Orderly Progressions in Stepwise Electrode Potentials of 4d and 5d Hexafluorometallate Complexes in Acetonitrile

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Successive reversible E° values for the redox couples $[MF_6]^{z/z-1}$ ($z = 0$, -1, -2) where M = Ta, W, Re, Os and Nb, Mo, (Tc), Ru, detected by cyclic voltammetry in MeCN over a 6 V range, follow linear progressions related to central ion nuclear and electronic structure for $d^0 \to d^1$, $d^1 \to d^2$, and $d^2 \to d^3$ while deviations observed for $d^3 \to d^4$ and subsequent couples are attributable to spin-pairing effects; corresponding $4d^{n/n+1}$ and $5d^{n/n+1}$ couples are almost uniformly separated by 1.0 V.

The relative stabilities of various oxidation states of the heavy transition metal hexafluorides are of interest and practical importance but in the past have been inferred mainly from qualitative observations. Reversible $[WF_6]^{0/1-}$ and $[MoF_6]^{0/1-}$ couples were first observed by Bond et al.,[1] in pioneering cyclic voltammetric measurements in anhydrous hydrogen fluoride solution, and we recently demonstrated similar behaviour for $[WF_6]^{0/1-}$ in stringently purified acetonitrile.[2] We now report that many such complex fluorides can be studied in this conventional electrochemical solvent which makes such measurements more accessible, and (crucially) directly compatible on a familiar potential scale with the wealth of data on other systems. In the vacuum-tight cell, it is most effective to refer potentials directly to the Ag^+/Ag couple measured in situ. Diffusion-limited electrodeposition of Ag is found not to interfere with more negative voltammetric processes.

For example, $AgMoF_6$ displays three equally spaced one-electron steps, corresponding to the $M^{VI/V}$, $M^{V/IV}$, and $M^{IV/III}$ couples (Figure 1). Similar well defined reversible behaviour is observed for all the heavy metal hexafluoride complexes so far studied, presenting a hitherto unrecognized orderly array of one-electron couples. The systematic pattern which emerges is apparent in Figure 2 which presents the stepwise electrode potentials as a function of periodic core charge; $E_{\frac{1}{2}}$
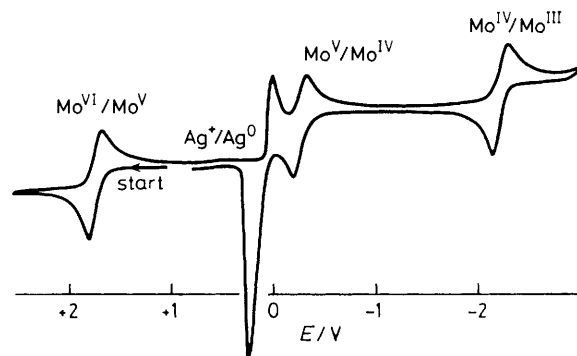

Figure 1. Cyclic voltammogram (c.v.) of $AgMoF_6$: scan rate 100 mV s^{-1}, at Pt wire electrode in MeCN/Bu$_4$NBF$_4$(0.1 M)/AgMoF$_6$ (0.005 M).

data for 2nd row elements are offset by 1.0 V in order to overlay them with 3rd row data and emphasize the close parallel between them. Appreciation of these regularities enables estimation of $E_{\frac{1}{2}}$ for inaccessible couples and for the missing $[TcF_6]^{z/z-1}$ sequence, e.g., +3.0 V ($Tc^{VI/V}$), +0.85 V ($Tc^{V/IV}$), and -2.5 V ($Tc^{IV/III}$) vs. Ag^+/Ag.

Table 1

Equilibrium type	Cell reaction (example)					E_{cell}
(a) Congeneric iso-electronic couples[a]	$[TaF_6]^{2-}$ d^1	+	$[NbF_6]^{1-}$ d^0	→ $[TaF_6]^{1-}$ d^0	+ $[NbF_6]^{2-}$ d^1	+1.0 V
(b) Adjacent iso-electronic couples[b]	$[TaF_6]^{2-}$ d^1	+	$[WF_6]$ d^0	→ $[TaF_6]^{-}$ d^0	+ $[WF_6]^{-}$ d^1	+3.2 V
(c) Successive couples (disproportionation)[a]	$[WF_6]^{-}$ d^1	+	$[WF_6]^{-}$ d^1	→ $[WF_6]$ d^0	+ $[WF_6]^{2-}$ d^2	−2.0 V
(d) Adjacent isovalent couples[b]	$[TaF_6]^{2-}$ d^1	+	$[WF_6]^{-}$ d^1	→ $[TaF_6]^{-}$ d^0	+ $[WF_6]^{2-}$ d^2	+1.2 V

