Electrochemical Reduction of Trimetallic $[M(M'S_4)_2]^{2-}$ Ions ($M = Ni^{II}$, Pd^{II}, or Pt^{II}; $M' = Mo$ or W)

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Summary Trimetallic $[M(M'S_4)_2]^{2-}$ ions ($M = Ni^{II}$, Pd^{II}, or Pt^{II}; $M' = Mo$ or W) exhibit reversible electrochemical reduction in nonaqueous solvents; the existence of formal monovalent ($M = Ni$ or Pd) and zerovalent ($M = Ni$, Pd, or Pt) complexes is indicated.

The thioanions $[MoS_4]^{2-}$ and $[WS_4]^{2-}$ function as bidentate chelating ligands in the square-planar trimetallic complexes $[Ni(MoS_4)_2]^{2-}$, $[Ni(WS_4)_2]^{2-}$, and $[Pt(WS_4)_2]^{2-}$ first reported by Müller and his co-workers.[1] We have prepared the remaining members of this series, $[Pd(MoS_4)_2]^{2-}$, $[Pd(WS_4)_2]^{2-}$, and $[Pt(MoS_4)_2]^{2-}$, and have observed that all these compounds undergo novel electrochemical reactions.

The new complexes were prepared by reaction of aqueous solutions of K_2PdCl_4 or K_2PtCl_4 with aqueous acetonitrile solutions of the ammonium salts of the thiometallate ions, followed by precipitation of the products with an excess of tetra-alkylammonium halide.† The use of mixed solvents was found to greatly enhance the yields and purities of all compounds.

Cyclic voltammograms of each compound were measured using the three-electrode technique in acetonitrile or dimethylformamide (DMF) solvent, 0·1 M in Et_4NClO_4 supporting electrolyte, at room temperature (23 ± 2 °C). Voltages were measured relative to a saturated calomel electrode (S.C.E.). The ferrocene–ferricinium ion redox couple was used as an external standard.

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† All new compounds gave satisfactory elemental analyses.

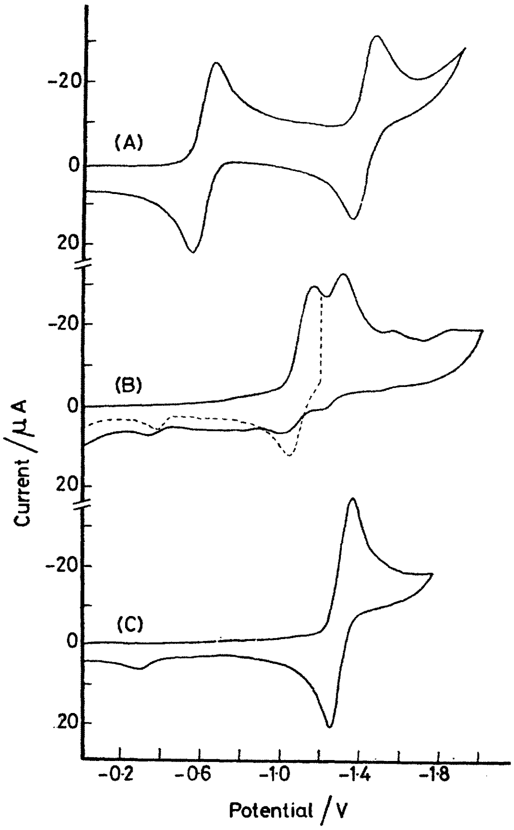

FIGURE. Cyclic voltammograms of (A) $(\mathrm{Pr_4N})_2[\mathrm{Ni(MoS_4)_2}]$, (B) $(\mathrm{Et_4N})_2[\mathrm{Pd(MoS_4)}]$, and (C) $(\mathrm{Et_4N})_2[\mathrm{Pt(MoS_4)_2}]$ in DMF–$\mathrm{Et_4NClO_4}$. Sample concentrations 10^{-3} M, scan rate 3 V $\mathrm{min^{-1}}$, potentials *vs.* S.C.E.

The Figure (A), a typical cyclic voltammogram obtained from $[\mathrm{Ni(MoS_4)_2}]^{2-}$, shows two reversible one-electron reductions at −0·60 and −1·40 V *vs.* S.C.E. The analogous Pd complex [Figure (B)] shows two closely spaced reductions, the first one being reversible if the scan direction is reversed shortly after the current maximum (dashed line), and the second irreversible up to 500 mV $\mathrm{s^{-1}}$ scan rate. The scan of $[\mathrm{Pt(MoS_4)_2}]^{2-}$ [Figure (C)] exhibits one reduction process which, on the basis of peak shape and peak current, involves two electrons. When $[\mathrm{Pt(WS_4)_2}]^{2-}$ was studied in MeCN with $\mathrm{Et_4NBr}$ supporting electrolyte, evidence of a shoulder on the positive side of the reduction wave was seen.

