Formation of Metal Heptafluorotungstates(VI) in Acetonitrile †

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Thallium(I) and copper(II) fluorides react with tungsten hexafluoride in acetonitrile and the soluble adducts $TlF \cdot WF_6$ and $CuF_2 \cdot 2WF_6 \cdot 5MeCN$ are isolated from solution. The adducts are formulated as metal heptafluorotungstates(VI). The hexafluorotungstate(V) anion behaves as a fluoride-ion donor in MeCN, reacting with WF_6 to give the WF_7^- anion as one product.

SEVERAL studies of the behaviour of tungsten hexafluoride towards ionic fluorides have been reported,[1,2] the reactions being carried out in the presence of bromine and bromine trifluoride,[1a] iodine pentafluoride,[1b] or chlorine trifluoride,[1c] or in the absence of a liquid phase.[2] The 1 : 1 or 1 : 2 $WF_6 \cdot MF$ (M = Na, Cs, or NH_4) adducts obtained have, in some cases,[1] been formulated as $M[WF_7]$ or $M_2[WF_8]$ salts, mainly on the basis of *X*-ray powder diffraction data. Similar adducts between WF_6 and nitryl or nitrosyl fluorides [3] appear, from their i.r. spectra,[3a] to contain $[NO_2]^+$ or $[NO]^+$ cations. However the presence in solution of the anions $[WF_7]^-$ and $[WF_8]^{2-}$ has not been demonstrated.

This paper describes the formation in acetonitrile of soluble heptafluorotungstate(VI) salts. A related investigation of the reactions between WF_6 and metals in MeCN is described elsewhere.[4]

RESULTS AND DISCUSSION

Preparation and Solution Behaviour of Metal Fluoride–Tungsten Hexafluoride Adducts.—Anhydrous thallium(I) and copper(II) fluorides are sparingly soluble in MeCN but dissolve readily in the presence of WF_6, a blue solution being obtained in the latter case. When the mole ratios $WF_6 : TlF$ and $WF_6 : CuF_2$ are respectively $\geqslant 1 : 1$ and $\geqslant 2 : 1$, the solids remaining after removal of volatile material correspond to $TlF \cdot WF_6$, white, and $CuF_2 \cdot 2WF_6 \cdot 5MeCN$, blue. They are involatile at room temperature, moisture sensitive, particularly the Cu^{II} adduct, and are soluble in MeCN without apparent decomposition. The Cu^{II} adduct exhibits a broad e.p.r. signal, $\langle g \rangle$ 2·172, at room temperature. It reacts with copper metal in MeCN to give a yellow solution from which a Cu^{I} compound is isolated. The Tl^{I} and Cu^{II} adducts are characterised from their analysis and vibrational spectra ‡ as $Tl[WF_7]$ and $[Cu(NCMe)_5][WF_7]_2$. Their ^{19}F n.m.r. spectra, which are discussed below, provide supporting evidence.

The compounds contain a strong characteristic band at *ca.* 705 cm^{-1} in both their solid and solution Raman spectra. Bands attributable to WF_6,[5] particularly its a_{1g} mode at *ca.* 770 cm^{-1}, are absent. The i.r. spectra of the solids contain a strong band at 620 cm^{-1} which may be compared with a similar band in the spectra of $[WF_7]^-$ salts having Group I, $[NO]^+$, or $[NO_2]^+$ cations,[6,3a] and the spectrum of the Cu^{II} compound indicates the presence of co-ordinated MeCN.

As expected, the position of the strong band (presumably a W–F stretching mode) in the Raman spectra is intermediate between those of the analogous bands in the isoelectronic $[TaF_7]^{2-}$ (640 or 651 cm^{-1}) [7] and ReF_7 (736 cm^{-1}) [8] compounds. Qualitatively the vibrational spectrum of $Tl[WF_7]$ is more like that of ReF_7 than $[TaF_7]^{2-}$,

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† No reprints available.

‡ The details of the vibrational spectra are deposited as a Supplementary Publication (SUP 21292, 2 pp.). For details of this Scheme see *J.C.S. Dalton*, 1974, Index issue, ' Notice to Authors No. 7.'

[1] (*a*) B. Cox, D. W. A. Sharp, and A. G. Sharpe, *J. Chem. Soc.*, 1956, 1242; (*b*) G. B. Hargreaves and R. D. Peacock, *J. Chem. Soc.*, 1958, 2170; (*c*) N. S. Nikolaev and V. F. Sukhoverkhov, *Doklady Akad. Nauk S.S.S.R.*, 1961, **136**, 621.

