

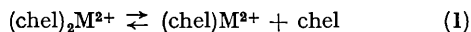
Association of Perchlorate Ion with Complex Ions of Palladium and Platinum

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EVIDENCE for the association of the perchlorate ion with cations in aqueous solution is extremely slight and inconclusive.¹ In 75% dioxan-25% water solution, however, nickel and zinc ion show reduced activity toward complex formation with acetylacetonone when sodium perchlorate is added in substantial amounts.² Hathaway and Underhill have shown that there is considerable interaction between the perchlorate ion and certain metal ions in the solid.³

In the course of work on solutions of nitrate and perchlorate salts in nitromethane, we encountered weak electrolyte behaviour.⁴ Certain complex palladium and platinum nitrates were strongly associated while corresponding perchlorates usually proved to be strong electrolytes. Two perchlorate salts, *viz.* $(\text{chel})_2\text{M}(\text{ClO}_4)_2$, where $\text{chel} = \text{PhS}\cdot\text{C}_3\text{H}_6\cdot\text{SPh}$ and $\text{M} = \text{Pd}$ or Pt , exhibited somewhat low solution conductivities in nitromethane although they behaved normally in methanol and *NN*-dimethylformamide. The adsorption spectra of solutions in nitromethane underwent a change on dilution which indicated a dissociation:

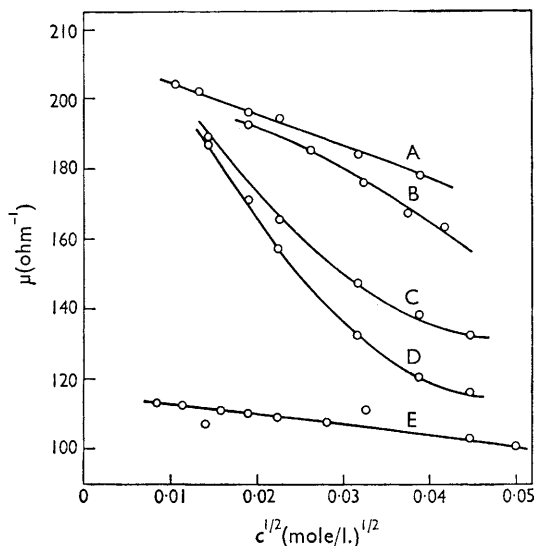
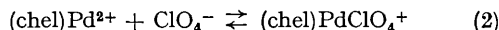


The change was reversed by adding excess of the chelating ligand.

It is apparent that the metal atoms in the species on the right hand side of the equation must be associated with two additional atoms in order to retain the normal co-ordination number of four. As the solvent molecules are very weak donors in this case, there is an opportunity for perchlorate to compete favourably in co-ordination. An attempt to isolate $(\text{chel})\text{Pd}(\text{ClO}_4)_2$ led only to the formation of an intractable oil.

The plot of the molar conductivity of $(\text{chel})_2\text{Pd}(\text{ClO}_4)_2$ shown in the Figure (curve D) indicates that the linear Onsager relation is not obeyed and, in the concentration range studied, the values lie between the likely ranges for 2:1 and 1:1 strong electrolytes. Examples of plots typical of such electrolytes are included in the

Figure for comparison (curves A and E). Curve D is suggestive of a weak electrolyte equilibrium:



Plots of molar conductivity at 25° in nitromethane against (concn.)^{1/2}

Curve A, $[(\text{Ph}_2\text{P})_2\text{C}_2\text{H}_4]_2\text{Pt}(\text{ClO}_4)_2$

Curve B, $\{(\text{PhS})_2\text{C}_2\text{H}_4\}_2\text{Pd}(\text{ClO}_4)_2$

Curve C, $\{(\text{PhS})_2\text{C}_3\text{H}_6\}_2\text{Pd}(\text{ClO}_4)_2$
+ $(\text{PhS})_2\text{C}_3\text{H}_6$ (0.007M)

Curve D, $\{(\text{PhS})_2\text{C}_3\text{H}_6\}_2\text{Ph}(\text{ClO}_4)_2$

Curve E, $[\text{Et}_4\text{N}]\text{ClO}_4$

It seems that the curve is approaching the linearity of a 1:1 electrolyte at higher concentrations, thus implying that only one perchlorate ion is associated to any appreciable extent. Curve C shows the effect of adding a 0.007 M-excess of $\text{PhS}\cdot\text{C}_3\text{H}_6\cdot\text{SPh}$ which further justifies the postulate of equilibrium (1). By decreasing the chelate ring size from six to five members, a considerable increase in ring

¹ M. M. Jones, E. A. Jones, D. F. Harmon, and R. T. Semmes, *J. Amer. Chem. Soc.*, 1961, **83**, 2038.

² L. G. Van Uitert, W. C. Fernelius, and B. E. Douglas, *J. Amer. Chem. Soc.*, 1953, **75**, 2739.

³ B. J. Hathaway and A. W. Underhill, *J.*, 1961, 3091.

⁴ J. Pluščec and A. D. Westland, *J.*, in the press.

⁵ L. A. Chugaeff and A. G. Kobljansky, *Z. anorg. Chem.*, 1913, **83**, 8, 159.

stability is effected.⁵ Curve B is a plot of the molar conductivity of $(\text{PhS}\cdot\text{C}_2\text{H}_4\cdot\text{SPh})_2\text{Pd}(\text{ClO}_4)_2$, which is only slightly decomposed to the mono-chelate in nitromethane. Similar results were obtained for $(\text{chel})_2\text{Pt}(\text{ClO}_4)_2$.

Since it is necessary for the metal atom to make

co-ordination sites available in order for ion association to take place, it follows that the associated species probably contains perchlorate in the first co-ordination sphere.

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