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REDOX REACTIONS INVOLVING MOLYBDENUM, TUNGSTEN AND URANIUM HEXAFLUORIDES IN ACETONITRILE

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SUMMARY

The redox properties of molybdenum, tungsten and uranium hexafluorides in acetonitrile at 298 K have been compared with other redox couples using cyclic voltammetry, and by carrying out appropriate redox reactions under carefully controlled conditions. The order of oxidizing ability established is $UF_6 > MoF_6 > NO^+ >$ solvated $Cu^{2+} \geqslant WF_6$. The position of the solvated Tl^{3+} cation probably lies between MoF_6 and Cu^{2+} Reactions which occur in the Cu metal/solvated Cu^{n+} (n = 1 or 2)/WF_6 system are accounted for by redox and fluoride-ion-transfer equilibria.

INTRODUCTION

The oxidizing abilities of molybdenum tungsten and uranium hexafluorides have attracted considerable attention. Their electron affinities have been determined by various methods, for example ion cyclotron resonance spectroscopy [1], molecular-beam reactions with alkali metals [2], thermochemistry of hexafluorometallate(V) salts [3], and effusion mass spectrometry [4]. Although there is some disagreement as to their precise values, particularly for MoF_6, most data indicate that the order of electron affinities is $UF_6 > MoF_6 > WF_6$. This order is also indicated by the electronic spectra of the hexafluorides' charge transfer complexes [5], and is consistent with their gas-phase redox chemistry [6].

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The redox couples MF_6/MF_6^-, M = Mo and W, have been identified in anhydrous hydrogen fluoride [7] and in acetonitrile [8] by cyclic voltammetry. In both solvents MoF_6 is the stronger oxidant, the difference in half-wave potentials, $E_{\frac{1}{2}}$ V, being ca. 1 V. The oxidation of several metals by MoF_6, WF_6, or UF_6 in MeCN was reported several years ago [9], but detailed comparisons among their oxidizing abilities and those of other redox couples in MeCN could not be made. This has now been accomplished by a combination of cyclic voltammetry and the study of selected redox reactions under defined conditions.

RESULTS AND DISCUSSION

Cyclic voltammetry

Cyclic voltammetry of hexafluorometallate(V) and heptafluorotungstate(VI) salts in purified acetonitrile was performed using the evacuable, Pyrex cell shown in Figure 1.

The cell consists of three sections, made from 24 and 15-10 mm dia. tubing, and joined by B.14 and B.19 greaseless 'O'-ring joints. Connections to vacuum and to storage ampoules for reference, bridging, and working electrolytes, and for the solvent are by P.T.F.E., Pyrex stop-cocks. The working, reference, and bridge compartments of the cell are connected using unfired 'Vycor' tips joined to glass (4 mm dia.) by heat shrunk P.T.F.E. tubing. The reference electrode is $Ag°/Ag^+$ (0.1 mol dm^{-3} in MeCN) and both working and auxiliary electrodes are Pt wire (1.0 mm dia.). The wires are vacuum sealed by spot welding them to tungsten wire and sheathing the assembly in uranium glass. Solutions for cyclic voltammetry are prepared as follows. The degassed cell is transferred to an argon atmosphere glove box and the storage ampoules loaded with silver nitrate solution (2 cm^3, 0.1 mol dm^{-3} in MeCN). tetraethylammonium tetrafluoroborate solution (2 cm^3 and 8 cm^3, 0.1 mol dm^{-3} in MeCN respectively, for bridging and working compartments), and the solute, which is contained in a frangible ampoule. The apparatus is re-evacuated, and the solutions degassed and tipped into their respective compartments. After determining the working potential range of the Et_4NBF_4, MeCN solution, the frangible ampoule is broken and the solute dissolved. Solutions so prepared can be studied over a period of hours before hydrolysis is detectable.

