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# Some Properties of 2,2' -Bipyridine, 1,10-Phenanthroline and Their Metal Complexes

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# Some Properties of 2,2′-Bipyridine, 1,10-Phenanthroline and Their Metal Complexes

Three recent long reviews[1,2,3] deal with 2,2′-bipyridine, 1,10-phenanthroline and their metal complexes. The three reviews are all chiefly concerned with thermal reactions in aqueous solution and they all contain at least 30 structural formulas of species in which the ligand is depicted as modified, either by addition of water across a double bond or by addition of a nucleophile (usually $OH^-$ or $CN^-$) to a C atom of a heteroaromatic ring. In some cases the adducts were said to take part in equilibria (either with the free or complexed ligand) and in other cases the adducts were postulated to be intermediate in reaction sequences *without overall chemical change in the ligand.* In this extra step in a reaction mechanism, a nucleophile is supposed to be transferred from the ligand to the metal center.[4]

F. P. Dwyer (1910–1962) discussed metal–nitrogen double bonding in complexes of pyridine, 2,2-bipyridine, and 1,10-phenanthroline in the section subtitled "The Reactivity of Coordinated Molecules" of an article[5] published soon after his death. He considered that the analogy between coordination to a metal and quarternization of the nitrogen is closer than that between metal coordination and protonation "though certainly not equivalent." He also states that little is known of the reactivity of these ligands in complexes or whether, for instance, the phenanthroline ring is sensitized or stabilized to disruptive oxidation on coordination.

In the past 10 years, much abortive effort has been expended on attempts to isolate ligand adducts, or to detect them in systems

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undergoing nucleophilic substitution. Constable[2] and Serpone *et al.*[3] agree that there is no structural evidence for such intermediates, but nevertheless large sections of their reviews are devoted to demonstrating the inadequacy or inaccuracy of the published data which was supposed to characterize such species and to discussing either why they do not exist, or what happens when the electronic structures of the ligands are so drastically modified, by substituents, that they do chemically react with solvent and base. The questions thus arise as to why, when no ligand reaction is observed, these authors consider it necessary to describe in such detail the ways in which such adduct intermediates were sought and not found, and also as to why they not only expected to exist but also are still "eagerly awaited"?[6] The answers can perhaps partly be found in Ref. 1 where the author concluded that some of the thermodynamic, structural and kinetic properties of 2,2′-bipyridine, 1,10-phenanthroline and their complexes were "anomalous in that no ready explanation was available in molecular terms." We cannot find such anomalous properties and also show here that the complexes are in fact tractable within the framework of "classical" coordination chemistry.

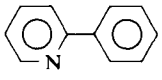
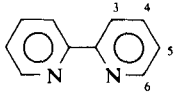
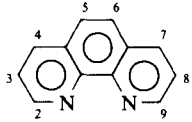
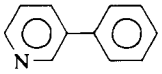
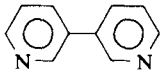
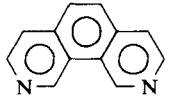
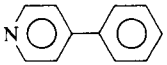
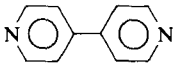


## EQUILIBRIA

The $pK_A$ values of the conjugate acids of 2,2′-bipyridine and 1,10-phenanthroline are included in Table I. In disagreement with Ref. 1, we do not find it anomalous that the potentially chelate ligands are reluctant to accept a second proton. This can be reasonably attributed to stabilization of the monoprotonated form by H bonding between the two N's and/or to destabilization of the diprotonated form by electrostatic repulsion between the protons on the N atoms in a planar *cis* configuration. Both effects would be expected to be larger for the more rigid 1,10-phenanthroline, in qualitative agreement with the trend in $pK_A$ values. A more detailed discussion is hampered by our lack of knowledge of the energy of the barrier for rotation of the two rings of 2,2′-bipyridine which, when unprotonated, has the *trans* configuration both in solution[9] and in the solid state.[10] For biphenyl the height of the rotational barriers have been calculated[11] as 3.7 kcal/mole for a twist angle between the rings $\theta$ of 90° and 2.5

TABLE I

$pK_A$ values for protonated pyridine and some derivatives: "a" from Ref. 7; others from Ref. 8

| L | $pK_{LH^+}$ | L | $pK_{LH^+}$ | $pK_{LH_2^{2+}}$ | L | $pK_{LH^+}$ | $pK_{LH_2^{2+}}$ |
|---|---|---|---|---|---|---|---|
|  | 5.2 | | | | | | |
|  | 4.48 |  | 4.3[a] | −0.2[a] |  | 4.9[a] | −1.6[a] |
|  | 4.80 |  | 4.60 | 3.0 |  | ~4.0 | ~2.4 |
|  | 5.55 |  | 4.82 | 3.17 | | | |

kcal/mole at $\theta = 0°$. It is relevant that the calculated minimum energy corresponds to $\theta$ in the gas phase (40–45°). For biphenyl $\theta$ is 20–25° in solution.[11] It is therefore reasonable not only that the height of the barrier for 2,2′-bipyridine is small compared with $\Delta H°$ for monoprotonation (approximately 16 kcal/mole)[7] but also that the *cis* structure for the monoprotonated cation, which was "frozen" in crystals of 2,2′-bipyridinium(1+)(2,2′-bipyridine)oxodiperoxovanadate(1−)[12], may approximate that in solution. In crystals of 2,2′-bipyridinium(2+)bis(fluorosulphate) the diprotonated cation is distorted 31.5° from the ideal *trans* configuration.[13] In strongly acid solutions, the mono- and diprotonated 2,2′-bipyridinium cations adopt skew transoid configurations with averaged interplanar angles of approximately 30° and 60°, respectively.[14]

