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FERRICENIUM HEXAFLUOROMOLYBDATE(V) -TUNGSTATE(V) AND -URANATE (V) PREPARATION AND ELECTROCHEMICAL IDENTIFICATION

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SUMMARY

Ferrocene is oxidized by molybdenum, tungsten or uranium hexafluoride in Freon 11 to give ferricenium hexafluoromolybdate(V) -tungstate(V) and -uranate(V), which were identified by electrochemical methods. A previously unknown reduction process of uranium, UF_6^-/U^{IV} at -2.38V vs S.C.E. has been observed.

INTRODUCTION

Ferrocene, $Fe(C_5H_5)_2$, has been oxidized in aqueous media by various metal systems, for example Fe^{III} [1], Cu^{II} [2], Ag^I [3], to give blue ferricenium salts of the form $[Fe(C_5H_5)_2]^+ X^-$. The redox potential of the process $Fe(C_5H_5)_2/[Fe(C_5H_5)_2]^+$ has been the subject of extensive studies in aqueous and non-aqueous solutions [4]. More recently the stability and reversibility of this redox couple has enabled its use as an internal reference in electrochemical studies of other redox systems, such as hexafluorometallates [5] and hexachlorometallates [6]. The redox couples MF_6/MF_6^-, M = Mo, W, and U have been studied previously by cyclic voltammetry in acetonitrile [7] and with the help of an external Ag^0/Ag^+ reference electrode [8]. We now report that the oxidizing abilities of molybdenum, tungsten and uranium hexafluorides can be used to prepare stable ferricenium salts, which can be identified by the known redox couples of the hexafluorometallates and the ferricenium cation.

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RESULTS AND DISCUSSION

Addition of molybdenum, tungsten and uranium hexafluoride to a frozen solution of ferrocene in $CFCl_3$ results, upon subsequent warming, in the formation of dark blue ferricenium salts of the form $[Fe(C_5H_5)_2]^+[MF_6]^-$, M = Mo, W, and U. The infrared spectra of the new salts are consistent with the presence of octahedral MF_6^- anions and ferricenium cations. The strong band ν_3 for MoF_6^- is observed at 600 cm^{-1}, for WF_6^- ν_3 is at 599 cm^{-1} and ν_3 for UF_6^- occurs at 511 cm^{-1}. The bands are assigned by analogy with previously reported MF_6^- salts [9].
Table 1 summarizes the i.r. data; frequency assignments are made by comparison with other ferricenium cations [10].

TABLE 1

The i.r. spectra (cm^{-1}) of $[Fe(C_5H_5)_2][MF_6]$, M = Mo, W and U

MoF_6^-	WF_6^-	UF_6^-	Assignment [10]
3106 (m)	3114 (m)	3110 (s)	CH stretching
	2918 (w)	2923 (m)	
1524 (w)			
1415 (m)	1417 (m)	1417 (s)	antisym C-C stretching
1197 (m)		1198 (m)	CH bending ($\parallel$)
1123 (vw)		1125 (w)	
1105 (s)	1105 (w)	1106 (w)	CH bending ($\parallel$)
	1024 (s)		
1000 (s)	1001 (s)	1001 (m)	CH bending ($\parallel$)
972 (s)	976 (m)	971 (m)	
933 (s)			
854 (s)	858 (s)	858 (s)	CH bending ($\perp$)
738 (s)		740 (w)	
	702 (m)		
	641 (s)		
601 (vs)	599 (vs)	511 (vs)	$\nu_3 MF_6^-$
490 (s)	494 (w)		antisym. ring tilt
		440 (m,br)	
420 (m)	420 (m,sh)		antisym. ring-metal-stretching

vw = very weak, w = weak, m = medium, s = strong, vs = very strong, br = broad, sh = shoulder

Raman spectra of the ferricenium compounds could not be obtained due to decomposition of the intensely coloured samples by the laser light. NMR spectra could not be obtained due to the paramagnetism of the complex salts. Mass spectra for all three compounds show the MF_5^+ and the $[Fe(C_5H_5)_2]^+$ ion. Molecular ion peaks were not observed.