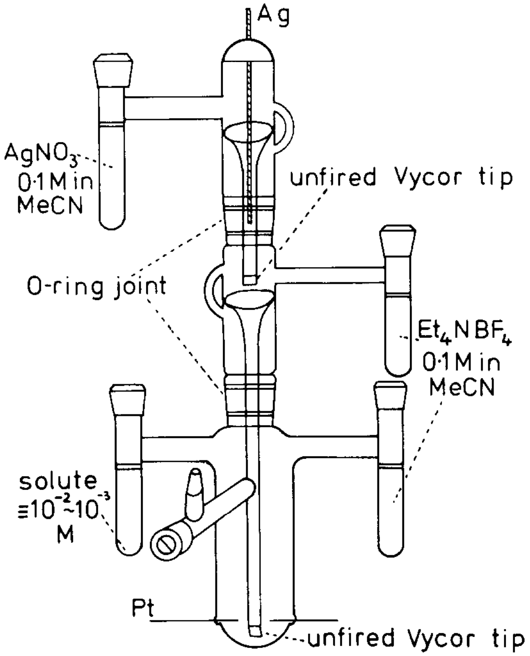

Fig. 1. Evacuable cell for cyclic voltammetry

The cyclic voltammogram of ferrocene (10^{-3} mol dm^{-3} in 0.1 mol dm^{-3} Et_4NBF_4, MeCN solution) recorded using this cell coupled to a potentiostat (CV-1A, Bioanalytical Systems Inc.) and XY recorder, consists of a quasi-reversible wave. The half-wave potential, $E_{\frac{1}{2}}$, is +0.07 V vs. Ag^+ (0.1 mol dm^{-3})/Ag°, the peak-to-peak separation, ΔEp, being 0.10 V at a scan rate 0.10 V s^{-1}. Decreasing the scan rate produces a smaller peak-to-peak separation.

$NOPF_6$, studied under identical conditions, gives rise to a quasi-reversible wave which is assigned to the couple NO^+/NO, $E_{\frac{1}{2}}$= +0.87 V and ΔEp = 0.27 V. The lack of complete reversibility in this case may be a consequence of a change in geometry between the oxidized and reduced forms as the NO^+ cation appears to be very effectively solvated by MeCN [10].

The results of cyclic voltammetry of hexafluorometallates(V), MF_6^-, M = U, Mo, and W, and heptafluorotungstates(VI), obtained under identical conditions, are given in Table 1. Assignments of the couples MF_6/MF_6^- and MF_6^-/M^{IV}, M = Mo or W, were made by comparisons with previous studies of alkali metal and silver(I) salts [8]. Cu^{II}/Cu^I couples were assigned by comparisons with data obtained from their PF_6^- salts [11]. In all cases the agreement between $E_{\frac{1}{2}}$ values is satisfactory, but peak-to-peak separations are somewhat greater than in previous work possibly due to the presence of more than one electroactive species in solution. Broad waves are particularly evident in solutions containing WF_6^- and WF_7^- anions. It is possible that the WF_7^-/W^V couple is not even quasi-reversible in MeCN. However, what is evident is a marked decrease in the oxidizing ability of W^{VI} by the addition of a F^- anion to WF_6.

The waves assigned to the UF_6/UF_6^- couple are very distorted, ΔEp = 0.44 - 0.49 V, and occur close to the solvent limit. UF_6 is known to undergo a slow reduction in MeCN [9], therefore the lack of reversibility is not unexpected. However, the data do imply that UF_6 is that strongest one-electron oxidant of those examined.

Waves assignable to the Tl^{III}/Tl^I couple could not be observed in solutions of Tl^I fluoro-anion salts and the wave, $E_{\frac{1}{2}}$ = +0.45 V, tentatively assigned to Tl^{III}/Tl^I in Tl^{III} hexafluoromolybdate(V) solutions was broad, ΔEp = 0.30 V, and ill-defined.