Stability constants for metal complexes of the title ligands[7] show no irregularities when the ground-state electronic configuration of the metal ion remains unchanged. This is illustrated in Fig. 1. Even when there is a change of electronic configuration ($Fe^{2+}$), or coordination number ($Cu^{2+}$), the effect of substituting 1,10-phenanthroline (phen) for 2,2′-bipyridine (bpy) is constant within the experimental error of the data. This is illustrated in Table II for some *tris* complexes. The standard enthalpy changes and the activation energies for aquation (acid hydrolysis) also conform with such correlations.[7,16]

Pyridine (py) is among the ligands studied by Jannik Bjerrum[17]: he found no anomalies in the equilibrium constants. It is therefore not surprising that the report,[4] that aqueous solutions of $Pt(py)_4Cl_2^{2+}$ contain appreciable concentrations of the conjugate base of covalent hydrate, has been shown to be incorrect.[18] Values of a "$pK_A$" for this complex as different as 3.4 and 7.2 were calculated (see references in Ref. 3) from measurements of the pH of millimolar solutions. Seddon *et al.*[18] now report that "By the use of a wide range of physical and spectroscopic techniques (including $^1H$, $^{13}C$ and $^{195}Pt$ NMR spectroscopy and time- and concentration-dependent pH measurements) we have unambiguously shown that the result presented by Gillard as evidence for covalent-hydration is due to the presence of a small amount of a strong acid impurity." Also Grinberg *et al.* in 1966[19] found that, in contrast to the analogous mixed $NH_3$,py complexes, the tetrapyridino complex could not be *titrated* as an acid. The pyridine complexes are not discussed further here.

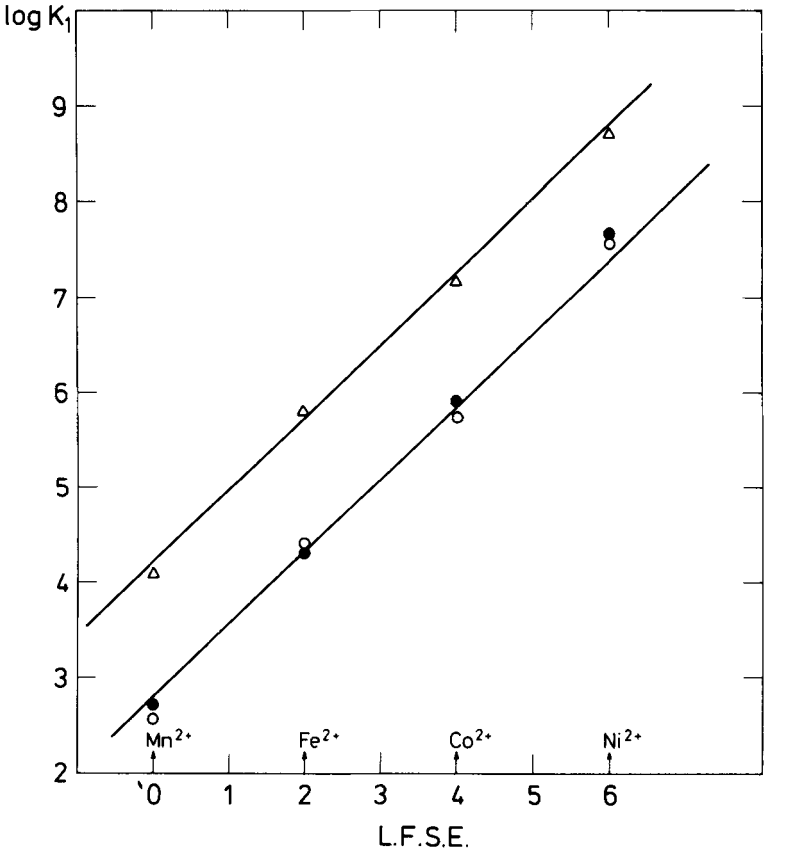



FIGURE 1 Log $K_1$ vs. the relative ligand field stabilization energies for some divalent transition metal ions. $M^{2+} + \widehat{N\,N} \overset{K_1}{\rightleftharpoons} M(\widehat{N\,N})^{2+}$. ●, $\widehat{N\,N}$ = ethylenediamine (from Ref. 15). ○, $\widehat{N\,N}$ = 2,2'-bipyridine : △, $\widehat{N\,N}$ = 1,10-phenanthroline (from Ref. 7). Medium and temperature as in Table II.

