

Equilibria in Complexes of Heterocyclic Ligands

By R. D. GILLARD* and J. R. LYONS

(The Chemical Laboratory, University of Kent at Canterbury, Canterbury, Kent)

Summary Changes with pH of the spectroscopic properties of aqueous solutions of bipyridyl complexes of platinum(II) are attributed to a reaction not at the metal ion but of the ligand, at its 6-position.

AMONG the best studied complexes formed in protic media are those involving co-ordination to metal ions of heterocyclic bases, such as pyridine, 2,2'-bipyridine, or 1,10-phenanthroline, and their derivatives.¹ We report here evidence for nucleophilic attack by hydroxide ion on the ligand in the bis-(2,2'-bipyridyl)platinum(II) ion and its 5,5'-dimethyl analogue.

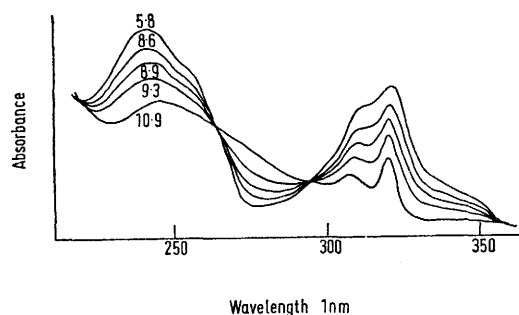
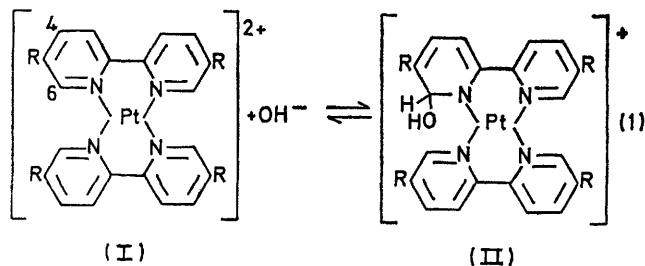


FIGURE 1. Electronic spectrum of aqueous $[\text{Pt}(\text{bipy})_2](\text{ClO}_4)_2$ as a function of pH.

The large changes in the electronic spectrum which occur on the addition of base (Figure 1) are attributed to equilibrium (1). These spectroscopic changes are complete in the time of mixing and are fully reversed by acidification.



Hydrolysis of the complexes is extremely slow under the conditions used. The apparent $\text{p}K$ for change, determined from the pH-dependence of the electronic spectrum, is 9.0 ± 0.2 ($\text{R}=\text{H}$) and 9.5 ± 0.3 ($\text{R}=\text{Me}$). Bis-(5,5'-dimethyl-2,2'-bipyridyl)palladium(II) ion exhibits the same type of behaviour, but decomposes on lengthy exposure to base ($\text{p}K = 8.2 \pm 0.3$). The changes occur with hydroxide but not chloride, so 5-co-ordinate structures for (II) are unlikely.

