

SIX CO-ORDINATION BY Pd (II) ION

By

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The characteristic shape of predominant complexes of Pd (II) ion is square planer¹⁻³. However, in special cases, there are indications⁴⁻⁶ that additional, though weaker, bonds may be formed in the vacant octahedral sites due to axial interactions above and below the square plane. Sundaram and Sandell⁷ have indicated the existance of weak PdCl₅ and PdCl₆ complexes which was later confirmed by Grindberg and Kiseleva⁸ from spectrophotometric studies. In this communication, the existance of octahedral complexes of Pd (II) Ion with 3-picoline in 10% DMF-water and 15% DMSO-water media has been indicated from polarographic measurements and the results interpreted in the light of statistical and symmetry considerations.

EXPERIMENTAL

Materials. All chemicals used were of reagent grade. 1.0 M Sodium sulphate and 0.001% gelatin in final solutions were respectively used as base electrolyte and maxima suppressor in 0.5 mM solutions of Pd (NO₃)₂. The experimental technique is the same as described earlier⁹.

The Pd (II)-3-picoline system could not be studied in aqueous media due to the presence of oiliness in solution which appeared when the two are mixed. 10% DMF or 15% DMSO were used to

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dissolve the oiliness; these being the optimum amounts of non-aqueous component because while lower percentage in each case failed to dissolve oiliness, the higher concentration on the other hand precipitated out the base electrolyte.

All the potential measurements were made against S. C. E. at 32° C throughout the investigations.

RESULTS

The polarography of solutions containing 0.5 M PdNO₃, 1 M Na₂SO₄, 0.001% gelatin and varying amounts of 3-picoline with final concentrations (V/V) of the non-aqueous components as stated revealed a single well defined diffusion controlled reduction wave involving two electrons in each case. Since the value of $E_{\frac{1}{2}}$ at zero ligand concentration can not be obtained experimentally due to

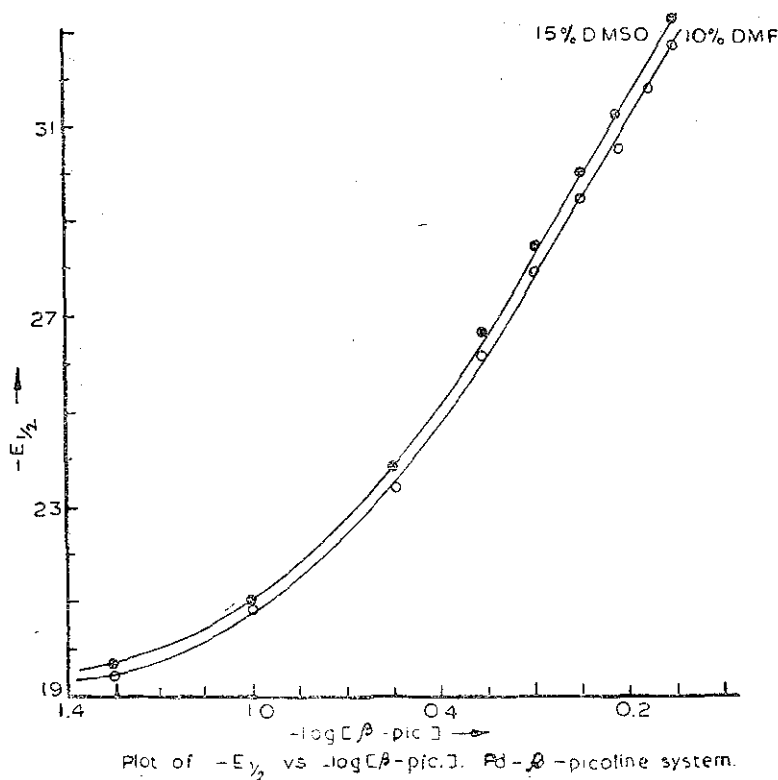


Fig. 1

anodic dissolution of mercury, the extrapolated value was used as done previously by other workers.¹⁰⁻¹¹ Now knowing change in half-wave potential as a function of ligand concentration (Fig. 1), the method of DeFord and Hume¹² as improved by Irwing¹³ was applied to determine the formation constants of the stepwise complexes of Pd (II) with 3-picoline.