Redox reactions between NO^+ and Cu^I hexafluorometallates(V)

The oxidation of Cu metal to Cu^{II} in MeCN by the NO^+ cation has been reported previously [12]. The $E_{\frac{1}{2}}$ data, Table 1, indicate that this is to be expected, and that WF_6^-, but not MoF_6^-, should be oxidized. The reverse behaviour, reduction of MoF_6 but not WF_6 by NO, has been shown to occur in the gas phase [6]. Spectrophotometric titrations at 298 K in MeCN, Table 2, demonstrate the oxidation $Cu^I \rightarrow Cu^{II}$ by NO^+ in three hexafluoroanion salts. The behaviour with PF_6^- or MoF_6^- as counter anion is almost identical, but the extent of Cu^{II} formation at comparable initial $[NO^+] : [Cu^I]$ ratios when WF_6^- is the counter anion is smaller, due to the oxidation $WF_6^- \rightarrow WF_6$. The Raman spectrum of a solution in which the initial ratio $[Cu^I] : [NO^+] : [WF_6^-] = 1 : 1 : 1$ shows the presence of WF_6 but not WF_6^- nor WF_7^-, suggesting that oxidation of WF_6^- is complete. Under these conditions only 12% of the Cu^I originally present is oxidized, Table 2.

TABLE 1

Half-wave potentials, $E_{\frac{1}{2}}$ V vs. Ag^+(0.1 mol dm^{-3})/Ag° in MeCN[*]

Solute[†]	REDOX COUPLE								
	UF_6/UF_6^-	MoF_6/MoF_6^-	Cu^{II}/Cu^I	WF_6/WF_6^-	MoF_6^-/Mo^{IV}	$Cu^I/Cu°$	$Tl^I/Tl°$	WF_7^-/W^V	WF_6^-/W^{IV}
$Cu^{II}(UF_6)_2 5MeCN$	+2.31 (0.44)		+0.70 (0.11)			-0.71			
$Tl^{III}(UF_6)_3 4MeCN$	+2.33 (0.49)						-1.06		
$Tl^{III}(MoF_6)_3 5MeCN$		+1.60 (0.15)			-0.34 (0.18)		-1.15		
$Cu^{II}(MoF_6)_2 5MeCN$		+1.65 (0.08)	+0.71 (0.10)		-0.36 (0.10)	-0.70			
$Cu^I(MoF_6) 4MeCN$		+1.60 (0.10)	+0.75 (0.10)		-0.35 (0.20)	-0.73			
$Cu^I(WF_6) 4MeCN$			+0.74 (0.20)	+0.51 (0.22)		-0.68			-1.50 (0.20)
$Cu^{II}(WF_7)_2 5MeCN$			+0.69 (0.23)			-0.72		-1.27 (0.20)	
$(Bu^n_4N^+)(WF_6^-, WF_7^-)$				+0.51 (0.22)				-1.26 (0.25)	-1.52 (0.15)
Tl^IWF_7							-0.93	-1.22 (0.20)	

[*] Peak-to-peak separations in parentheses.

[†] $10^{-2} \sim 10^{-3}$ mol dm^{-3}

Redox chemistry derived from copper metal, metal hexafluoride reacti in MeCN

The $E_{\frac{1}{2}}$ data in Table 1 indicate that both MoF_6 and UF_6 are capable of oxidizing Cu metal to Cu^{II} in MeCN, and that Cu^{I} and Mo^{IV} are accessible by reduction with Cu metal. With one exception, this is in keeping with synthetic experience. Cu^{II} and Cu^{I} hexafluoromolybdates(V) and hexafluorouranates(V) have been prepared by this means [9], the only additional consideration being that in the reduction of Cu^{II} hexafluorouranate(V), a fresh Cu metal surface is required [13]. Although the reduction of Cu^{II} to Cu^{I} in the hexafluoromolybdate(V) by Cu metal is rapid and exothermic in MeCN at 298 K, the half-life for a reaction in which $[Cu^{II}]$ was initially 0.024 mol dm^{-3} is ca. 30 min, reduction of MoF_6^- to MoF_6^{2-} by Cu metal was not observed. Yellow $Cu^{I}(MoF_6)$, 4MeCN was the only product isolated. MoF_6^{2-} salts of some alkali metal cations have been isolated by reduction of MoF_6^- with iodide anion in sulphur dioxide however [14].

