

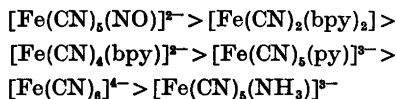
were found to show the same pattern with a maximum in the Job plot at a Co:Fe ratio of about 2:1.

Each of the complexes in Table 1 were found to follow Beer's law at concentrations used in the Job experiments. $[\text{Fe}(\text{CN})_5(\text{H}_2\text{O})]^{3+}$ and $[\text{Fe}(\text{CN})_5(\text{NO}_2)]^{4-}$ also react with the two $[\text{Co}(\text{his})_2]^+$ isomers to give brown species, but the behaviour of these two iron(II) complexes is more complicated since their solutions do not comply with Beer's law.

Conclusions. The experimental results suggest that two of the cyanoiron(II) complexes, $[\text{Fe}(\text{CN})_5(\text{py})]^{3-}$ and $[\text{Fe}(\text{CN})_5(\text{NH}_3)]^{3-}$, form tricenter μ -cyano-iron(II)dicobalt(III) species with each of the two $[\text{Co}(\text{his})_2]^+$ isomers. This is in analogy with the mode of reaction found for $[\text{Fe}(\text{CN})_6]^{4-}$, which has been studied in more detail.¹

Of the factors controlling the formation of a stable Co-NC-Fe-CN-Co chain the redox properties of the iron center and the charge of the iron(II) complex are likely to be important.

The standard redox potentials for the Fe(II)/Fe(III) couples⁸⁻¹⁰ presumably decrease in the order



Our experiments have shown that only the three more reducing of these iron(II) complexes form μ -cyano species. The same three complexes are also the more favoured with regard to coulombic interaction with the positively charged cobalt(III) complexes.

The electrochemistry of the new tricenter compounds appears to be interesting. The Co-(III)-NC-Fe(II)-CN-Co(III) moiety may undergo a one-electron oxidation as well as a two-electron reduction.

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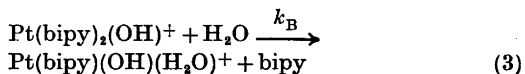
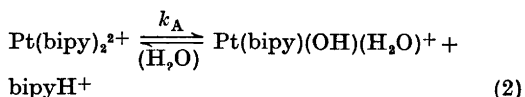
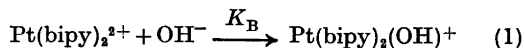
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The Base Hydrolysis of Bis(2,2'-bipyridyl)platinum(II) Perchlorate

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The cation $[\text{Pt}(\text{bipy})_2]^{2+}$ of the title compound reacts with aqueous acid and base as follows:



These reactions are followed by fast proton equilibration of the products of the slow steps 2 and 3 and by the very slow dissociation of the second (bipy) ligand.

Equilibrium 1 is fast as is evidenced by the pH dependence of the compositions of the solutions, resulting in the changes of ultraviolet absorption which were reported by Gillard *et al.*¹⁻³ These authors envisage attachment of OH to a carbon atom of the ligand with no increase in the coordination number of the metal ion. Although we have, ourselves, shown^{4,5} that the oxidation of OH^- by $\text{Fe}(\text{bipy})_3^{3+}$ and related oxidising complexes occurs through "a highly reactive precursor complex $[\text{Fe}(\text{bipy})_2\text{R}\cdot\text{OH}]^{2+}$ where $\text{R}\cdot\text{OH}$ is probably the pseudo-base of a radical formed by addition of an electron to a ligand which approaches the structure of a quaternary cation" we consider it likely that $\text{Pt}(\text{bipy})_2^{2+}$ in solution contains coordinated water. Such water would be acid and equilibrium 1 thus involve addition of OH^- to the metal ion. The fact that neither $\text{Pt}(\text{py})_4^{2+}$ (py = pyridine) nor $\text{Pt}(\text{bipy})(\text{py})_2^{2+}$ show pH dependent spectral behaviour similar to that of $\text{Pt}(\text{bipy})_2^{2+}$ suggests to us that distorted square planar coordination is necessary for equilibria such as (1) and that this is a consequence of the steric, not of the chemical properties of the coordinated ligands. Two molecules of bipy, or of 1,10-phenanthroline, cannot form unstrained square planar complexes because of steric interaction between the H atoms at the 6,6' and 2,9 positions, respectively. This strain may be relieved by distortion - as may easily be seen from models.

