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COVALENT HYDRATION AND PSEUDOBASE FORMATION IN TRANSITION METAL POLYPYRIDYL COMPLEXES: REALITY OR MYTH?

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A. INTRODUCTION

Transition metal–polypyridine complexes (2,2′-bipyridine (bpy) and 1,10-phenanthroline (phen) and their substituted derivatives) continue to provide interesting photochemical and photophysical results in the unraveling of structure–reactivity relationships in excited states [1–3], as well as supporting attempts to convert and store solar energy [4,5]. The understanding of these structure–reactivity correlations clearly depends on the knowledge of these same relationships for the ground state complexes. One component in such studies is solution medium effects, and the question often asked is how and to what extent do changes in solution medium (solvent, pH, etc.) affect the nature and the reactivity of such excited- and ground-state species. A particular emphasis of our investigations in recent years has been to probe

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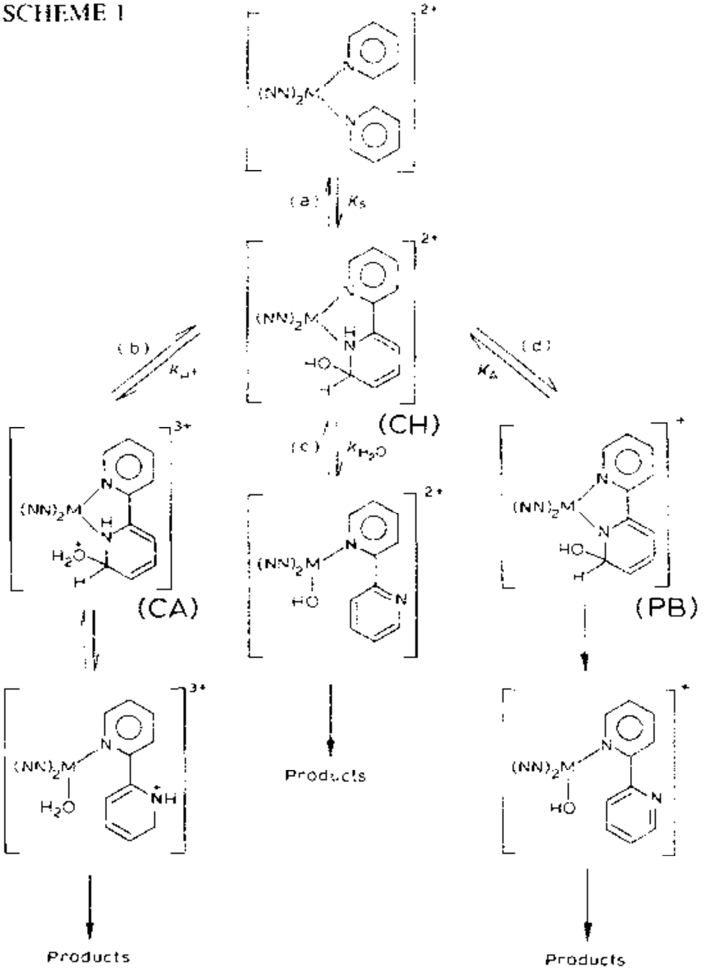
the nature of these polypyridyl complexes in aqueous solutions inasmuch as many presumed "anomalies" [6–25] exist in their aqueous chemistry (e.g. kinetics, stabilities, reactivities). Gillard has summarized many of these so-called "anomalies" [6] which have led him to postulate an interesting explanation for rationalizing some of the properties of bpy and phen metal complexes (and the ligands themselves). He begins with the postulate that quaternization of the nitrogen in these N-heterocyclic molecules, whether by H^+, alkyl, aryl, oxide or metal ion, leads to similar electronic changes in the pyridyl ring, and consequently, to similar reactivity in the ligands. Borrowing from the organic literature and employing metal complexes, the process of

SCHEME 1



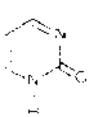
quaternizing is illustrated in Scheme 1 (step a) for a typical $M(NN)_3^{2+}$ cation (in Scheme 1 bpy is used and the charges have been omitted for clarity). The equilibrium step K_s depicts the attack of H_2O on the C-6 carbon adjacent to N (i.e. —C=N—) to form the covalent hydrate [26,27] (**CH**) species with the N now quaternized; deprotonation of the quaternized N leads to formation of the pseudobase (**PB**). Scheme 1 also illustrates two additional fates for the covalent hydrate. It can react (k_{H_2O}) by an intramolecular shift of OH within the **CH** to give the open-ended bpy species, and it can be protonated (k_{H^+}) to form the conjugate acid (**CA**). Both these species and the pseudobase can react further by an intramolecular shift of H_2O and OH, respectively, onto the metal, also giving open-ended bpy species from which substituted or reduced products may be formed [6].