TABLE 2

Oxidation of Cu^{I} hexafluoroanion salts by NO^+ in MeCN at 298 K

10^2 Concentration (mol dm^{-3})			Ratio
$[Cu^{I}]_o$	$[NO^+]_o$	$[Cu^{II}]$ *	$[Cu^{II}]/[Cu^{I}]_o$
(a) Cu^{I} hexafluorophosphate			
3.8	3.8	2.3	0.61
3.8	7.6	3.3	0.87
3.8	9.4	3.4	0.89
(b) Cu^{I} hexafluoromolybdate(V)			
3.8	1.2	1.0	0.26
3.8	4.0	3.0	0.79
3.8	8.9	3.3	0.87
(c) Cu^{I} hexafluorotungstate(V)			
4.2	4.3	0.5	0.12
2.5	4.0	1.3	0.52
2.4	4.9	2.0	0.83
3.0	7.5	2.4	0.80

* Determined spectrophotometrically after 15 min.

Analogous chemistry involving WF_6 is more complicated for two reasons, the similar values of the Cu^{II}/Cu^{I} and WF_6/WF_6^- potentials, Table 1, and the ease with which WF_6^- reacts with WF_6 in MeCN to give WF_7^- [10,15]. Although $Cu(NCMe)_6^{2+}$, WF_6^-, and WF_7^- can all be identified in solution from reactions of Cu metal with WF_6 in MeCN depending on the conditions used, the only solid compound isolable in a pure state is $[Cu^{I}(NCMe)_4][WF_6]$, cf. ref. [9]. It has been proposed in the preliminary communication [16] that this behaviour is due to the redox, equation 1, and F^- ion transfer, equation 2, equilibria in which all species are solvated by MeCN.

$$Cu^{+} + WF_6 \underset{}{\overset{K_1}{\rightleftharpoons}} Cu^{2+} + WF_6^- \qquad (1)$$

$$WF_6^- + WF_6 \underset{}{\overset{K_2}{\rightleftharpoons}} WF_7^- + WF_5 \qquad (2)$$

The redox equilibrium (1) is temperature dependent, Cu^{2+} being favoured at 230 K [16]. Equilibrium (2) is important when WF_6 is reduced by iodide ion, as the tetra-n-butylammonium salt, in MeCN. The products are I_2 and a mixture of WF_6^- and WF_7^- salts. This is in contrast to the situation in SO_2, from which alkali metal hexafluorotungstates(V) have been prepared in a pure state [17]. In the analogous reaction involving MoF_6 in MeCN, further oxidation of I_2 occurs to give $[I(NCMe)_2][MoF_6]$ [18] and there is no evidence for heptafluoromolybdate(VI) formation.

The species $Cu(NCMe)_6^{2+}$, WF_6^-, WF_7^-, and WF_6 are unambiguously identified in solution by electronic or Raman spectroscopy, but identification of solvated WF_5, presumably WF_5, NCMe, is more problematic. A Raman active band at 755 cm^{-1} has been assigned to this species [10], and is observed, in company with WF_7^-, in this work. When a large excess of WF_6 is present the band shifts to 722 cm^{-1}.

The species in solution, identified by Raman spectroscopy, from redox reactions at 298 K between WF_6^- and Cu^{II}, and between Cu^{I}, counter-ions PF_6^- or WF_6^-, and WF_6, are given in Tables 3 and 4. Raman spectra obtained from the reaction of copper(I) hexafluorotungstate(V), $[Cu^{I}]$ = 0.106 mol dm^{-3}, with WF_6, $[WF_6]$ = 0.21 mol dm^{-3}, are shown in Figure 2.