## STRUCTURES

The authors of recent papers giving results of crystal structures of phen and bpy complexes[20–26] have chiefly been concerned first with the way in which the strain, which would result from the close approach of H atoms of opposing ligands, in a planar structure is

TABLE II

Cumulative stability constants $\beta_3$: $M^{2+} + 3\,\widehat{N\,N} \overset{\beta_3}{\rightleftharpoons} M(\widehat{N\,N})_3^{2+}$ from Ref. 7. 0.1 M aqueous $NaNO_3$ + $NaClO_4$, 25 °C

| $M^{2+}$ | $\widehat{N\,N}$ = 1,10-phenanthroline log $\beta_3$ | $\widehat{N\,N}$ = 2,2'-bipyridine log $\beta_3$ |
|---|---|---|
| $Mn^{2+}$ | 10.4 | 5.9 |
| $Fe^{2+}$ | 21.2 | 17.4 |
| $Co^{2+}$ | 19.9 | 16.0 |
| $Ni^{2+}$ | 24.7 | 20.2 |
| $Cu^{2+}$ | 20.9 | 17.2 |
| $Zn^{2+}$ | 17.1 | 13.4 |

relieved, and second with structural evidence for $\pi$ back-bonding to the ligands. It is of interest here that the structures are now known for the complete series $Co(bpy)_3^{n+}$, $n = 1$, 2 and 3. There is no reason for reformulation of the Co(I) (or Rh(I)*bis*) complex as the H adduct suggested in Ref. 1. These complexes are in no way anomalous: for the Co(I) complex it is already known that the bond distances, and reactivity,[26,27] fit very nicely with that expected from increasing back-bonding accompanying the decrease in metal ion oxidation state.

The isolation of $Pt(phen)_2CN^+$, in which the crystal structure shows one long Pt–N bond,[28] is of considerable interest when considering mechanisms of substitution reactions of phen complexes. The significance of this is discussed in the next section.

The structure of a C-bonded bipyridine complex is given in Fig. 2. This can be considered an end product of a reaction series in which the first step is a loss of a proton from the 3 position (see Table I for system of numbering). This is reasonable because D/H exchange of the H-3 has been observed for $Ru(bpy)_3^{2+}$ [30] and for $Os(bpy)_3^{2+}$.[31] Slower exchange occurs at H-5 (see Fig. 3[32] and also Ref. 33). Such D/H exchange has only been observed in mixed solvent solutions of strong bases. In agreement with the earlier workers,[30,31] we find no exchange in 0.02 M to 0.35 M NaOD solutions of $Ru(bpy)_3^{2+}$ in $D_2O$ and also no D/H exchange for the free ligands and the phenanthroline complexes. For $Os(bpy)_3^{2+}$ the exchange rate of the H-3 has been shown not only to be first order in complex but also first order in $OH^-$ concentration in the same medium as given in the legend to Fig. 3; the rate decreases with increase of water concentration.[31]

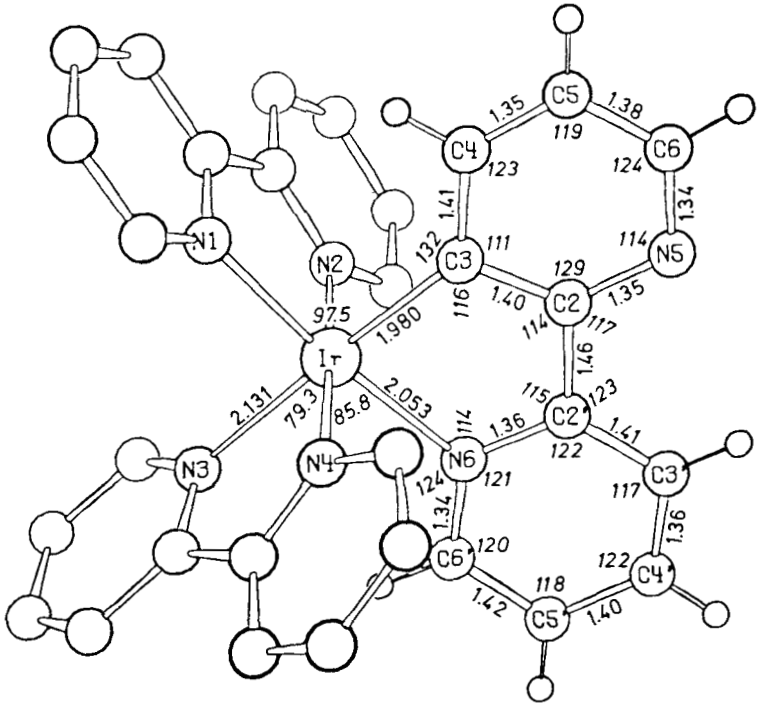



FIGURE 2 A perspective view of the cation of (2,2'-bipyridinyl-C,N')-bis(2,2'-bipyridine-N,N')iridium(III)-bisperchlorate-water (1/3). Reproduced by permission from Inorganic Chemistry **22**, 3429 (1983).

The "alarming"[34] suggestion that base hydrolysis of bpy complexes may occur by a conjugate base mechanism can fortunately be tested. We find no D/H exchange in the ligand produced during base hydrolysis of the Pt(II), Fe(II) and Cr(III) complexes discussed in the next section. For the small group of trivalent complexes where *oxidation of the ligand* accompanies reduction of the metal center (also discussed in some detail below) a conjugate base path cannot be eliminated because the ligand is destroyed. However, for these reactions, the rates for the phenanthroline complexes are much greater than those for the bipyridine complexes[35] so that an extra path would be required for the phen systems.