The electrochemistry of the ferricenium salts has been investigated by direct current (d.c.) and alternating current (a.c.) methods using the ferrocene/ferricenium redox couple as internal reference. The measured potentials of the redox couples (vs S.C.E.) were found to be independent of the choice of CH_2Cl_2 or MeCN as solvent and are consistent with previously reported voltammetric studies. For all three MF_6^- compounds the one electron oxidation to MF_6 has been observed; the quasi-reversible half-wave potential of UF_6^-/UF_6 occurs at +2.76 [8], MoF_6^-/MoF_6 at +2.08V [7,8], and WF_6^-/WF_6 at +1.08V [7,8]. One electron reduction to the metal IV occurs for MoF_6^-/MoF_6^{2-} at ca. +0.1V [7,8] and for WF_6^-/W^{IV} at -0.91V [7,8].

TABLE 2

Half-wave potentials, E [V] vs S.C.E.* of $[Fe(C_5H_5)_2][MF_6]$, M = Mo, W, U.

	REDOX COUPLE				
Metal	V/VI	V/IV	IV/III	solvent	electrolyte
Mo	+2.08 (160)	ca.+0.1$^+$ (100)	-1.95	MeCN	0.1M$[Et_4N][PF_6]$
W	+1.08 (180)	-0.91 (220)		CH_2Cl_2	0.5M$[Bu_4N][PF_6]$
U	+2.76 (400)	-2.38		MeCN	0.1M$[Et_4N][PF_6]$

$^+$ Obscured by $Fe(C_5H_5)_2/[Fe(C_5H_5)_2]^+$ couple

* Half-width (mV) in parentheses. Criterion for reversible (a.c.) wave for one-electron step is a half-width of 90 mV [11].

The corresponding reduction of the uranium complex UF_6^-/U^{IV} at a strongly reducing potential of -2.38V appears to be observed here for the first time. Only the molybdenum complex has a second reduction: MoF_6^{2-}/Mo^{III} at -1.95V [7].

In this study the half-wave potentials of the ferrocene/ ferricenium couple has been established at +0.16V vs S.C.E. Table 2 lists the electrochemical date for the ferricenium salts with potentials generally given as obtained in the (a.c.) mode.

The observed redox potentials are in agreement with the spontaneous chemical reduction of the hexafluorides by ferrocene, equation 1. Further reduction of the hexafluorometallates or oxidation of the ferricenium (e.q. equation 2,3 and 4) are clearly not thermodynamically feasible.

$$Fe(C_5H_5)_2 + MF_6 \Longrightarrow [Fe(C_5H_5)_2]^+[MF_6]^- \qquad (1)$$

$$2Fe(C_5H_5)_2 + MF_6 \not\Longrightarrow [Fe(C_5H_5)_2]_2^+[MF_6]^{2-} \qquad (2)$$

$$Fe(C_5H_5)_2 + MF_6 \not\Longrightarrow [Fe(C_5H_5)_2]^{2+}[MF_6]^{2-} \qquad (3)$$

$$Fe(C_5H_5)_2 + 2MF_6 \not\Longrightarrow [Fe(C_5H_5)_2]^{2+}[MF_6]_2^- \qquad (4)$$

(M = Mo, W, U)

All three ferricenium salts were subjected to vacuum pyrolysis at 200°C and to chemical reduction with aqueous $Na_2S_2O_3$. In both cases only ferrocene could be isolated. There was no evidence that fluorination of the C_5H_5 ligands had occured. A previous report on the synthesis of monofluoroferrocene has since been questioned [12].

EXPERIMENTAL

Conventional vacuum line and glove box techniques were used throughout. Glass systems were flamed out prior to use.

