The Orderly Progression of Redox Behaviour of 4d- and 5d-Hexachlorometallate Complexes

Graham A. Heath,[a] Klaus A. Moock,[b] David W. A. Sharp,[b] and Lesley J. Yellowlees[b]

[a] *Department of Chemistry, University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ, U.K.*
[b] *Department of Chemistry, University of Glasgow, Glasgow G12 8QQ, U.K.*

A comprehensive study of the redox behaviour of 4d- and 5d-hexachlorometallates (Zr to Pd and Ta to Pt, omitting only Tc) has been undertaken in methylene chloride; the successive reversible E° values for the redox couples $[MCl_6]^{z/z-1}$ ($z = 0, -1, -2, -3$) follow orderly trends which have been interpreted in terms of core-charge and inter-electronic correlation terms, and the redox behaviour of the hexachlorometallates is compared to that of the hexafluorometallates.

We previously demonstrated that the successive E° values for the couples $[MF_6]^{z/z-1}$ ($z = 0, -1 -2$) where M = Ta, W, Re, Os, Nb, Mo, Ru, in acetonitrile show a remarkable linear progression related to central ion core charge and configuration, deviating at d^3/d^4 couples in response to spin-pairing effects.[1] We have now made an extensive study of the corresponding family of 4d- and 5d-hexachlorometallates (Zr to Pd and Ta to Pt, omitting for the present only Tc) which provides the opportunity for testing the generality of such redox progressions. Pioneering studies of individual systems such as $[MoCl_6]^{2-}$,[2] $[OsCl_6]^{-}$,[3] and $[WCl_6]^{-}$,[4] in diverse media, have appeared elsewhere.

The chloride systems have been studied in methylene chloride (CH_2Cl_2) to preclude solvolysis {*e.g.* WCl_6 in

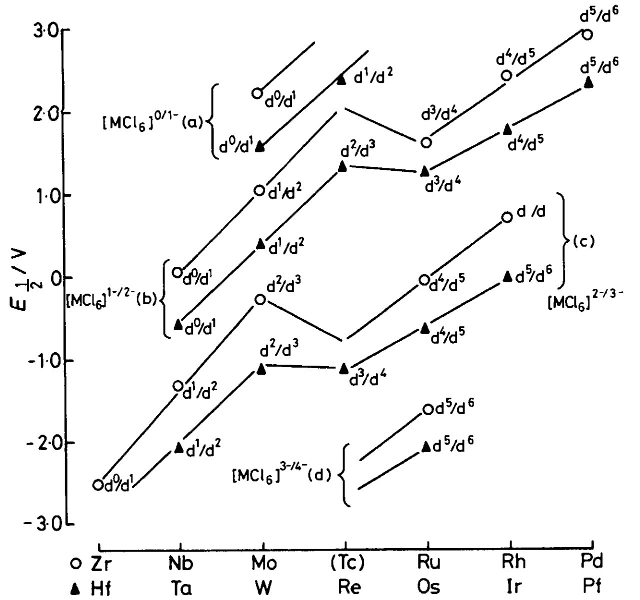

Figure 1. Trends in half-wave potentials, $E_{\frac{1}{2}}$ in V, of $[MCl_6]^{z/z-1}$ couples in CH_2Cl_2; ○: 4d-hexachlorometallates; ▲: 5d-hexachlorometallates. (a) $z = 0$; (b) $z = -1$; (c) $z = -2$; (d) $z = -3$.

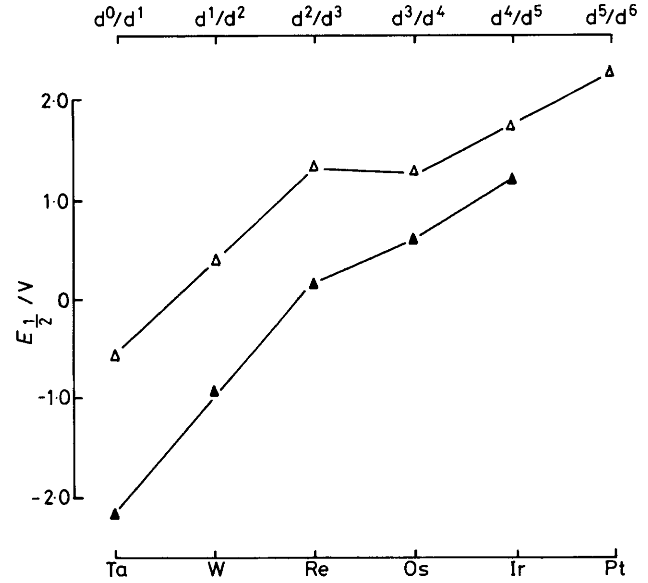

Figure 2. Comparison of half-wave potentials for $[MX_6]^{1-/2-}$ couples of 5d-hexafluorometallates (▲; X = F) and hexachlorometallates (△; X = Cl).