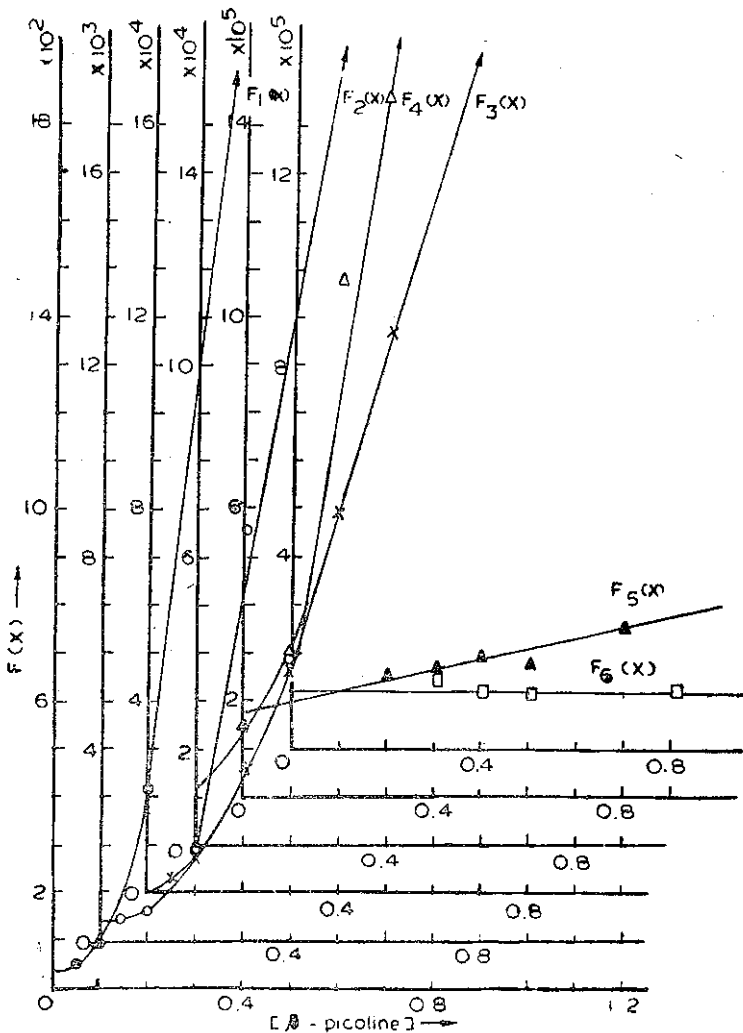


Fig. 2

The following values were obtained :

Overall Formation Constant	15% DMSO	10% DMF
β_1	30	25
β_2	300	200
β_3	500	1500
β_4	12000	15000
β_5	182000	75000
β_6	2080000	203000

The derived functions for the two systems are plotted in figures 2 and 3.

DISCUSSION

Since cumulative formation constant K_i has the relationship $\beta_i = K_1 \times K_2 \times K_3 \times \dots \times K_i$ with overall formation constant, our values for the systems under investigation are as follows :

Cumulative Formation Constant	15% DMSO	10% DMF
K_1	30	25
K_2	10	8
K_3	1.7	7.5
K_4	24	10
K_5	15.2	5
K_6	1.2	2.7

The trends in the formation constants are significant. The first three constants display the usual feature in so far as they progressively decrease in magnitude. From purely statistical considerations the higher complexes have lesser number of vacant ligand positions to be occupied which explains the lowering of formation constants from K_1 to K_3 . However, for the four co-ordinate complex, symmetry considerations overweigh statistical factors. Therefore, once the 1 : 3 complex has been formed, it has a strong tendency to 'catch' another ligand to attain an highly stable co-ordination number of four. The square planer 1 : 4 complex could attain octahedral configuration by co-ordinating two ligands with weak bond strength on the two sides of the square plane due to axial interactions. This, indeed, is

confirmed by the decreasing values of K_5 and K_6 for the higher complexes. Similar results have been obtained by Gozzi and Pantani¹⁴ for Rhodium complexes with chloride ions.

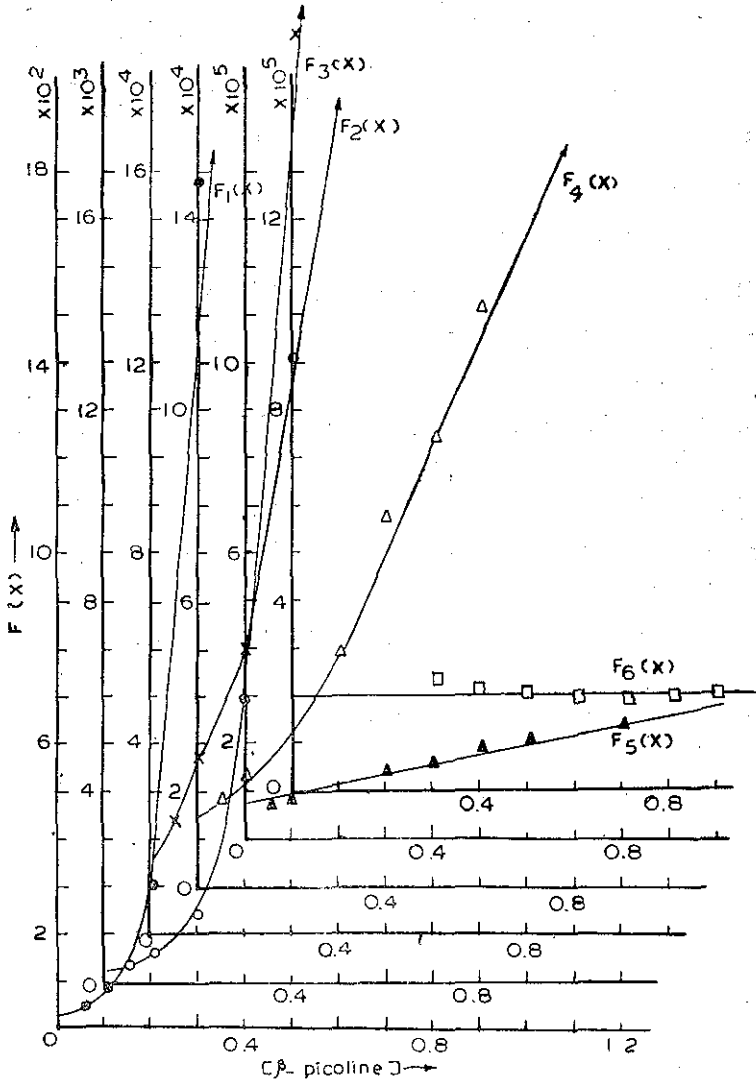


Fig. 3

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