TABLE 3

Oxidation of WF_6^- by Cu^{II} in MeCN at 298 K. Species identified by Raman spectroscopy

Initial concentration mol dm^{-3}		Species identified		
[WF_6^-]*	[Cu^{II}]†	WF_6^-	WF_7^-	WF_6
0.06	0.133	-	-	✓
0.10	0.133	-	✓	✓
0.12	0.133	✓	✓	✓

* As the Cu^I salt; † counter anion PF_6^-

The oxidation of Cu^I by WF_6 in MeCN at 298 K is conveniently followed by monitoring the solution's electronic spectrum after each WF_6 addition, and the latter part of one such experiment is shown in Figure 3. Addition of WF_6 to Cu^I hexafluorophosphate in MeCN, initial [Cu^I] = 0.112 mol dm^{-3}, results in the formation of Cu^{II}. The maximum [Cu^{II}] observed is 0.064 mol dm^{-3} which is approximately 57% of that theoretically attainable and requires a large excess of WF_6, mole ratio $Cu^I : WF_6 \simeq 1:13$. Removal of all volatile material leaves a mixture in which $Cu^{II} : Cu^I = 1:4$. Similar behaviour is observed using Cu^I hexafluorotungstate(V). For example, the maximum concentration of Cu^{II} observed in a mixture for which [Cu^I] was initially 0.100 mol dm^{-3}, is 0.054 mol dm^{-3} and occurs at $Cu^I : WF_6 \simeq 1:18$. The greater mole ratio required is a reflection of the additional WF_6^- concentration in the latter case. The solid isolated from this reaction has $Cu^{II} : Cu^I = 1:9$.

The electronic spectra of both systems contain a broad, weak band, ν_{max} = 25,000 cm^{-1} (PF_6^- salt), 26,300 cm^{-1} (WF_6^- salt) which is distinct from absorptions due to WF_6^-, ν_{max} = 27,800 (ξ = 7), 20,000 cm^{-1} (ξ = 1.5) in the spectrum of Cu^I hexafluorotungstate(V). The band intensity increases as [WF_6] increases, Figure 3, and is tentatively assigned to solvated WF_5.

TABLE 4

Oxidation of Cu^I by WF_6 in MeCN at 298 K. Species identified by Raman spectroscopy

Initial concentration, mol, dm^{-3}		Species identified			
$[Cu^I]_0$	$[WF_6]_0$	WF_6^-	WF_7^-	WF_6	'WF_5'
(a) Cu^I hexafluorophosphate + WF_6					
0.106	0.02	-	✓	-	-
0.106	0.05	-	✓	-	obscured
0.106	0.07	-	✓	✓	by
0.106	0.18*	-	✓	✓	PF_6^-
(b) Cu^I hexafluorotungstate(V) + WF_6					
0.110	0.02	✓	✓	-	✓
0.110	0.05	✓	✓	✓	✓
0.110	0.075	✓	✓	✓	✓
0.106	0.21	-	✓	✓	✓
0.106	0.59	-	✓	✓	✓
0.106	0.64+	-	✓	✓	✓