[2] H. C. Clark and H. J. Emeléus, *J. Chem. Soc.*, 1957, 4778; S. Katz, *Inorg. Chem.*, 1964, **3**, 1598; *ibid.*, 1966, **5**, 666.

[3] (*a*) J. R. Geichman, E. A. Smith, and P. R. Ogle, *Inorg. Chem.*, 1963, **2**, 1012; (*b*) N. Bartlett, S. P. Beaton, and N. K. Jha, *Chem. Comm.*, 1966, 168.

[4] (*a*) A. Prescott, D. W. A. Sharp, and J. M. Winfield, *J.C.S. Chem. Comm.*, 1973, 668; (*b*) *J.C.S. Dalton*, following paper.

[5] B. Weinstock and G. L. Goodman, *Adv. Chem. Phys.*, 1965, **9**, 169; H. J. Clase, A. M. Noble, and J. M. Winfield, *Spectrochim. Acta*, 1969, **25A**, 293.

[6] R. D. Peacock and D. W. A. Sharp, *J. Chem. Soc.*, 1959, 2763.

[7] O. L. Keller, jun., and A. Chetham-Strode, *Inorg. Chem.*, 1966, **5**, 367; W. P. Griffith and T. D. Wickins, *J. Chem. Soc.* (*A*), 1967, 675.

[8] H. H. Claassen, E. L. Gasner, and H. Selig, *J. Chem. Phys.*, 1968, **49**, 1803.

but assignment of a structure to $[WF_7]^-$ from the present data is not possible.

The ^{19}F n.m.r. spectra of Tl^{I} and Cu^{II} heptafluorotungstates(VI) in MeCN are consistent with, although do not prove, the existence of $[WF_7]^-$. Single line (width at half-height 50 Hz) spectra are observed in each case, Tl^{I} δ 144, Cu^{II} δ 142 p.p.m., to higher field than WF_6 in MeCN, δ 166 p.p.m. Interestingly Cu^{II} has little effect on the chemical shift of $[WF_7]^-$, suggesting, as does the similar half widths in the Tl^{I} and Cu^{II} salts, that there is no strong interaction between the ions in solution. Addition of WF_6 to a $Tl[WF_7]$ solution results in a shift of the n.m.r. signal to lower applied field. Separate signals were not observed indicating rapid exchange between WF_6 and $[WF_7]^-$, although the Raman spectrum of the solution indicates the presence of the two species. Similarly, exchange between $W^{18}F_6$ and $Tl[WF_7]$ in MeCN is complete within 1 h at room temperature.* The ability of $[WF_7]^-$ to act as a fluoride-ion donor is illustrated also by the behaviour of $Tl[WF_7]$ towards arsenic pentafluoride. The ^{19}F n.m.r. spectrum of the mixture in MeCN consists of a 1 : 1 : 1 : 1 quartet, δ −76 p.p.m., $^1J_{AsF}$ 930 Hz, assigned to $[AsF_6]^-$, and a single peak, δ 168 (width at half-height 150 Hz), assigned to WF_6.

Of the fluoro-anions isoelectronic with $[WF_7]^-$ only $[TaF_7]^{2-}$ has been observed in solution.[7] The dissociation $[MF_7]^{n-} \longrightarrow [MF_6]^{(n-1)-} + F^-$ occurs in aqueous solution where $n = 3$ and M = Zr [9] or Hf,[10] in aqueous HF where $n = 2$ and M = Nb,[11] and in anhydrous HF where $n = 2$ and M = Ta.[12] The $[TaF_7]^{2-}$ anion exists only in solutions which have a high fluoride ion activity. In the present work the formation of $[WF_7]^-$ from WF_6 and F^- ion must be favoured by the poor solvating properties of MeCN towards F^- ion. There is no evidence of a reaction in solution between $Tl[WF_7]$ and TlF, or of the formation of a 1 : 1 $CuF_2{\cdot}WF_6$ adduct, suggesting that $[WF_7]^-$ is a weaker fluoride-ion acceptor than $[WF_6]$.

