Inertness of the Trimethylplatinum(IV) Aquo-ion to Electrochemical Reduction

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Summary The polarogram of the trimethylplatinum(IV) ion has four well separated waves at such negative potentials as to indicate the extreme robustness of the $(H_2O)_3{\cdot}Pt^{IV}Me_3^+$ complex.

THE structure of the trimethylplatinum(IV) aquo-ion $[Me_3Pt(H_2O)_3]^+$ in which the methyl groups have a *fac*-orientation about the metal, has been established by ^1H (ref. 1) and ^{17}O n.m.r.[2] spectroscopy and by Raman spectroscopy.[3] The inertness of the metal–carbon bonds, rare in transition-metal chemistry, precludes e.m.f. measurements; we report here a preliminary polarographic investigation, which illustrates the reduction sequence and emphasises the robustness of the complex.

Solutions of the ion were prepared by shaking together stoicheiometric amounts of trimethylplatinum(IV) iodide and silver sulphate in water, and removing the precipitated silver iodide. The ^1H n.m.r. spectrum of the filtrate confirmed the presence of the trisaquo-ion. Ordinary direct and derivative mercury-drop polarograms were obtained on solutions *ca.* 7×10^{-3}M in $Me_3Pt_{aq}^+$ and 0·5M in sodium sulphate. N.m.r. spectra[1] and conductance measurements[4] show that the sulphate ion does not enter the co-ordination sphere of the metal at this concentration. A conventional divided H-cell with, as reference, 0·5M-Na_2SO_4| Hg_2SO_4| Hg, was used. Repeated scans on several samples clearly show (Figure) four waves with half-wave potentials at *ca.* −1·05, −1·35, −1·55, and −1·8 V against the Hg_2SO_4 electrode used. The waves are irreversible, with slight maxima. Both features, the four-fold wave and, more notably, the highly negative potentials required for the reductions, stand in marked contrast with observations[5] on other platinum(IV) complexes, which show usually one (IV → II), sometimes two (IV → II and II → 0?) or occasionally, a trace of a third (IV → III) wave, at potentials more positive by 0·7—1·3 V than those we report. The four waves of the Figure are to be ascribed *prima facie* to succeeding one-, two-, three-, and four- electron reductions, though the final wave could be hydrogen discharge catalysed by the complex or a product.[6] Reduction in solution by ordinary reductants[5] is clearly unlikely.

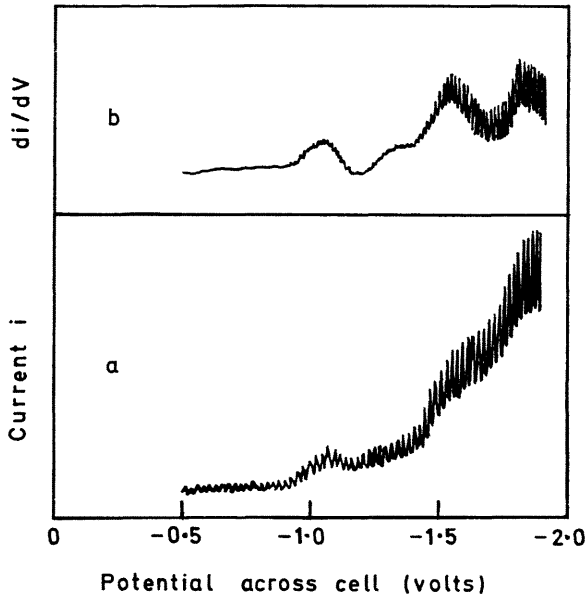

FIGURE. *Polarogram for reduction at dropping mercury electrode of* $Me_3Pt(OH_2)_3^+$ *in* 0·5 M-Na_2SO_4 *solution.* $Na_2SO_4|Hg_2SO_4|Hg$ *reference*; 25 °C. A: *Direct*; B: *Derivative.*

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