* Solid isolated from this mixture contained WF_7^- but no WF_6^-

\+ Solid isolated from this mixture contained WF_6^- and WF_7^-

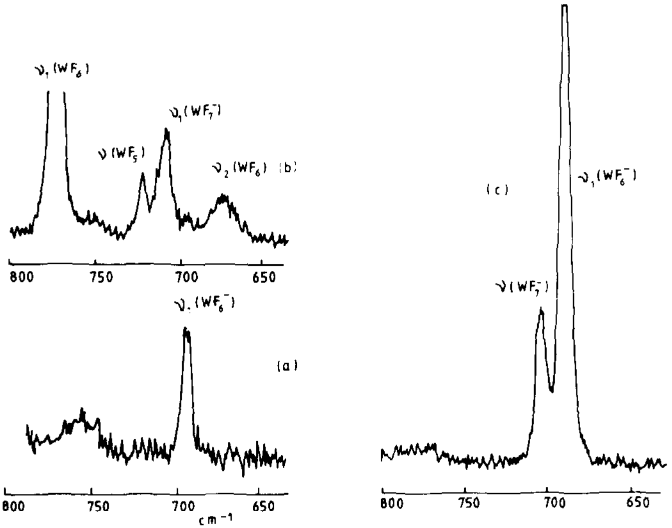

Fig. 2. Raman spectra of Cu^I hexafluorotungstate(V)(0.106 mol dm^{-3}) + WF_6 (0.21 mol dm^{-3}) in MeCN; (a) before addition of WF_6, (b) reaction mixture, (c) solid isolated from solution.

Evaluation of the equilibrium constants for equations 1 and 2, K_1 and K_2, was not possible as only $[Cu^{II}]$ could be determined and even these measurements are biased when the volume of WF_6 present becomes significant. However, the results obtained indicate that $K_2 > K_1$. A small value for the latter is expected in view of the order of $E_{\frac{1}{2}}$ values found , Table 1.

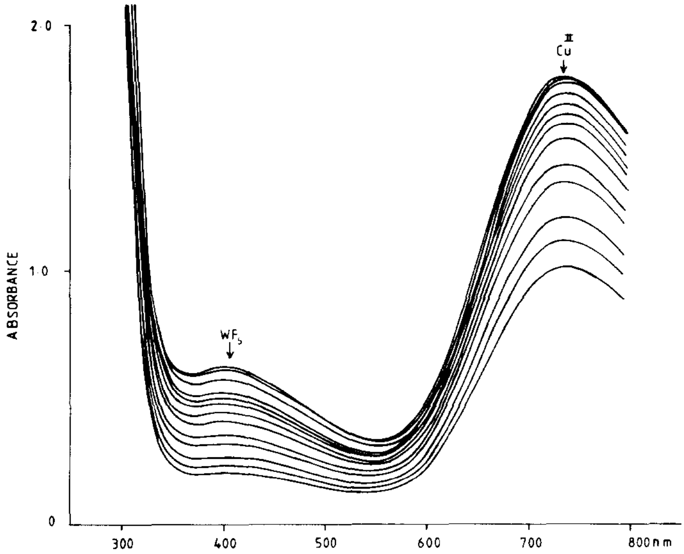

Fig. 3. Electronic spectra of Cu^I hexafluorophosphate (initial $[Cu^I]$ = 0.112 mol dm^{-3}) + WF_6 (1.33 to 5.60 mmol) reaction mixtures.

Oxidation of thallium metal by MoF_6 or UF_6. Properties of $Tl^{III}/MoF_6)_3$, 5MeCn.

Oxidation of Tl metal by MoF_6 in MeCN at 298 K results in a pale green solution, ν_{max} = 15,600 cm^{-1}, which rapidly becomes dark green-blue. The electronic spectral band is not observed in MoF_6, MeCN solutions, therefore it must originate from charge transfer involving MoF_6^- and/or a thallium species. A pure Tl^{III} salt, colourless $Tl^{III}(MoF_6)_3$, 5MeCN [9], is isolated only if the mole ratio MoF_6 : Tl° is high, and if the concentration of MoF_6 is > ca. 1 mol dm^{-3}. If these conditions are not met, yellow solids are formed in which Tl : Mo = ca. 1:2, Table 5.

TABLE 5

Oxidation of Tl metal by MoF_6 in MeCN

Tl metal	MoF_6	$[MoF_6]_0$	Product	
mmol	mmol	mol dm^{-3}	Colour	Tl : Mo
0.49	4.7	0.94	white	1 : 3.0
1.88	10.7	2.14	white	1 : 2.9
1.53	5.4	1.08	yellow	1 : 2.2
0.98	1.4	0.06	yellow	1 : 2.0*

* Unreacted Tl metal present.