Thus, for bipy it is possible to retain the 4 N atoms of the ligands in a plane and distort the two rings about 30 degrees towards the *trans* configuration of the ligands, while for the more rigid 1,10-phenanthroline the steric interaction cannot be relieved in a structure with square plane coordination. Steric hindrance is also eliminated in *cis*-bis octahedral complexes (see Ref. 7 for discussion). Analogously, addition of a fifth (mono-dentate) ligand could also form a sterically unhindered five-coordinate Pt(II) complex similar to that well documented as the trigonal bipyramidal intermediate in substitutions at d^8 electron configuration metal ions. Pt(bipy)₂(OH)⁺ formed according to equilibrium 1 would in this case be expected to be an intermediate in the base hydrolysis reaction and, by combining the value for $pK_B = 4.76$ (see experimental) with the kinetic data given in the table, we find that this is so. Changes in pK_B with temperature are, within the experimental error, equal to those due to the fast protonic equilibrium of the buffer. The loss of a proton from water loosely bound to the Pt in Pt(bipy)₂²⁺ would also explain the specificity of equilibrium 1 to OH⁻. The data in the table for k_B , using reaction rate theory, give $\Delta H^\ddagger = 22.1$ kcal/mol; $\Delta S^\ddagger = -13.5$ cal/(mol K).

We consider that the new experimental data reported here clearly demonstrate that the unified mechanism given in Ref. 2, which purports to explain unusual properties of all diimine complexes in basic solution in the terms of ligand reactions only, cannot be accepted.

Experimental. Solutions of Pt(bipy)₂(ClO₄)₂ (6×10^{-6} M to 5×10^{-5} M) were found to obey Beers Law (220 to 350 nm) in each of a series of buffers (pH 2 to 12) and also in 0.01 NaOH and in 0.01 M HCl. From data at 16 wave-

Table 1. Rate constants for hydrolysis of Pt(bipy)₂²⁺ (k_A) and Pt(bipy)₂(OH)⁺ (k_B). Ionic strength 0.10 M with NaCl.

Temp. °C	Medium 0.01 M	Constant ^a s ⁻¹
25	NaOH	$10^7 k_B = 4.0 \pm 0.1$
25	borax	$10^7 k = 1.8 \pm 0.1$
25	borax	$10^7 k$ calc. ^b = 1.86
45	NaOH	$10^6 k_B = 4.50 \pm 0.08$
45	borax	$10^6 k = 1.90 \pm 0.04$
60	NaOH	$10^5 k_B = 2.3 \pm 0.3$
60	borax	$10^5 k = 1.10 \pm 0.03$
60	HCl	$10^5 k_A^c = 0.058 \pm 0.002$

^a $k = \alpha k_A + (1 - \alpha)k_B$; $(1 - \alpha)/\alpha = K_B[\text{OH}^-]$

^b k calc. = $(1 - \alpha)k_B$ using $pK_B = 4.76$ together with $\log [\text{OH}^-] = -4.82$ in medium.

^c First half-life only.

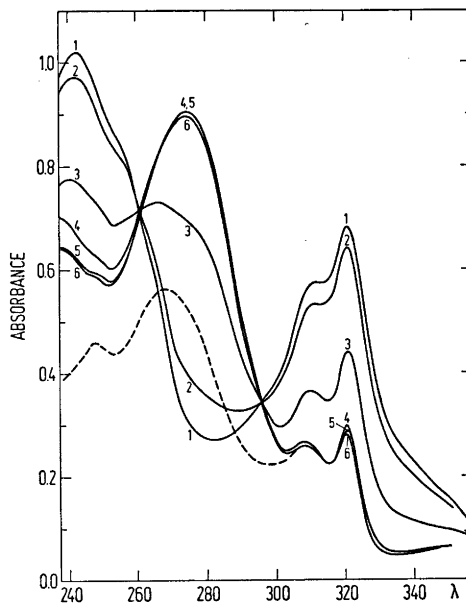


Fig. 1. Hydrolysis of 3.35×10^{-5} M Pt(bipy)₂(ClO₄)₂ in 0.01 M borax. Ionic strength 0.10 M, 60 °C. (Spectra measured at room temperature). — Absorption spectra of reaction solutions.

No.	1	2	3	4	5	6
Time (h)	0	4	23	95	119	265

--- Absorption spectrum of aqueous phase of 5 after chloroform extraction. This is also the spectrum of 3.35×10^{-5} M Pt(bipy)(OH)₂ in the medium and this coincides with 5 above 305 nm. 5 minus --- is the absorption spectrum of 3.35×10^{-5} dipy in the medium.

lengths and at an ionic strength of 0.1 M, pK_B for equilibrium 1 is 4.76 ± 0.01 at 25 °C.

The rate of appearance of free bipy according to reactions 2 and 3 was followed spectrophotometrically after extraction into chloroform. First order plots were obtained and the rate constants calculated from these agreed with those from the time dependence of the changes in the spectra of the reaction mixtures as illustrated in Fig. 1.

Pt(py)₄Cl₂·3H₂O was a sample from the collection of S. M. Jørgensen. The other complexes were prepared by published methods. Extinction coefficients all agreed with the literature values.

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