Table 1. Half-wave potentials of $[MCl_6]^{z/z-1}$ couples (*vs.* s.c.e.) in CH_2Cl_2.[a]

		Oxidation state of metal		
Metal (M)	$M^{VI/V}$	$M^{V/IV}$	$M^{IV/III}$	$M^{III/II}$
Hf			−3.1[b]	
Ta		−0.55	−2.05	
W	+1.59	+0.40	−1.15	
Re	+2.35	+1.33	−1.12	
Os		+1.28	−0.64	−2.0
Ir		+1.74	−0.02	
Pt		+2.30		
Zr			−2.53	
Nb		+0.08	−1.32	
Mo	+2.20	+1.05	−0.28	
(Tc)		+2.0[c]	−0.8[c]	
Ru		+1.61	−0.05	−1.6
Rh		+2.43	+0.72	
Pd		+2.92		

[a] $[Fecp_2]^+/[Fecp_2]$ (cp = cyclopentadienyl) is observed at +0.48 V *vs.* s.c.e. in CH_2Cl_2 but cannot generally be used as an internal reference. [b] Extrapolated potential outside solvent range. [c] Interpolated potentials.

acetonitrile (MeCN) gives $[WCl_4(MeCN)_2]^5\}$. Where it has been possible to study the same species in both solvents (*e.g.* $[OsCl_6]^{2-}$) the redox processes are observed at similar potentials. Soluble tetrabutylammonium salts $[(C_4H_9)_4N]_2[MCl_6]$ in organic solvents were prepared by cation exchange methods from the relevant potassium salt (for M = Pt, Ir, Re, Os, Ru) or by reaction of the chlorometallate in the presence of tetrabutylammonium chloride (M = Mo, Ta, Nb, W, Zr, Hf, Pd, Ru, Rh). The most effective inert electrolytes were tetrabutylammonium tetrafluoroborate and hexafluorophosphate. Major experimental challenges implicit in this work were the control of hydrolysis (*e.g.* $[MoCl_6]^-$ gives $[MoOCl_5]^{2-}$), condensation equilibria (*e.g.* $RhCl_6^{3-} \rightarrow Rh_2Cl_9^{3-}$), and aggressive Lewis acid exchange (*e.g.* $TaCl_5$ in the presence of $[R_4N][BF_4]$ gives $[TaCl_6]^-$ and $[TaF_6]^-$). These difficulties necessitated the use of stringent vacuum line procedures, fast time-domain techniques and low temperature voltammetry and will be detailed elsewhere. The E° potential for every reversible hexachlorometallate couple $[MCl_6]^{z/z-1}$ was measured *vs.* $[IrCl_6]^{1-/2-/3-}$ which was added to the system as an internal reference. The half-wave potentials for $[R_4N]_2[IrCl_6]$ were independently established in CH_2Cl_2 with a conventional non-aqueous electrode.

The E° values [relative to saturated calomel electrode (s.c.e.)] for the reversible $[MCl_6]^{z/z-1}$ couples are given in Table 1 and the data are plotted in Figure 1 as a function of periodic core charge (increasing atomic number). The reversibility of the couples given in Table 1 suggests that previously unknown species, for example hexachloroplatinate(V), $[PtCl_6]^-$, hexachloromolybdate(VI), $MoCl_6$,† hexachlorozirconate(III), $[ZrCl_6]^{3-}$ can be prepared and studied by electrochemical methods. We emphasise here the profoundly general implications of the orderly trends contained in Figure 1 which may be analysed as previously in terms of central ion core-charge and inter-electronic correlation terms. In particular, the typical separation between successive couples $[MCl_6]^{z/z-1}$ and $[MCl_6]^{z-1/z-2}$ for any one element (vertical separation between parallel lines on Figure 1) is substantially smaller than for the hexafluorides (typically 1.4 V *vs.* 2.0 V), directly reflecting electron–electron correlations within the t_2 manifold, and in accord with anticipated nephelauxetic effects.

Across each transition series the progressions in redox potentials for isovalent complexes show comparable gradients for chlorides and fluorides (Figure 2). (We have recently

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† The species hexachloromolybdate(VI) has been reported previously (ref. 6) although its formation was questioned later. The potential at which this species is formed shows that it should indeed be a compound stable enough for characterisation.

extended the $[MF_6]^{z/z-1}$ data to include the reversible d^4/d^5 couple for $[IrF_6]^{2-}$.) Some convergence is observed such that the difference in stability of corresponding high oxidation state fluoride and chloride complexes is smaller for the later elements (and least for the maximum oxidation states, *e.g.* $[MoCl_6]^{0/1-}$ = +2.20 V; $[MoF_6]^{0/1-}$ = +2.08 V). This comparison has been made exact by direct measurement in CH_2Cl_2 of selected fluorides and chlorides coexisting in the same electrochemical cell.

A notable implication of the strictly parallel redox behaviour of 2nd and 3rd row hexahalogenometallates (Figure 2) is that the spin-orbit coupling energy effects anticipated to cause measurable deviations between corresponding 4d and 5d electrode potentials do not emerge except possibly at the d^3/d^4 couple. We note that it is this couple which is calculated to contain the largest spin-orbit coupling energy contribution, thereby favouring reduction of the 3rd row element.[7]

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