The yellow solids are spectroscopically identical to $Tl^{III}(MoF_6)_3$, 5MeCN, except that the absorption edge in their electronic spectra occurs at lower energy. They are oxidized by MoF_6 in MeCN to the Tl^{III} salt and appear to react slowly with Tl metal, unlike $Tl^{III}(MoF_6)_3$, 5MeCN. The solids are formulated as Tl^I, Tl^{III} mixtures with MoF_6^- as counter ion. Although their composition is variable, the atomic ratio Tl : Mo is always near 1 : 2. UF_6 shows similar behaviour, and to ensure the preparation of pure Tl^{III} hexafluorouranate(V) [9], the UF_6 concentration should be at least 1 mol dm^{-3}.

The vibrational spectrum of $Tl^{III}(MoF_6)$, 5MeCN contains bands due to coordinated MeCN, 2322 $\nu(CN)$, 2293 comb., 950 $\nu(CC)$, and 390 cm^{-1} $\delta(CCN)$, and to MoF_6^-, 675 pol.(ν_1), 640(ν_3), and 250 cm^{-1} (ν_4). Its electronic spectrum in MeCN consists of two weak bands, ν_{max} = 33,600, 30,800(sh) cm^{-1}, analogous to bands at 34,500 and 30,300 cm^{-1} in Cu^I hexafluoromolybdate(V). The bands are in reasonable agreement with two of those reported for solid $CsMoF_6$ [19], but assignments are not possible.
Cu^I hexafluorotungstate(V), assignments are not possible.

$Tl^{III}(MoF_6)_3$, 5MeCN oxidizes Cu^I to Cu^{II} in MeCN at 298 K, although the reaction is not complete. In reactions for which $[Cu^I]$ and $[Tl^{III}]$ were initially 0.040 and 0.019 - 0.032 mol dm^{-3} respectively, the final $[Cu^{II}]$ is 60-78% of that expected for the stoicheiometry, Tl^{III} : Cu^I = 1:2. Cu^I is also oxidized by the yellow Tl^{III}, Tl^I solid in MeCN.
Thallium(I), as the PF_6^-, salt, does not appear to be oxidized by WF_6, Cu^{II}, or NO^+ in MeCN at 298 K.

The reactions of Tl^{III} and Tl^{I} in MeCN imply that the Tl^{III}/Tl^{I} couple is less oxidizing than is MoF_6/MoF_6^- but more so than is Cu^{II}/Cu^{I}. A high concentration of MoF_6 is required to achieve complete oxidation to Tl^{III} at ambient temperature, indicating a kinetic barrier to be overcome in the two electron transfer process. The synthetic results are at variance with those obtained from cyclic voltammetry, however, the latter are indeterminant.

EXPERIMENTAL

Standard vacuum and glove box techniques were used throughout. Reagent purification and the procedures for spectroscopic studies and cyclic voltammetry (except where described above) were as previously described [10, 11, 13]. Solvated metal cation hexafluorometallates(V) and heptafluorotungstates(VI) were prepared by literature methods [9, 13, 15, 20] or by simple extensions thereof. The salts were characterized by their spectra and in some cases analysis, metals being determined by atomic absorption spectroscopy, nitrogen by the Kjeldahl method, and other microanalyses by Malissa and Reuter, F.R.G. Their vibrational spectra, except for Tl^{I} salts, contained bands characteristic of coordinated MeCN and the appropriate anion. Bands due to co-ordinated H_2O and metal-oxygen moieties were absent. Cu^{II} salts showed the d-d band due to distorted octahedral $Cu(NCMe)_6^{2+}$ at 740 nm in their electronic spectra. The molar extinction coefficient, ξ, was determined as 28 mol^{-1} dm^3 cm^{-1} in the PF_6^- salt, and this was used to determine $[Cu^{II}]$ in spectrophotometric titrations. Solutions for these were prepared using a microburette in a glove box or <u>in vacuo</u>, with the solutes contained in frangible ampoules.