The progression of first reduction potentials to more negative values as the mass of the central metal increases is evident in the Figure. In sharp contrast, there is negligible change in first reduction potentials when the central metal atoms are held constant but the ligand is changed from $[\mathrm{MoS_4}]^{2-}$ to $[\mathrm{WS_4}]^{2-}$ (Table). The second reduction of these complexes is more sensitive to the ligand than the first reduction, although the magnitude of this effect is much less than that of changing the central metal atom on the first reduction potentials.

TABLE

Complex	Reduction potentials[a] $E_{\frac{1}{2}}(1)$/V	 $E_{\frac{1}{2}}(2)$/V
$[\mathrm{Ni(MoS_4)_2}]^{2-}$	−0·61	−1·40
$[\mathrm{Ni(WS_4)_2}]^{2-}$	−0·61	−1·57
$[\mathrm{Pd(MoS_4)_2}]^{2-}$	−1·09	−1·24
$[\mathrm{Pd(WS_4)_2}]^{2-}$	−1·05	−1·28
$[\mathrm{Pt(MoS_4)_2}]^{2-}$	−1·30	b
$[\mathrm{Pt(WS_4)_2}]^{2-}$	−1·35	b

[a] DMF solution. 0·1 M $\mathrm{Et_4NClO_4}$ supporting electrolyte, potentials *vs.* S.C.E. [b] See text.

The behaviour of the Ni complexes is most readily interpreted as sequential reduction at the central metal atom, as shown in equation (1). The first reduction of the Pd complexes is similarly consistent with formation of a $\mathrm{Pd^I}$ complex. The irreversibility of the second Pd reduction and the 2-electron Pt wave is indicative of a more complex situation.

$$[\mathrm{Ni^{II}(MS_4)_2}]^{2-} \overset{e^-}{\rightleftharpoons} [\mathrm{Ni^{I}(MS_4)_2}]^{3-} \overset{e^-}{\rightleftharpoons} [\mathrm{Ni^{0}(MS_4)_2}]^{4-} \qquad (1)$$
$$\mathrm{M = Mo\ or\ W}$$

The anomalous behaviour of the $\mathrm{Pt^{II}}$ complexes is consistent with overlap of two different electrode processes, which is partially resolved in $[\mathrm{Pt(WS_4)_2}]^{2-}$. This situation has been described theoretically by Polcyn and Shain,[2] and was recently precedented by Geiger[3] in his study of the reduction of $[\mathrm{Pt(mnt)_2}]^{2-}$ (mnt = $[\mathrm{S_2C_2(CN)_2}]^{2-}$).

Geiger[3] argued that his results were in agreement with a change in the occupied orbitals between $[\mathrm{Pd(mnt)_2}]^{3-}$ (half-filled b_{1g}, metal-centred) and $[\mathrm{Pt(mnt)_2}]^{3-}$ (half-filled a_g, ligand-centred, but close enough in energy to b_{1g} such that the second reduction resulted in half filling b_{1g}) which resulted in the anomalous electrochemical behaviour of $[\mathrm{Pt(mnt)_2}]^{2-}$. An a_g ground state was previously established in $[\mathrm{Au(mnt)_2}]^{2-}$ (isoelectronic with $[\mathrm{Pt(mnt)_2}]^{3-}$) by Schlupp and Maki.[4]

Our observation that the second reduction of the $[\mathrm{Ni(M'S_4)_2}]^{2-}$ species is reversible while that of the Pd complexes is irreversible, coupled with the trend of the first reduction to occur at more negative potentials as the mass of the central metal atom is increased, suggests that in these $[\mathrm{MS_4}]^{2-}$ complexes the energy levels become quite close at Pd, with b_{1g} lower, and become indistinguishable at Pt, where the two reductions overlap almost entirely. The two reductions of the Ni complexes thus fill the b_{1g} orbital, while at Pd b_{1g} is first half-occupied, then a_g is half-filled, and the relative energies in the case of Pt are so close as to be coincident under our conditions.

This work was supported by the Research Corporation and the Brown University Materials Research Laboratory.

(*Received*, 23*rd August* 1978; *Com.* 926.)

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