

Letter

A Nuclear Magnetic Resonance Study of Dicyano-2,2'-bipyridylplatinum(II)

GWYNETH NORD and B. V. AGARWALA *

Chemical Laboratory I (Inorganic Chemistry),
The H. C. Ørsted Institute University
of Copenhagen, DK-2100 Copenhagen,
Denmark

The supposed existence of so-called "covalently hydrated" forms of the Pt(II) complexes and of the free ligands has been used to give credence to the suggestion² that such ligand adducts are significant as intermediates in substitution and redox reactions of many other transition metal 2,2'-bipyridine and 1,10-phenanthroline complexes. These include the divalent and trivalent *tris* complexes of Fe, Ru and Os.

The nucleophiles OH⁻ and CN⁻ have recently been proven^{3,4} to be directly coordinated to the metal ion both in Pt(bpy)₂OH⁺ and in Pt(phen)₂CN⁺.** This is in direct contradiction to

* On leave from the University of Allahabad, India.

** bpy is 2,2'-bipyridine; phen is 1,10-phenanthroline.

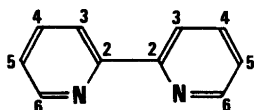


Fig. 1. System of numbering.

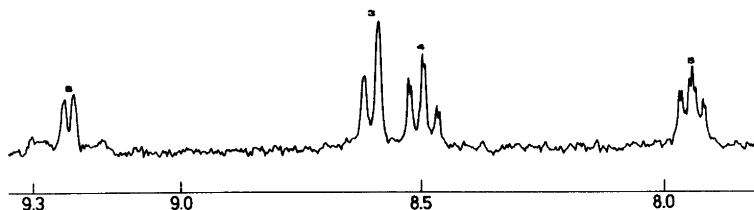


Fig. 2. 270 MHz ¹H NMR spectrum of 2.46×10^{-3} M Pt(bpy)(CN)₂ in D₂O – [D₆]-DMSO 30/70 (v/v) (T = 373 K, 217 scans). The system of numbering is given in Fig. 1.

earlier conclusions drawn by other workers who have postulated a "covalent hydration hypothesis",¹ *i.e.* the reversible formation of species in which the nucleophile is attached to a carbon atom of the aromatic ligand. This hypothesis is partly based upon new features in the ¹H NMR spectrum of Pt(bpy)(CN)₂ which are said to appear on cooling (to 298 K) solutions in aqueous dimethylsulfoxide. In view of the poor resolution of the reported spectra,⁵ and of our earlier disagreement³ with this interpretation of such spectral changes, we have reinvestigated this system.

The ¹H NMR spectrum of Pt(bpy)(CN)₂ at 373 K is given in Fig. 2. This is very simple and similar to that of the uncomplexed ligand in the same solvent (Fig. 3). It is noteworthy that the average position of the lowest field, H(6), signals for the complex is 9.23 p.p.m. On cooling to 298 K the solubility decreases but there are only barely perceptible changes in the positions of all the signals and there is *no new signal* at 6.77 p.p.m. as reported in Ref. 5. The spectrum given in this reference at 373 K is incomplete because the H(6) signals are missing. The authors specifically state⁵ that the signal at lowest field is at 8.73 p.p.m., *i.e.* about where we find the H(3) signals. They nevertheless divide all the H's among the signals of their incomplete spectrum and using differences between these and a spectrum at 298 K (which cannot be reproduced under the given conditions) state that the "new signal" at 6.77 p.p.m. is unequivocally assigned in a ligand adduct. This ligand adduct is depicted with OH bound to the 6 position, *i.e.* the position for which we find the signals at 9.23 p.p.m.

In view of the fact that the published structural evidence⁶ for covalent hydration of uncomplexed bpy and phen has now also been shown⁷ to be

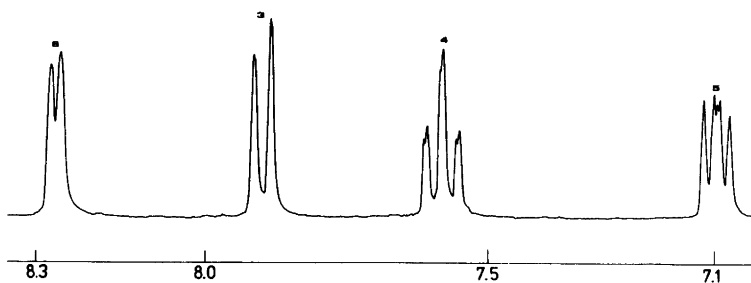


Fig. 3. 270 MHz ^1H NMR spectrum of bpy in $\text{D}_2\text{O}-[\text{D}_6]\text{-DMSO}$ 30/70 (v/v) ($T=300$ K, 200 scans).

spurious, it would seem that the only *direct* evidence for covalent hydration is based on this one new band which does *not* belong to this complex.

