between F^- ion and MoF_6.

The reactions described above provide the first unambiguous demonstration that MoF_6 is a stronger oxidising agent than WF_6. Previous comparisons [2] involved situations in which WF_6 did not react. The behaviour of the hexafluorides is qualitatively in accord with recent estimates of their electron affinities.[14] The role of the acetonitrile, in addition to providing a suitable

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[10] B. D. Cutforth, C. G. Davies, P. A. W. Dean, R. J. Gillespie, P. R. Ireland, and P. K. Ummat, *Inorg. Chem.*, 1973, **12**, 1343; B. D. Cutforth, R. J. Gillespie, and P. R. Ireland *J.C.S. Chem. Comm.*, 1973, 723; I. D. Brown, B. D. Cutforth, C. G. Davies, R. J. Gillespie, P. R. Ireland, and J. E. Vekris, *Canad. J. Chem.*, 1974, **52**, 791.

[11] J. Schröder and F. J. Grewe, *Chem. Ber.*, 1970, **103**, 1536.

[12] M. Mercer, T. J. Ouellette, C. T. Ratcliffe, and D. W. A. Sharp, *J. Chem. Soc.* (*A*), 1969, 2532; J. C. Fuggle, D. W. A. Sharp, and J. M. Winfield, *J. Fluorine Chem.*, 1971/72, **1**, 427.

[13] S. Brownstein, *Canad. J. Chem.*, 1973, **51**, 2530.

[14] J. Burgess, I. Haigh, R. D. Peacock, and P. Taylor, *J.C.S. Dalton*, 1974, 1064.

dielectric medium, is in the solvation of the metal cations. Although it is too weak a donor to stabilise abnormally high or low oxidation states of most *d* block elements,[15] it is crucial in stabilising Cu^{I} and Cu^{II}, Ag^{I} and Ag^{II}, and Tl^{I} and Tl^{III}.[16]

EXPERIMENTAL

Experimental methods used were as described elsewhere,[6] except for the following. Electronic reflectance spectra were obtained using a Perkin-Elmer 450 instrument, samples being mounted between silica plates separated by a Teflon spacer. Analysis are by Bernhard; analytical figures for fluoride are often not good because of partial hydrolysis of the complexes and because of interference by metal ions during the analysis. Molybdenum hexafluoride (Alfa) was purified in a manner similar to WF_6.[6] Metals used were at least 99·9%. Metal foil (Co, Ni, Cu, Ag, Zn, or Cd) or metal wire (Pb) was degreased and a fresh surface exposed with abrasive paper. Mn Pieces were broken to obtain splinters and Tl rod was freshly cut. Redistilled Hg was used as received. AnalaR pyridine was dried over activated molecular sieves.

Reactions between Hexafluorides and Metals.—No reaction was observed between WF_6 and dry MeCN even after several weeks at room temperature, however some reaction was apparent between MoF_6 and MeCN after 12 h. A mixture of MF_6 and MeCN was distilled onto a small quantity of metal, which had been degassed for at least 0·5 h. Reactions occurred at ambient temperature. Those between WF_6 and Cu, Ag, Tl, or Pb were complete within 1 h but Co, Ni, Zn, or Cd required shaking for up to 3 days before reaction was complete. Reactions between MoF_6 and metals often appeared to be slower than the corresponding reactions with WF_6 and in some cases reaction with the solvent occurred before an adequate yield of product could be isolated.

In moist MeCN Ag metal reacted with MoF_6 to give a yellow compound, more resistant to hydrolysis than Ag^{II} hexafluoromolybdate(V). This compound contained a strong band in its i.r. spectrum at 1 030 cm^{-1}, a region characteristic of the Mo=O linkage.[17] It was formulated as $Ag^{II}Mo^{V}OF_5 \cdot 4MeCN$ (Found: C, 19·0; H, 3·4; F, 20·0. $C_8H_{12}F_5N_4OAgMo$ requires C, 20·4; H, 2·7; F, 19·8%). Addition of pyridine to the solution gave an orange solid formulated as $Ag^{II}Mo^{V}OF_5 \cdot 3py$ (Found: C, 33·1; H, 3·4 F, 17·5; N, 8·0. $C_{15}H_{15}F_5N_3OAgMo$ requires C, 32·6; H, 2·7; F, 17·2; N, 7·6%).

We thank Mrs. A. Pettrigrew, Dr. A. P. Lane, Dr. A. L. Porte, and Mrs. A. McConnell (University of Strathclyde) for help in obtaining the spectra, and the S.R.C. for a grant towards the Raman spectrometer. A. P. gratefully acknowledges the award of a Turner and Newall Fellowship.

[4/1777 *Received, 28th August, 1974*]

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[15] B. J. Hathaway and D. G. Holah, *J. Chem. Soc.*, 1965, 537.

[16] V. A. Pleskov, *Zhur. fiz. Khim.*, 1948, **22**, 351; I. M. Kolthoff and J. F. Coetzee, *J. Amer. Chem. Soc.*, 1957, **79**, 1852; H. L. Yeager and B. Kratochvil, *J. Phys. Chem.*, 1969, **73**, 1963.

[17] I. R. Beattie, K. M. S. Livingston, D. J. Reynolds, and G. A. Ozin, *J. Chem. Soc. (A)*, 1970, 1210.