Volatile fluorides, MoF_6 (Ozark-Mahoning), WF_6 (Ozark-Mahoning), and UF_6 (Hoechst AG), were purified using a published procedure [9]. Ferrocene was sublimed and recrystallised before use. Freon 11 (Hoechst AG) and CH_2Cl_2 (Merck, analytical grade) were dried by distilling from P_2O_5 under argon and stored over activated 3Å molecular sieves. MeCN (Merck, analytical grade) was purified and dried as previously described [13].

I.r. spectra were recorded on a Perkin Elmer 883 spectrometer, the samples analysed as KBr discs. Mass spectra were obtained on a Varian MAT 711, 80 eV, observed intensities include all isotopes on the basis of ^{56}Fe. Microanalyses were performed by Beller, Göttingen, F.R.G.

Electrochemical measurements were made with a PAR model 173 potentiostat in combination with a PAR model 124A Lock-in amplifier and a universal programmer (F.U. Berlin). Voltammograms were recorded on a Linseis LY 18100 X-Y-Y recorder. Electrochemical experiments were conducted as previously described [14].

Preparation of Ferricenium hexafluorometallates(V), $[Fe(C_5H_5)_2][MF_6]$, M = Mo,W,U

5.4 Mmol metal hexafluoride, MoF_6, WF_6 or UF_6, was added to a frozen solution of 5.4 mmol ferrocene in 20 ml Freon 11 followed by the condensation of another small amount (5ml) Freon 11 onto the frozen mixture. On warming to room temperature a blue-grey precipitate formed at once and the mixture was stirred for about 15 minutes. Removal of all volatile material left the products as dark blue solids in quantitative yield. The air and moisture sensitive salts all have melting points above 300°C.

Analysis:Found C, 29.56; H, 2.89; F, 28.4; Fe, 14.17; Mo, 23.9. $[Fe(C_5H_5)_2][MoF_6]$ req. C, 30.32; H, 2.53; F, 28.8; Fe, 14.11; Mo, 24.24%. Found C, 25.08; H, 2.39; F, 22.7; Fe, 11.0; W, 38.8 $[Fe(C_5H_5)_2][WF_6]$ req. C, 24.81; H, 2.07; F, 23.57; Fe, 11.55; W, 38.0%.Found C, 19.78; H, 1.77; F, 24.1; Fe, 11.92; U, 41.5. $[Fe(C_5H_5)_2][UF_6]$ req. C, 22.31; H, 1.86; F, 21.19; Fe,10.38; U, 44.25%.

Mass spectra: calcd. for $C_{10}H_{10}F_6FeMo$ m/e 395.78, found m/e 193 (MF_5^+, 4.3%), 186 ($FeC_{10}H_{10}^+$, 100), 185 ($FeC_{10}H_9^+$, 2.4), 184 ($FeC_{10}H_8^+$, 9.5), 121 ($FeC_5H_5^+$, 38), 56 (Fe^+, 14.3). calcd. for $C_{10}H_{10}F_6FeW$ m/e 483.69, found m/e 279 (WF_5^+, 5.9%), 260 (WF_4^+, 6.5),241 (WF_3^+, 1.2), 222 (WF_2^+, 1.0), 186 ($FeC_{10}H_{10}^+$, 100), 185 ($FeC_{10}H_9^+$, 3,0), 184 ($FeC_{10}H_8^+$, 9.2), 121 ($FeC_5H_5^+$, 35), 56 (Fe^+, 11.2). calcd. for $C_{10}H_{10}F_6FeU$ m/e 537.87, found m/e 333 (UF_5^+, 0.4%), 186 ($FeC_{10}H_{10}^+$, 100), 185 ($FeC_{10}H_9^+$, 2.1), 184 ($FeC_{10}H_8^+$, 8.4), 121 ($FeC_5H_5^+$, 16.5), 56 (Fe^+, 5.5).

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