Reaction of Hexafluorotungstate(V) *Ion with Tungsten Hexafluoride in Acetonitrile.*—The behaviour of hexafluorotungstate(V) salts towards fluoride-ion acceptors in CH_2Cl_2 or liquid SO_2 has recently been discussed in terms of the disproportionation of $[WF_6]^-$ and concurrent formation of complex anions.[13] We find that $[WF_6]^-$ acts as a fluoride-ion donor to arsenic or phosphorus pentafluorides. Addition of AsF_5 or PF_5 to Ag^{I} hexafluorotungstate(V) [4] in MeCN produces the $[AsF_6]^-$ or $[PF_6]^-$ anions, which are identified by their ^{19}F n.m.r. spectra, $[AsF_6]^-$ δ −61 p.p.m., $^1J_{AsF}$ 940 Hz, $[PF_6]^-$ δ −64 p.p.m., $^1J_{PF}$ 704 Hz, and for $[AsF_6]^-$ by its ^{75}As INDOR spectrum, $^1J_{AsF}$ 955 Hz. The solids isolated from these solutions are mixtures, but their i.r. spectra indicate that $[AsF_6]^-$ or $[PF_6]^-$ are present.

Similar behaviour is observed between silver(I) hexafluorotungstate(V) and WF_6. The Raman spectrum of a mixture in MeCN contains three strongly polarised bands, two of which at 770 and 695 cm^{-1} are assigned to WF_6 [5] and $[WF_6]^-$ (ref. 4) respectively. The intensity of the third band, at 705 cm^{-1}, increases with increasing WF_6 concentration, and by analogy with the spectra * is assigned to $[WF_7]^-$. No attempt was made to isolate a solid from this reaction, but a yellow solid isolated from the reaction of cadmium(II) hexafluorotungstate(V) [4] with a large excess of WF_6 is formulated, from its analysis and spectra, as predominantly $Cd[WF_7]_2{\cdot}5MeCN$.

The other product from these reactions is presumably solvated tungsten pentafluoride. No spectroscopic evidence for its formation could be obtained, although the pale yellow colour of silver(I) hexafluorotungstate(V) deepens when WF_6 is added. Solid WF_5 disproportionates at room temperature,[14] and there is some evidence that it disproportionates in MeCN. A broad peak (width at half height 160 Hz, δ 166 p.p.m.) in the ^{19}F n.m.r. spectrum of the $[WF_6]^-$–AsF_5 solution is assigned to WF_6, possibly exchanging with another species. The other product isolated from the reaction of cadmium(II) hexafluorotungstate(V) with WF_6 is a small quantity of brown solid. It was not obtained in sufficient quantities for analysis, but is characterised by a band at 580 cm^{-1} in its Raman spectrum, and it may be a tungsten(IV) compound.

EXPERIMENTAL

All manipulations were performed in a Pyrex vacuum system or in a Lintott inert-atmosphere box, H_2O and O_2 concentrations <15 p.p.m. Raman and i.r. spectra were obtained using Spex Ramalog and Perkin-Elmer 457 instruments. Samples for Raman spectra were contained in thin-wall Pyrex capillaries; i.r. spectra were obtained as Nujol mulls between AgCl plates. ^{19}F N.m.r. spectra at 56·4 MHz were obtained using a Jeol C60 HL instrument on 0·5—1·0M-solutions. Spectra were externally referenced w.r.t. WF_6 or CCl_3F, and are expressed as δ values (positive to low field of CCl_3F). A Schomandl frequency synthesiser and XY recorder were used to obtain the ^{75}As INDOR spectrum. The e.p.r. spectrum was recorded using a Decca X3 spectrometer combined with a Newport 11 in magnet system, the powdered sample being sealed in a quartz tube. Analyses were by Bernhardt.

Tungsten hexafluoride (Alfa), arsenic pentafluoride (PCR Inc), and phosphorus pentafluoride (Matheson) were purified by trap-to-trap distillation and stored over NaF. Acetonitrile (B.D.H.) was purified and dried by several refluxes over P_2O_5, and stored *in vacuo* over Linde 4A molecular sieves. Thallium(I) and copper(II) fluorides (K and K Laboratories and Ozark Mahoning respectively) were used as received, being always handled in the inert-atmosphere box. Their stated purity was $\geqslant 99{\cdot}5\%$. Silver(I) and cadmium(II) hexafluorotungstates(V) were prepared as described elsewhere.[4]

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[9] L. Kolditz and A. Feltz, *Z. anorg. Chem.*, 1961, **310**, 195.

[10] P. A. W. Dean and D. F. Evans, *J. Chem. Soc.* (*A*), 1967, 698.

[11] O. L. Keller, jun., *Inorg. Chem.*, 1963, **2**, 783.

[12] N. A. Matwiyoff, L. B. Asprey, and W. E. Wageman, *Inorg. Chem.*, 1970, **9**, 2014.

[13] S. Brownstein, *J. Inorg. Nuclear Chem.*, 1973, **35**, 3575.