The $^{1}H$ NMR (and also $^{13}C$) spectra of both bpy and phen complexes are useful for "finger printing" the stereochemistry in solution.

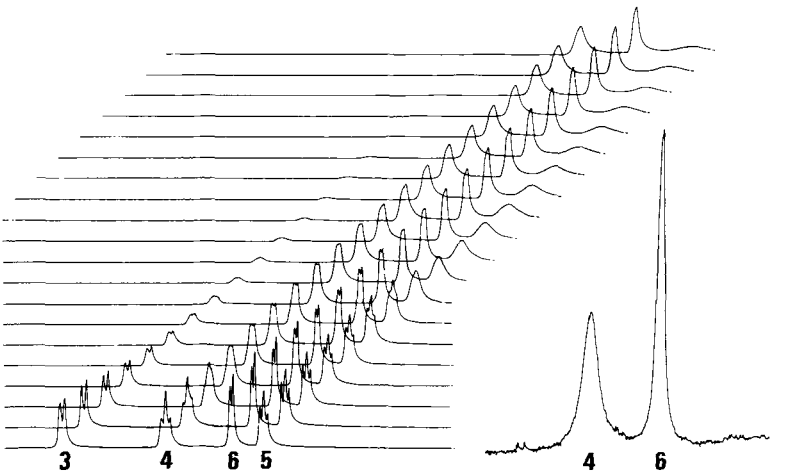



FIGURE 3 Time dependence of 270 MHz $^1H$ NMR spectrum at 300 K of 0.031 M $Ru(bpy)_3Cl_2.6\ H_2O$ in 0.10 M NaOH. The solvent is $D_2O$ : DMSO 1/10 (v/v). The spectra were measured at time intervals of 900 s and displaced (for clarity) after each measurement. The integrated signals for the H-3 and H-3′ decrease exponentially ($t_{½}$ = 3465 s) until ~83% D/H exchange has occurred. After this time the exchange rate at the 3 positions increases and exchange at the 5 positions becomes detectable. The insert is a magnified spectrum of the solution after 24 h illustrating that at this time D/H exchange at the 3 and 5 positions is effectively complete.

This is illustrated for bpy in Fig. 4 (a)–(d). The profile of planar complexes resembles that of the ligand while in *cis* bis complexes that is not so. The two rings of the ligand are now no longer magnetically equivalent; one-half of the H-6 protons of bpy are directly above the plane of an aromatic ring, and therefore more shielded and their resonance signals moved upfield. In the *tris* complexes all H-6 protons are shielded and shifted. In agreement with this it is the shifts of these protons which are least effected by solvent change (see Table III). For phen it is the 9 protons which are shielded (see, e.g., Figs. 7(a) and 7(b) of Ref. 36. and also Ref. 37). The misinterpretation of "extra lines" in the NMR spectra as due to ligand adducts is described fully in Ref. 3. Since this last review the more complicated NMR spectra of the $Ir(bpy)_2(bpy\ C\text{-}N)^{2+}$ cation have been interpreted.[29,38] A consideration of Fig. 2 shows that it is now the 4 proton in the C-bonded ring which is shielded by another ring. From Fig. 4(a) it is apparent that the resonance signal of the 4 proton in the

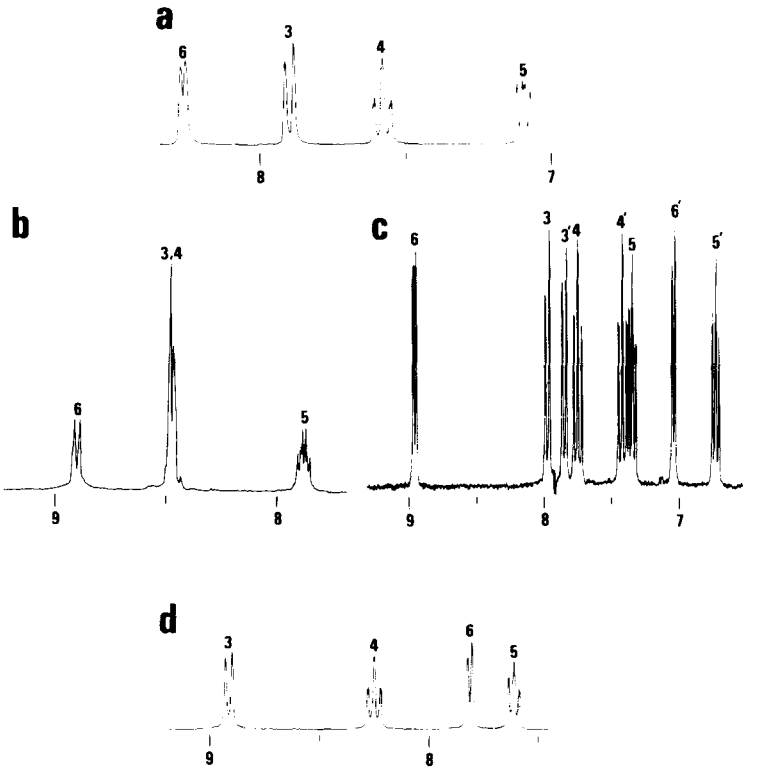



FIGURE 4 270 MHz $^1H$ NMR spectra at 300 K. The abscissa is $\delta$ and is given in parts per million vs. $Me_4Si$. (a) bpy in $D_2O$ : DMSO, 30/70 (v/v). (b) $[Pt(bpy)_2](NO_3)_2$ in $D_2O$. (c) $[Ir(bpy)_2Cl_2]Cl$ in $D_2O$. (d) $[Ru(bpy)_3]Cl_2.6\ H_2O$ in DMSO.

free ligand is already at higher field than that of the 6 proton, so that an equivalent relative shift to that in the N-bonded complex would result, as found, in a signal for H-4 at higher field even than that in the free ligand. This signal is not, as stated in Ref. 4, due to a ligand adduct.

