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THE BEHAVIOUR OF COPPER AND THALLIUM HEXAFLUOROMOLYBDATES(V) IN ACETONITRILE

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Copper(I), copper(II), and thallium(III) hexafluoromolybdates(V), prepared by the oxidation of the metals in acetonitrile with molybdenum hexafluoride (A. Prescott, D.W.A.Sharp, and J.M. Winfield, J. Chem. Soc., Dalton Trans., 1975, 963) have been investigated by cyclic voltametry. Half wave potentials, $E_{\frac{1}{2}}$ V vs. Ag^+/Ag were obtained using a evacuable cell equipped with an external Ag^+/Ag electrode, enabling strict anerobic conditions to be maintained. A number of reversible or quasi-reversible electron transfer processes have been observed, enabling comparison with synthetic work to be made. Results for Cu^I and Cu^{II} hexafluoromolybdates(V) are in accord with preparative experience. MoF_6, $Mo^{VI}/Mo^{V}E_{\frac{1}{2}}$ = +1.600V, oxidises Cu metal to Cu^{II} in MeCN, and Cu^{II} is reduced by Cu^0 to Cu^I, $Cu^{II}/Cu^{I}E_{\frac{1}{2}}$ = +0.750 or +0.710V for Cu^I and Cu^{II} solutes respectively, $Cu^I/Cu^0E_{\frac{1}{2}}$ = -0.720V not reversible. A wave at $E_{\frac{1}{2}}$ = -0.350V is assigned to Mo^V/Mo^{IV} by analogy with Ag^I hexafluoromolybdate (D.W.A. Sharp, unpublished work). $E_{\frac{1}{2}}$ data for I_2 in MeCN, I_2/I_3^- = 0.280, I_3^-/I^- = -0.116V, suggest that reduction of MoF_6^- by I^- is not likely, in contrast to the situation in SO_2 (A.J. Edwards and R.D. Peacock, Chem. Ind., 1960, 1441). Reduction of MoF_6^- by Cu^0 in MeCN should be feasible, but appears to be very slow. Pure $T\ell^{III}$ hexafluoromolybdate(V) is obtained from $T\ell^0$ and MoF_6 only when the mole ratio $MoF_6:T\ell>5:1$. Smaller ratios produce yellow solids in which $Mo:T\ell$ is ca. 2:1. $T\ell^{III}$ is a stronger oxidising agent than Cu^{II} in MeCN, as oxidation of Cu^I by $T\ell^{III}$ is rapid and quantitative. However a reversible electron transfer wave assignable to $T\ell^{III}/T\ell^{I}$ is not observed in the expected range +1.600 to +0.710V possibly because of solute-electrode interactions.

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REDOX BEHAVIOUR IN HEXAFLUOROMETALLATE SYSTEMS

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The electrochemical processes $[MF_6]^{n-} \rightleftharpoons [MF_6]^{-n+1}$ have been studied by cyclic voltammetry and polarography in acetonitrile for a series of transition metals. The observed potentials show correspondence with the number of d electrons and emphasise quantitatively the expected greater oxidising power of second-row elements over third-row elements. There are breaks in the plots of E_0 against the number of d electrons at $d^3 \rightarrow d^4$ corresponding to the spin pairing in the d^4 state.

Metal	VI/V	V/IV	IV/III	Metal	VI/V	V/IV	IV/III
Nb	-	-1.55	<-3.0	Ta	-	-2.55	<-3.0
Mo	+1.70	-0.35	-2.25	W	+0.70	-1.30	<-3.0
Tc	-	-	-	Re	+2.00	-0.20	<-3.0
Ru	>3.0	+0.85	-1.25	Os	+2.90	+0.25	-2.3

(volts vs. Ag^+/Ag)