Recent work by Nord and co-workers [28–31] has seriously questioned the validity, indeed the premise [28] upon which covalent hydrate formation in bpy and phen metal complexes is based. Our own work [32–38] on polypyridyl metal complexes and that of others [39–43] have failed to demonstrate the existence of covalent hydrates in these species. Hence, the lack of stable covalently hydrated species in polypyridyl metal complexes, in general, poses serious doubt as to whether or not it is necessary to invoke structurally analogous reactive intermediates in mechanisms for reactions which do not involve an overall chemical change in the aromatic NN ligand [28]. The question has also been raised [28] as to the possibility that the properties which have been described by Gillard [6] as anomalous, may in some instances, reflect the inadequacy and/or the reliability of the experimental data. Luminescence spectral evidence has been presented in favour of covalent hydrates in the phen and bpy free bases [44,45]; but this has been questioned by Kotlicka and Grabowski [46]. Others have presented NMR and kinetic evidence for the formation of pseudobases in $M(NN)_3^{n+}$ complexes and phen with CN^- [47] and CH_3O^- [48] to argue for nucleophilic attack by neutral or anionic species on the organic ligand. In some cases, we have been unable to kinetically preclude the possible intermediacy of covalently hydrated species in the substitution reactions of $Cr(bpy)_3^{3+}$ and $Cr(phen)_3^{3+}$ complexes [1,32,33,38].

It is clear from the above discussion that much confusion and disagreement exist in the literature on the value and the very existence of covalent hydrates for bpy and phen metal complexes in aqueous solution. This article endeavours to explore some of the recent relevant data since Gillard's review in 1975 (where germane, even before) to evaluate the data and the arguments critically, and to present alternative explanations where possible. But first, it is important and instructive to consider briefly the organic literature on covalent hydrates and pseudobases in heterocyclic compounds (by no means is this meant to be extensive) to give the inorganic chemist a "feel" for what properties and conditions of substrate lead to the formation and stability of such species.

B. COVALENT HYDRATES IN HETEROCYCLIC COMPOUNDS [26,27,49]

Covalent hydration in nitrogen heteroaromatic compounds refers to hydration across a —C=N— bond. Definitive evidence prevails for the existence of covalent hydrates in these compounds; in some cases they have been suggested as reaction intermediates, as in the bromination of 2(1H)-pyrimidinone (**1**) [50], 4(3H)-pyrimidinones (**2**) [51] and 4(3H)-quinazolinone (**3**) [52]. Covalent hydration has been demonstrated in the families of compounds: 1,6-naphthyridines (**4**), quinazolines (**5**), quinazoline-3-oxides (**6**); 1,3,*x*- and 1,4,*x*-triazanaphthalenes (**7**), pteridines (**8**), tetraazanaphthalenes (**9**) and 8-azapurines (**10**) [26]; recently, covalent hydration has also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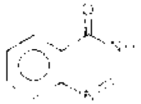
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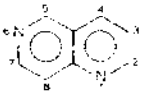
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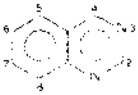
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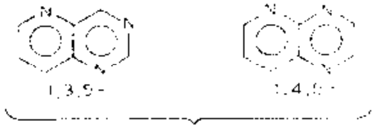
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1,4,5-

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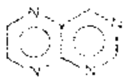
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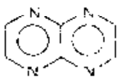
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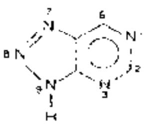
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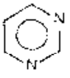
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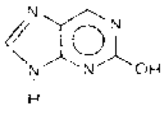
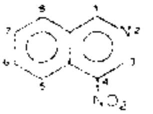