A well-documented feature of these complexes is ion pairing,[6] which also can cause shifts of the protons. Another phenomenon, which can result in drastic changes in the $^1H$ NMR spectra without chemical change in the ligand is "stacking."[39] This is attributed to intermolecular hydrophobic interactions between rings on different

TABLE III
Average proton chemical shifts: 270 MHz, 300 K.

| Complex | Solvent | $H_3$ | $H_4$ | $H_6$ | $H_5$ |
|---|---|---|---|---|---|
| $Fe(bpy)_3^{2+}$ | $D_2O$ | 8.26 | 7.81 | 7.21 | 7.08 |
| | DMSO | 8.93 | 8.30 | 7.48 | 7.61 |
| $Ru(bpy)_3^{2+}$ | $D_2O$ | 8.20 | 7.70 | 7.49 | 7.03 |
| | DMSO | 8.92 | 8.25 | 7.80 | 7.61 |
| $Os(bpy)_3^{2+}$ | $D_2O$ | 8.23 | 7.57 | 7.44 | 6.99 |
| | DMSO | 8.90 | 8.05 | 7.71 | 7.51 |

complexes and this effect increases with an increase in the concentration of complex. It has recently[40] been quantitatively accounted for in $D_2O$ solutions of $Ru(phen)_3^{2+}$, and also has been detected in crystals of a bpy complex.[41]



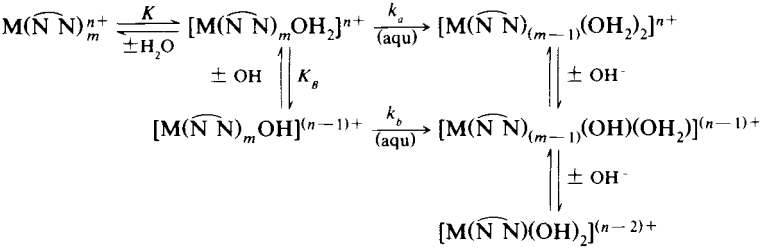
## REACTION KINETICS IN BASIC SOLUTION

We consider the following three groups of reactions: the mechanisms of these have all previously been discussed in terms of the Gillard hypothesis.[1-4]

1. Base hydrolysis with no accompanying change of the ligand (bpy or phen).
2. "Base hydrolysis" of complexes of 5 $NO_2$- and 5 $SO_3$-1,10-phenanthroline. These ligands reversibly react with base at the 6 position as do the free ligands. The overall stoichiometry of these systems is usually unknown.
3. Reduction of the *tris* bpy and *tris* phen complexes of Fe(III), Ru(III), and Os(III). The metal center is reduced and the ligand is irreversibly oxidized. The reaction schemes involve both parallel and consecutive reactions and the overall stoichiometry is very complicated.

1. We consider here the complexes $Pt(\widehat{N\ N})_2^{2+}$, $Cr(bpy)_3^{3+}$ and $Fe(\widehat{N\ N})_3^{2+}$ where $(\widehat{N\ N})$ is bpy or phen. The general reaction scheme

for $Pt(bpy)_2^{2+}$ [42] and $Cr(bpy)_3^{3+}$ [43] is given below; $m$ and $n$ are either 2 or 3.




The general rate law is

$$-\frac{1}{[\text{complex}]}\frac{d[\text{complex}]}{dt} = k_a + (k_b - k_a)\frac{K'_B[OH^-]}{1 + K'_B[OH^-]}$$

where $K'_B = KK_B[OH_2]$.

For both systems $k_a << k_b$, and it is the intermediate [M(N N)$_m$ OH]$^{(n-1)+}$ which has been the focus of dicussion.

In concentrated hydroxide solutions ($\geq 10^{-2}$ M) extra terms have been observed, not only for the Fe(II) complexes[44] (see later discussion) but also for $Cr(bpy)_3^{3+}$,[45] where under these conditions,

$$k_{obs} = \frac{k_b K'_B[OH^-]}{1 + K'_B[OH^-]} + c[OH^-] + c'[OH^-]^3$$

It is likely that these higher terms partly reflect the physics (change in salt medium, ion-pair formation) and not the chemistry of the systems. Nevertheless it is possible that they may in part arise from the acidity of the ligands. In alkaline solution, in the presence of $O_2$, all three ligands are lost in the Fe(II) systems. (The rate is, however, independent of the $O_2$ concentration). We find that no D/H exchange occurs during reaction of $Fe(bpy)_3$ and $Fe(phen)_3$ in 0.3 M NaOD in $D_2O$. Reaction of $Cr(bpy)_3^{3+}$ in 0.3 M NaOD in $D_2O$ gives $Cr(bpy)_2(OD)_2^+$ and bpy as products: a $CDCl_3$ extract of the bpy also gave an NMR spectrum which showed no exchange. It would

be of interest to examine the NMR spectrum of the bpy formed by complete dissociation of the product.