Analytical data were as follows: Found Cu, 9.2; Mo, 28.0. $Cu(MoF_6)_2$, 5MeCN req. Cu, 9.2; Mo, 27.9%. Found Cu, 14.4; Mo.22.6, $Cu(MoF_6)$, 4MeCN req. Cu, 14.5; Mo, 22.4% Found Cu, 6.9; N, 7.1. $Cu(WF_7)_2$, 5MeCN req. Cu, 7.0; N, 7.8%. Found C, 11.7; H, 1.4; F, 32.8; N, 6.9; Mo, 27.5; Tl, 19.8. $Tl^{III}(MoF_6)_3$, 5MeCN req. C, 11.6; H, 1.4; F, 32.9; N, 6.7; Mo, 27.7; Tl, 19.7%.

A mixture of dried tetra-*n*-butylammonium iodide (0.95 mmol) and WF_6 (5.50 mmol) in MeCN (5 ml) was allowed to react at room temperature. Iodine was immediately produced and was removed with other volatile material by vacuum sublimation. The residue, washed four times with MeCN to remove trace I_2, was a pale cream solid. Its vibrational spectrum contained strong bands at 705 (Raman) and 630 cm^{-1} (i.r.) due to WF_7^-, and at 695 (Raman) and 600 cm^{-1} (i.r.) due to WF_6^-.

Tl metal (*ca.* 2 mmol) was allowed to react with UF_6 (*ca.* 10 mmol) in MeCN (5 ml) at room temperature for 15 min. after which time all the metal had reacted. Removal of solvent and unchanged UF_6 left a pale green solid. Found C, 6.6; H, 0.7; F, 23.75; N, 3.8; Tl, 14.2; U, 50.4. $Tl(UF_6)_3$, 4MeCN req. C, 6.7; H, 0.8; F, 24.0; N, 3.9; Tl, 14.35; U, 50.1%. A reaction employing a similar quantity of UF_6 but a larger quantity of Tl metal, which did not all react, gave a solid whose analysis was identical, but if a significantly smaller quantity of UF_6 was used, the solid's analysis was C, 8.75; H, 1.1; F, 21.1; N, 5.1; Tl, 18.8; U, 44.5. $Tl(UF_6)_2$, 4MeCN req. C, 8.95; H, 1.1; F, 21.25; N, 5.2; Tl, 19.1; U, 44.4%. The three solids were identical spectroscopically to $Tl^{III}(UF_6)$, 5MeCN reported earlier [9].

A mixture of thallium(I) fluoride (4.7 mmol), PF_5 (4.4 mmol) and MeCN (5 ml), allowed to react at room temperature, gave initially a yellow solution which became colourless on shaking for several hours. A colourless solid was isolated, identified as $TlPF_6$ from its analysis (Found F, 32.2; P, 8.6; Tl, 58.4. $TlPF_6$ req. F, 32.6; P, 8.6; Tl, 58.5%) and spectra. Raman: $\nu_{max} = 742(\nu_1), 470(\nu_5)$ cm^{-1}; i.r.: ν_{max} $830(\nu_3), 560(\nu_4)$ cm^{-1}; ^{19}F n.m.r.: δ-73 p.p.m. w.r.t. CCl_3F, $^1J(PF)$ 707 Hz.

CONCLUSION

From a combination of cyclic voltammetry and redox chemistry the order of oxidizing ability in MeCN at 298 K is established as $UF_6 > MoF_6$ > solvated NO^+ > solvated $Cu^{2+} \gg WF_6$. Solvated Tl^{3+} lies probably between MoF_6 and Cu^{2+}. The redox reactions alone do not differentiate between UF_6 and MoF_6, but the chemical behaviour of WF_6 is clearly differentiated, both by its weaker oxidizing power and by its ability to participate in F^- ion transfer equilibria.

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