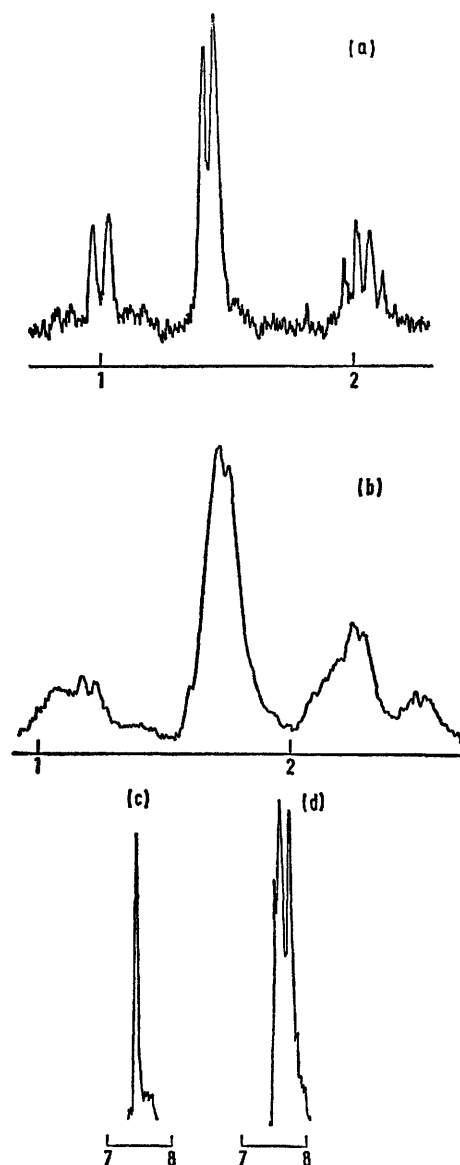


FIGURE 2. ^1H N.m.r. spectra at 100 MHz of (a) $[\text{Pt}(\text{bipy})_2](\text{NO}_3)_2$ in neutral D_2O ; (b) $[\text{Pt}(\text{bipy})_2](\text{NO}_3)_2$ in alkaline D_2O ; (c) methyl resonance of $[\text{Pt}(5,5'\text{-Me}_2\text{bipy})_2]\text{Cl}_2$ in neutral D_2O ; (d) $[\text{Pt}(5,5'\text{-Me}_2\text{bipy})_2]\text{Cl}_2$ in alkaline D_2O .

The nature of the species (II) in basic conditions is confirmed by the ^1H n.m.r. spectrum, which has been assigned by reference to the spectra of phenanthroline and its methyl-substituted derivatives [both complexed to platinum(II) and as the free ligands]. On basification, only the resonance of the 6,6'-protons suffers loss of intensity, which is accompanied by growth of a new peak at high field (Figures 2a and 2b). This change is fully reversed when the solution is neutralised, *i.e.* there is no specific exchange of any

aromatic hydrogen atom with the deuterium atoms of the solvent. Also, for $R = \text{Me}$, species (I) shows a single signal arising from the protons of the methyl group, whereas (II) shows at least three signals, arising from the inequivalence of the methyl groups (Figures 2c and 2d).

In heterocyclic molecules, where electron density has drained away from the ring through quaternisation of the nitrogen, nucleophilic attack at the carbon atom adjacent to the ring nitrogen is common² (and is frequently suggested as a kinetically significant fact). We suggest that 'quaternisation' by a metal ion may lead to similar low energy pathways for nucleophilic attack by solvent or other

Lewis base (although we do not observe the present striking spectroscopic features for all N-heterocyclic complexes).

Such equilibria could help to explain some anomalous features in the chemistry of such complexes including: (i) the spectroscopic change in alkaline solution of 5-nitro-phenanthroline and of its tris-complex with iron(II), attributed to deprotonation,³ but where, in the free molecule, we have been unable to detect exchange; and (ii) the rapid rate and detailed kinetic features of certain reactions of complexes of heterocyclic ligands.³

(Received, 8th February 1973; Com. 176.)

¹ W. W. Brandt, F. P. Dwyer, and E. C. Gyarmas, *Chem. Rev.*, 1954, **54**, 960; W. R. McWhinnie and J. D. Miller, *Adv. Inorg. Chem. Radiochem.*, 1969, **12**, 135; E. D. McKenzie, *Coordination Chem. Rev.*, 1971, **6**, 187.

² A. Albert, *Angew. Chem. Internat. Edn.*, 1967, **6**, 919; L. A. Paquette, 'Principles of Modern Heterocyclic Chemistry,' Benjamin, New York, 1968, pp. 235—239, pp. 289—290 and references therein; 'Heterocyclic Compounds—Pyridine and Derivatives,' ed. E. Klingsberg, Interscience, New York, Vol. II, 1961, Chs. III and IV by E. N. Shaw; also Vol. III, 1962, p. 3; 'Heterocyclic Compounds,' ed. R. C. Elderfield, Wiley, New York, 1952, Vol. 4, p. 203, p. 279 and p. 442.

³ J. Burgess and R. H. Prince, *J. Chem. Soc.*, 1965, 4697; D. W. Margerum, *J. Amer. Chem. Soc.*, 1957, **79**, 2728; D. W. Margerum and L. P. Morgenthaler, *J. Amer. Chem. Soc.*, 1962, **84**, 706; J. Burgess, *Inorg. Chim. Acta*, 1971, **5**, 133; *J.C.S. Dalton*, 1972, 1061; F. Basolo, J. G. Bergmann, R. E. Meeker, and R. G. Pearson, *J. Amer. Chem. Soc.*, 1956, **78**, 2676; M. L. Tobe, *Accounts Chem. Res.*, 1970, **3**, 377; F. Basolo and R. G. Pearson, 'Mechanisms of Inorganic Reactions,' Wiley, New York, 2nd edn., 1967, pp. 314ff. and references therein.