For the $Pt(bpy)_2$ system $K'_B$ is $10^{4.8}$ $M^{-1}$ at 25°C so that a small excess of base gives a solution containing effectively only $[Pt(bpy)_2OH]^+$. The pre-equilibrium is rapidly attained and $[Pt(bpy)_2OH]^+$ is long lived at room temperature ($t_{½}$ = 480 h at 25°C). The $^1H$ NMR spectrum of $Pt(bpy)_2$ is given in Fig. 4(b). This has a distorted square-planar structure but on the NMR time scale all four rings are equivalent. In basic $D_2O$ only pairs of the rings from the two ligands are equivalent[46] and the profile resembles that of Fig. 4(c). There is therefore a change from a distorted square-planar structure in neutral solutions to a five or six coordinated species in alkaline solutions, and in this latter the two ligands are *cis* to each other. The ligands are not chemically changed and since potentiometric titration has shown that the species contains on $OH^-$ this must be directly bonded to the metal center.[46]

The simplest mechanism for this system is therefore the associative mechanism generally accepted for substitution reactions in Pt(II). Two features of the system are worthy of speculative discussion: first, the fact that $OH^-$ is a good nucleophile for $Pt(bpy)_2^{2+}$ and second, the fact that $[Pt(bpy)_2OH]^{2+}$ is stabilized with regard to dissociation of bpy. Not only $OH^-$ but also $CN^-$ is a good nucleophile both for $Pt(bpy)_2^{2+}$ and for $Pt(phen)_2^{2+}$ [47] so that relief of steric strain on expansion of the coordination shell can explain the fast rate of formation of the intermediate. For $Pt(phen)_2^{2+}$ it is the $CN^-$ complex which is long lived and in this both phen ligands have been found to be equivalent on an NMR time scale. It has been suggested that $Pt(phen)_2CN^+$ is fluctional in solution, the contributing structures all containing one long Pt–N bond (as in the solid) and with the $CN^-$ in the plane of a tetragonal pyramid.[47] The long life of $Pt(bpy)_2OH^+$ may therefore reflect the difference in flexibility of the two different ligands. This would accord with a six-coordinated aquo-hydroxo-complex[46] stabilized because proton transfer enables $OH^-$ to exchange between the two sites, $OH^-$ and $OH_2$. The concurrent stretching of the Pt–N bond *trans* to coordinated water and contraction of that *trans* to coordinated hydroxide would be, as required, rapid on the NMR timescale.

The rates of *acid* hydrolysis of *tris* phen and bpy complexes of divalent first-transition-series metal ions have long been known. Ac-

tivation energies[16] parallel standard enthalpies for complex formation,[7] in accord with considerable bond-breaking in the transition state. For any one metal, the phen complex dissociates more slowly than the bpy complex (see earlier discussion), and also appropriate substitution in the ligand leads to a series of complexes for which the changes in rate parallel those in the $pK_A$ values of the corresponding protonated ligands.[48] This is illustrated in Fig. 5 for some 5-substituted 1,10-phenanthroline complexes of Fe(II) and also supports an interchange dissociative mechanism.

The *tris* bpy and phen complexes of Fe(II) are, however, unusual in that (unlike, e.g., the analogous complexes of Ni(II)) they dissociate much faster in *basic* than in acid solution.[44] This was earlier thought to be puzzling for complexes of the rigid phenanthroline ligand, but it is now known (see earlier discussion) that phen can be coordinated with one long metal–N bond. It can therefore move out of the plane and allow nucleophilic attack on the metal center. The special role of $OH^-$ (and also $CN^-$ and $N_3^-$)[44b] in the Fe(II) systems thus may well be "to destroy the octahedral symmetry and to facilitate the spin change" (see p. 236, Ref. 16).

The rate law for the hydrolysis of the Fe(II) *tris* complexes in dilute base is:

$$-d[\mathrm{Fe}(\widehat{\mathrm{N\ N}})_3^{2+}]/dt = k_1[\mathrm{Fe}(\widehat{\mathrm{N\ N}})_3^{2+}] + k_2[\mathrm{Fe}(\widehat{\mathrm{N\ N}})_3^{2+}][\mathrm{OH}^-].$$

There is no evidence for reactive intermediates. $k_1$ is, within the experimental errors, equal to the first-order constant for dissociation in acid solutions. Figure 5 illustrates that for a series of complexes of 5-substituted phen in basic solution, there is a rough correlation with the inductive effects of the 5-substituents. The activation parameters[49] show a large enthalpy–entropy compensation, usual for reactions between ions in solution, and it is relevant that all the activation parameters (including those for the 5-($NO_2$)phen complex) fit accurately on one isokinetic plot. This suggests a common mechanism and is of interest because the $k_2$ value for *tris* Fe(II) 5-($NO_2$)phen was only determined[49] in very dilute sodium hydroxide solutions in which the electronic spectrum of the complex was not detectably different from that in acid. Another species is present in more concentrated sodium hydroxide solutions (see 2 below). Both $k_1$ and $k_2$ in Fig. 5 therefore refer to the unmodified 5-($NO_2$)phen