[a] Charge redistribution and solvation terms for reactions a and c are self-cancelling. [b] For reactions b and c calculations using the Born equation yield values of ca. 0.1 eV,[4] substantially less than the effects considered here.
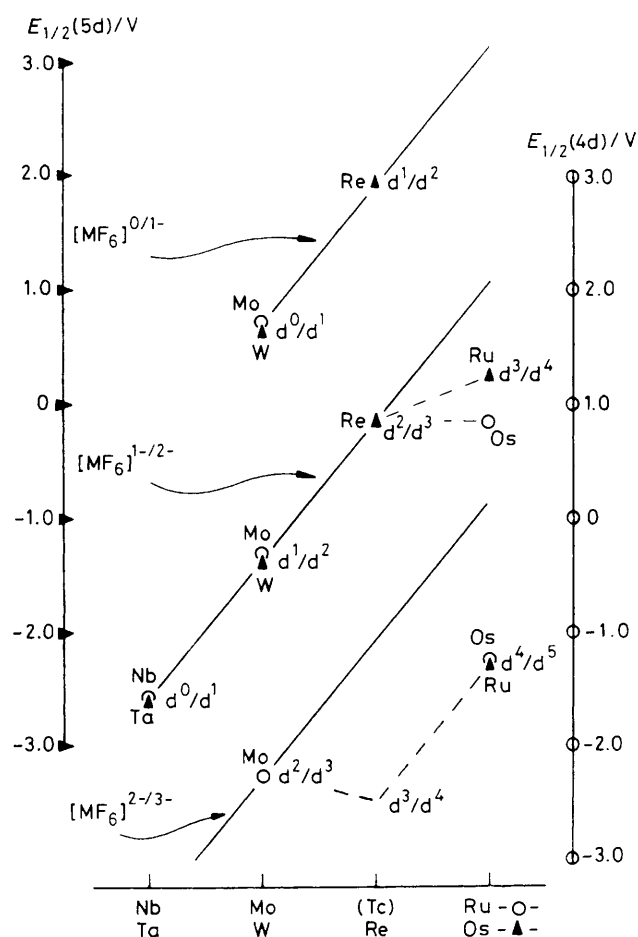

Figure 2. Trends in electrode potentials $[E_{1/2}/V]$: ○ = 4d elements and ▲ = 5d elements (vertical axis displacement 1.0 V). Full lines are all located strictly parallel to the Ta^V/IV–Re^V/IV tie-line. Potentials are referred to the forward (cathodic) c.v. peak potential for *in situ* Ag^+ reduction on Pt, at ca. −0.2 V *vs.* saturated calomel electrode.

The numerical data are best regarded in terms of thermodynamic cell reactions, by combining the electrode potentials in various significant ways as exemplified in reactions a to d (Table 1).

Reaction a defines the driving force for electron-transfer from $[TaF_6]^{2-}$ to $[NbF_6]^{1-}$, and typifies the relative stability

of the higher oxidation states in the 5d series. Combination of neighbouring couples within one series, such as $[TaF_6]^{1-/2-}$ and $[WF_6]^{0/1-}$ in reaction b, illustrates the preference of the transferred electron for the species of higher atomic number and shows the profound influence of core charge on iso-electronic energy levels. Equally, comparison of successive couples for one element, such as $[WF_6]^{0/1-}$ and $[WF_6]^{1-/2-}$ in reaction c, reflects the unfavourable energy of disproportionation (*i.e.*, electronic reorganisation at fixed core charge). Reactions such as d exemplify the anticipated increase in oxidising strength of isovalent ions across each series, which is seen to arise from the superimposed influence of core charge and electronic reorganisation.

The contribution of interelectronic correlation terms to the separation between $E°$ (d^{n-1}/d^n) and $E°$ (d^n/d^{n+1}) is uniformly $[r + k]$ for $n = 1, 2, 4$, and 5 but $[R−2k]$ for $n = 3$,† where r is the repulsion energy and k the exchange energy between any two parallel 4d (or 5d) electrons and R is the repulsion energy for electrons paired within one orbital.[3] The resulting prediction of approximately linear progression in $E°$ values, interrupted at the d^3/d^4 couple, is not altered by smooth variation of these parameters with changing atomic number or valency.

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3 G. A. Heath, unpublished calculations.

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† The same conclusion may be rigorously derived in terms of Racah parameters $\{[r + k] = A − 5B, [R − 2k] = A + 10B + 5C\}$.[3] Note that, although each electron added to the t_{2g} subshell contributes an increment 4 Dq in ligand field stabilisation energy this term is contained in every d^n/d^{n+1} couple and does not contribute to the *separation* in successive $E°$ values, even if 10 Dq varies smoothly across the series.