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

Reactions were carried out in Pyrex flasks fitted with PTFE, glass stop-cocks (West-Glass Inc. or Rotaflow).

Similar flasks, fitted with Raman or n.m.r. sample tubes, were used to obtain solutions for spectroscopic examination.

Reactions of WF_6 *with Metal Fluorides.*—A mixture of anhydrous TlF (3·5 mmol), WF_6 (4·9 mmol), and MeCN (0·83 g) was shaken for several hours at room temperature. A colourless solution was produced from which after removal of volatile material (1·23 g; required for a 1 : 1 reaction 1·23 g) a white solid was isolated. This was identified as *thallium*(I) *heptafluorotungstate*(VI) (3·45 mmol) (Found: F, 25·2; W, 34·2. F_7TlW requires F, 25·5; W, 35·3%). Similarly prepared from anhydrous CuF_2 was *pentakis(acetonitrile)copper*(II) *heptafluorotungstate*(VI) (Found: C, 14·0; H, 1·7; Cu, 7·0; F, 30·4; N, 7·5; W, 39·1. $C_{10}H_{15}CuF_{14}N_5W_2$ requires C, 13·3; H, 1·7; Cu, 7·0; F, 29·5; N, 7·8; W, 40·8%). Copper metal reacted with $[Cu(NCMe)_5][WF_7]_2$ (1 : 1 mol ratio) in MeCN during several hours at room temperature giving a yellow solution from which a yellow solid was isolated. Its analysis (Found: C, 17·5; H, 2·4; Cu, 10·6; F, 25·8; N, 10·2; W, 31·8. $C_8H_{12}CuF_7N_4W$ requires C, 17·6; H, 2·2; Cu, 11·7; F, 24·4; N, 10·3; W, 33·8%) was consistent with *tetrakis(acetonitrile)copper*(I) *heptafluorotungstate*(VI) but its vibrational spectrum indicated the presence of an additional species, possibly $[WF_7]^{2-}$ as WF_6 is reduced by Cu metal.[4b] Raman (solution) $\nu_{max.}$ 710 and 690 cm^{-1}, both strongly polarised. I.r. (mull) $\nu_{max.}$ 2310w, 2280w, 724m, 682m, and 619s cm^{-1}. Its ^{19}F n.m.r. spectrum consisted of a single peak δ 143 p.p.m.

In moist MeCN the products isolated from the above reactions contained oxofluoride impurities as shown by the presence of a strong band at *ca.* 1000 cm^{-1} in their i.r. spectra assigned to $\nu(W=O)$.[15]

Reactions of $[WF_6]^-$ *with Fluoride-ion Acceptors.*—The reactions occurring between silver(I) hexafluorotungstate(V) and WF_6, AsF_5, or PF_5 in MeCN were examined by Raman or ^{19}F n.m.r. spectroscopy. The n.m.r. parameters obtained were in reasonable agreement with those reported for the anions $[AsF_6]^-$ and $[PF_6]^-$ (ref. 16). The i.r. spectra of the solids isolated from the AsF_5 and PF_5 reactions contained bands at 705 cm^{-1} and at 835 and 560 cm^{-1}, respectively, characteristic of $[AsF_6]^-$ and $[PF_6]^+$.[17]

A large excess of WF_6 was added to a solution of cadmium(II) hexafluorotungstate(V) in MeCN and the mixture was shaken at room temperature for 24 h. Removal of volatile material left a yellow solid together with a small quantity of brown solid. The former was identified as predominantly *pentakis(acetonitrile)cadmium*(II) *heptafluorotungstate*(VI) (Found: C, 13·6; H, 1·9; Cd, 11·8; F, 29·5; W, 38·2. $C_{10}H_{15}CdF_{14}N_5W_2$ requires C, 12·6; H, 1·6; Cd, 11·8; F, 28·0; W, 38·7%). Its vibrational spectrum indicated that the $[WF_6]^-$ anion was also present. Raman (solution) $\nu_{max.}$ 705s,pol; (solid) $\nu_{max.}$ 695m and 707s cm^{-1}.

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[15] I. R. Beattie, K. M. S. Livingston, D. J. Reynolds, and G. A. Ozin, *J. Chem. Soc.* (*A*), 1970, 1210; L. B. Asprey, R. R. Ryan, and E. Fukushima, *Inorg. Chem.*, 1972, **11**, 3122.

[16] E. L. Muetterties and W. D. Phillips, *J. Amer. Chem. Soc.*, 1959, **81**, 1084.

[17] G. M. Begun and A. C. Rutenberg, *Inorg. Chem.*, 1967, **6**, 2212.