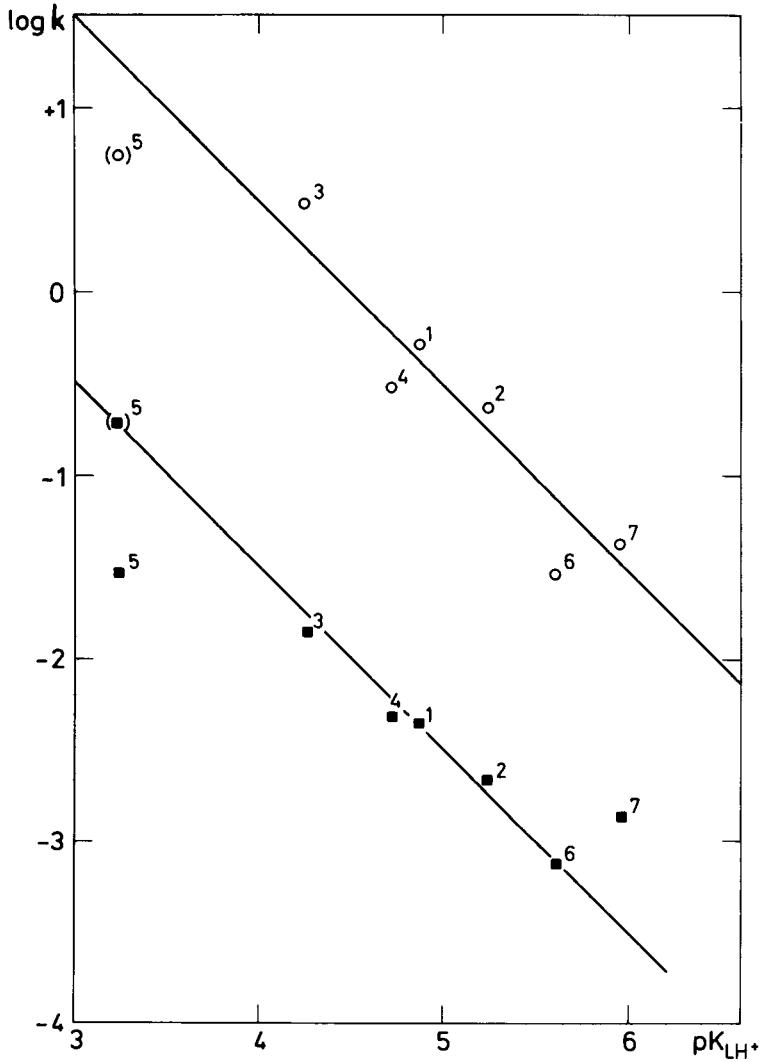



FIGURE 5 Logarithmic plot of rate constants for acid hydrolysis ■ (from Ref. 48) and base hydrolysis ○ (from Ref. 49) vs. $pK_A$ of protonated ligand. 1, phen; 2, 5-$(CH_3)$phen; 3, 5-(Cl)phen; 4, 5-$(C_6H_5)$phen; 5, 5-$(NO_2)$phen; 6, 5,6-$(CH_3)_2$phen; 7, 4,7-$(CH_3)_2$phen. See Table I for system of numbering.

ligand. The value for $k_1$ in parentheses for 5-($NO_2$)phen was obtained by extrapolation, as described in the next section, from measurements in aqueous sodium sulphate–sodium hydroxide at an ionic strength of 0.24 M, and is considerably higher than the $k_1$ reported in Ref. 48 from 1.0 M $H_2SO_4$. This suggests to us the possibility of the formation of more slowly reacting H-bonded 6-H-sulphate adducts. We find no evidence for any other adducts and also no anomalies which would require intermediates during dissociation, either in acid or in basic solutions.

2. 5-($NO_2$)phenanthroline and its complexes react reversibly with $OH^-$ at the 6 position. Analogous reactions have been reported with $^-OMe$ in methanol.[3] There seems to be disagreement[6] as to whether the product species is formed by proton loss from the 6 position or is a Meisenheimer complex.[50] We are unable to find a system for which the stoichiometry has been reported both of the fast formation of this species and also of the slow disruption of the complex containing it, although the many publications on this and similar systems have recently been reviewed.[6] The authors of this review do, however, list equilibrium constants and it was the value they give for the fast reaction of tris Fe(II) 5-($NO_2$)phen with $OH^-$ (143 $M^{-1}$) which we used together with data from Ref. 49 to extrapolate the $k_1$ value given in parentheses in Fig. 5 for the unmodified complex. It has long been known[49]; that modification of 5-($NO_2$)phen, by reaction with $OH^-$ at the 6 position, decreases the rate of its dissociation from the *tris* Fe(II) complex. We do not understand why this modified species is considered to be *mechanistically* significant[2,4,6] for the base hydrolysis either of the modified complex or for the parallel reaction of the unmodified 5-($NO_2$)phen complex.