The non-existence of stable covalently hydrated adducts poses the question as to whether or not it is necessary to postulate structurally analogous reactive intermediates in mechanisms for reactions which do not involve an overall chemical change in the aromatic ligand. It would seem possible that the properties which are described in Ref. 2 as "anomalous" really reflect the inadequacy or inaccuracy of the reported experimental data. The present evidence leads us to believe that the chemistry of these complexes does, in fact, allow interpretation in terms of known structures and simpler "classical" mechanisms. Certainly the results of the present work confirm our earlier conclusion^{3,13} that it is incorrect to assume that the properties of this important class of coordination complexes reflect the organic chemistry of the ligands.

Experimental. Red $\text{Pt}(\text{bpy})(\text{CN})_2$ was prepared according to Ref. 8. The analysis (C:H:N) was good and the IR spectrum agreed with that in Ref. 9. The crystals are yellow when wet. This colour change is analogous to that known for $\text{Pt}(\text{bpy})\text{Cl}_2$ and which has been attributed to the stacking of the complexes, so that Pt-Pt interactions occur in the red form.¹⁰ There are no significant differences in the molecular details between the red and yellow forms, but the planes of the molecules are not parallel in the yellow form, nor is there any Pt-Pt overlap.¹¹ At room temperature $\text{Pt}(\text{bpy})(\text{CN})_2$ is sparingly soluble both in water and in $\text{D}_2\text{O}-\text{DMSO}$ 30/70 (v/v). The solutions obey Beers law (210 nm to 360 nm, 4.0×10^{-6} M to 2.6×10^{-5} M) and the spectrum is "normal" for a bpy complex, e.g. the integrated area of the lower energy (long axis¹²) polarised $\pi-\pi^*$ transition ($\lambda_{\text{max}} = 314$ nm, $\epsilon_{\text{max}} = 1.56 \times 10^4$, in water) is approximately equal to that for bpyH^+ and one half that for $\text{Pt}(\text{bpy})_2^{2+}$. No new features appear in the absorption spectrum on heating or cooling the solutions. Heating a solution in $\text{D}_2\text{O}-\text{DMSO}$

30/70 (v/v) for two days at 363 K produced no significant (less than 2%) change in room temperature absorption.

The ^1H NMR measurements were made as in Ref. 3, using TMS as an internal standard.

Acknowledgements. The NMR spectrograph is the property of the Danish Natural Science Research Council. Thanks are due to Dr. K. Schaumburg for expert advice.

- Of some thirty publications, representative are a. Gillard, R. D. and Lyons, J. R. *J. Chem. Soc. Chem. Commun.* (1973) 585; b. Sagués, S. A. A., Gillard, R. D., Lancashire, R. J. and Williams, P. A. *J. Chem. Soc. Dalton Trans.* (1979) 193.
- Gillard, R. D. *Coord. Chem. Rev.* 16 (1975) 67.
- Farver, O., Mønsted, O. and Nord, G. *J. Am. Chem. Soc.* 101 (1979) 6118.
- Wernberg, O. and Hazell, A. *J. Chem. Soc. Dalton Trans.* (1980) 973.
- Gillard, R. D., Kane-Maguire, L. A. and Williams, P. A. *Transition Met. Chem.* 1 (1976) 247.
- Henry, M. S. and Hoffman, M. Z. *J. Am. Chem. Soc.* 99 (1977) 5201.
- Kotlicka, J. and Grabowski, Z. R. *Photochemistry II* (1979) 412.
- Bielli, E., Gidney, P. M., Gillard, R. D. and Heaton, B. T. *J. Chem. Soc. Dalton Trans.* (1974) 2133.
- Supplementary Tables* (Suppl. No. 2100) to Ref. 8.
- Osborn, R. S. and Rogers, D. *J. Chem. Dalton Trans.* (1974) 1002.
- Osborn, R. S. *Private communication* to Nord, G., May 1979.
- Bosnich, B. *Acta Chem. Research* 2 (1969) 266.
- Nord, G. *Acta Chem. Scand. A* 29 (1975) 270.

Received April 10, 1981.