3. Highly oxidizing complexes, like $IrCl_6^{2-}$ and $M(\widehat{N\ N})_3^{3+}$ (M = Fe, Ru, Os; $\widehat{N\ N}$ = phen or bpy) oxidize Co(II), Fe(II), Fe(III), Ni(II) and Cu(II) in basic solution in catalytic processes which produce dioxygen.[51–53] It has recently been found[52,53] that, in the *absence* of a catalyst, it is the ligand which is oxidized; under these conditions only about 90% of the reactant $M(\widehat{N\ N})_3^{3+}$ is reduced, without change in the coordination shell, to $M(\widehat{N\ N})_3^{2+}$. The complexes $Fe(bpy)_3^{3+}$ and $Fe(phen)_3^{3+}$ dissociate in the reacting solutions and the dissociated complexes are catalysts for $O_2$ formation. The authors of the most recent work[53] on the stoichiometry of the $Ru(bpy)_3^{3+}$–$OH^-$ system suggest that 2,2′-bipyridyl N-oxide, which was detected as a

product in the $Fe(bpy)_3$ $-OH^-$ system[52] (but is not found for the $Ru(bpy)_3^{2+}$–$OH^-$ system), may be produced in this parallel $O_2$ forming path. The rate of formation of $M(\widehat{N\ N})_3^{2+}$ (M = Fe, Os; $\widehat{N\ N}$ = phen or bpy or methyl-substituted derivatives of these ligands) is first order in $M(\widehat{N\ N})_3^{3+}$ and in $OH^-$ over a wide range of concentration of both reactants. Conditions have also been found where this is the major term in the rate law for the $Ru(bpy)_3^{3+}$–$OH^-$ system.[53] Scheme 1 is an attempt to summarize the reaction series arising from this second-order path.

These systems are the only ones known to the present author, for which one of the simplest mechanisms requires the rate-determining attack of $OH^-$ at a C atom of a coordinated imine ring. Thus the $[M(\widehat{N\ N})_3OH^{2+}]$ intermediate in the scheme has reasonably been depicted as the conjugate base of a covalent hydrate. This is, however, required to react further to give species in which the C–O bond *persists*, contrary to the suggested participation of such species in systems without overall change in the ligand.

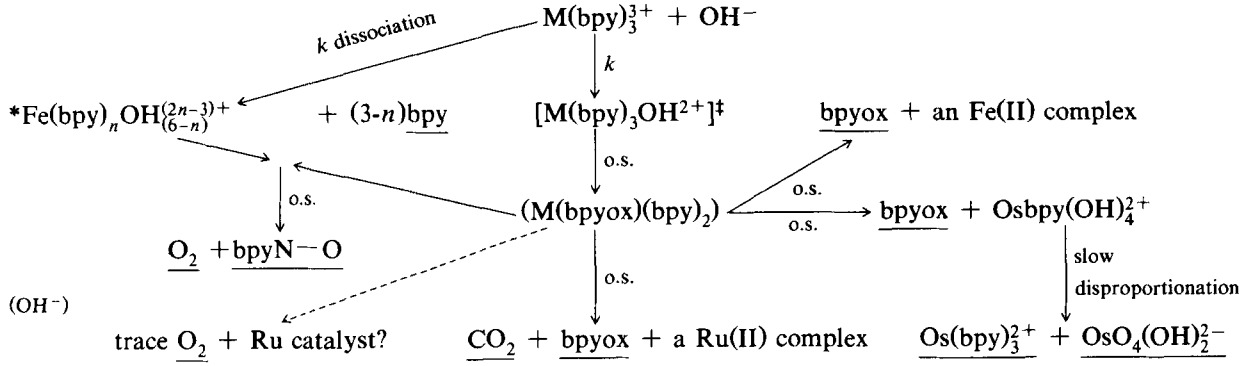


## CONCLUSIONS

Much of the recent work on the title complexes is confused, partly because of the difficulty in determining the stoichiometry of the reactions and partly because of the incomplete studies of systems for which no attempt to determine the stoichiometry has been made. In contrast to the rare redox systems where ligand oxidation does occur and where time-consuming stoichiometric studies have borne fruit, the stated aim of many workers with substitution reactions has been to detect intermediates which would conform with the Gillard hypothesis. All available data for substitution reactions in complexes of bpy, phen and their derivatives can be readily explained by nucleophilic substitution directly at the metal center according to the mechanisms which, because of their greater simplicity, have become an integral part of classical coordination chemistry. It is not only unnecessary but also unreasonable to introduce an extra step involving preliminary attack on a ligand because, for the rare systems where this probably does occur, it leads to irreversible destruction of the ligand.

Since the publication of Ref. 1 many workers appear to have

## SCHEME 1




o.s. = successive outer-sphere one-electron transfers, (+ M(bpy)$_3^{3+}$, − M(bpy)$_3^{2+}$)
M = Fe, Ru, Os; bpyox is used collectively for the products of the successive oxidation of a coordinated imine ring
* = catalyst
‡ = required by the rate law; identified products are underlined

become intoxicated by the excitement of searching for new and novel mechanisms, thereby losing the satisfaction of attempting to scientifically solve defined problems.

## SUMMARY

The many recent attempts to detect covalently hydrated imine-ring adducts in equilibrium with the title complexes have been abortive, because there are no anomalous properties which would require explanation, either in terms of these species or of their conjugate bases. For the rare reactions where nucleophilic attack on a carbon atom of an imine ring, coordinated to a metal ion, probably does occur it leads to irreversible chemical change of the ligand.



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