(13)

been shown for one-ring systems such as in the pyrimidine (**11**), and triazene (**12**) families [27]. Various techniques have been employed to demonstrate the existence of covalent hydrates; among others are (a) anomalous ionization constants, (b) ultraviolet and visible absorption spectra, (c) blocking effect of a methyl group, (d) mild oxidation to convert these "secondary" alcohols to the corresponding oxo compounds, (e) stopped-flow and continuous-flow (rapid) methods, (f) isolation of hydrates and hydrated salts, and (g) consecutive hydrations. Lately, the covalent character of the hydration has heen even more firmly established by mass spectroscopy, X-ray crystallography, and ^{1}H and ^{13}C NMR. Before the covalent hydration phenomenon can be established beyond all doubt, however, at least more than one technique should be applied. Albert and Armarego [26] suggest at least three. They also point out that the presence or absence of strongly held water of crystallization is to be regarded as a competitive phenomenon which makes no contribution to a diagnosis of covalent hydration. For example, 2-hydroxypurine (**13**) stubbornly retains a molecule of water at 130°C, but gives no indication of covalent hydration in any of the tests (a)–(f) above [26]. Also, covalent hydration has not been demonstrated in heteroaromatic compounds containing only one heteroatom, nor in systems possessing other heteroatoms in addition to nitrogen [26].

Generally, if a double bond is highly polarized it can attract a water molecule to within reacting distance. Two essential factors have been recognized for a molecule to produce an easily recognizable proportion of covalently hydrated species [26,27]. First, there must be a nucleus whose π-layer is deprived of electrons by two or more doubly-bound nitrogen atoms (such an atom has the approximate electron-withdrawing ability of a nitro group) in a ring, or by strongly inductive ($-$I) substituents, or by both influences together. Thus, the presence of several doubly-linked nitrogen atoms in an aromatic ring (especially in a *meta* position so that the separate effects are entirely additive) depletes the π-electron layer so strongly that aromatic stability is destroyed. Second, the covalent hydrate must be stabilized by "resonance". We hasten to point out, however, that these two factors are minimum requirements and do not necessarily lead to covalent hydration. For example, hydration has not been demonstrated (comparing UV spectra in cyclohexane, neutral water, and in dilute aqueous acid; no anomaly in the ionization constants; use of rapid reaction methods [53]) in the neutral and cationic species of 1,5-, 1,6-, 1,7- and 1,8-naphthyridines, even though the possible hydrated species might be resonance stabilized. Both electron deficiency and resonance stabilization are necessary for covalent hydration to be established. The necessity for electron deficiency is clearly shown by the following examples: the cation of 1,4,5-triazanaphthalene is anhydrous [54], but the cation of 1,4,5,8-tetraazanaphthalene is predominantly hydrated [55]; also, the 1,6-naphthyridine cation is anhydrous, whereas the cations of the 3-nitro and 8-nitro derivatives are predominantly hydrated [53]. The anhydrous nature of both the neutral and cationic species of 4-nitroisoquinoline (**14**) and 3-nitro-1,5-naphthyridine (**15**), for which hydration causes no extra resonance stabilization, demonstrates the essential requirement for such stabilization as much as electron deficiency. Substances (**14**) and (**15**) are to be contrasted with equally electron-deficient molecules which form strongly resonance-stabilized hydrates, namely, quinazoline (**5**) [56] and 1,3,5-triazanaphthalene (**7**) [57], respectively. Electron releasing substituents ($-NH_2$, $-OH$) decrease or prevent covalent hydration by diminishing the electron deficiency in the carbon atom. Multiple hydration has also been demonstrated by ^{1}H NMR for 1,4,5,8-tetraazanaphthalene to give (**16**) [58].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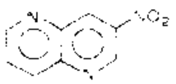
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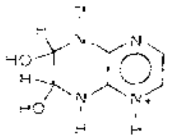
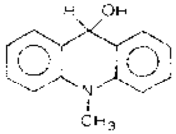

(16)

Covalent hydration and pseudobase (section C) formation that occurs when alkali (or MeO^-, CN^-, etc.) is added to a solution of a quaternary heterocycle [59] are two related phenomena [60,61]. The similarity between these two processes resides [26] in the conversion of an aromatic ring into a nonaromatic ring bearing a secondary alcohol group. The conditions for the production of this change are very different [26]. For example, *N*-methylacridine which is not hydrated gives the pseudobase (**17**) on addition of OH^-; but 2-aminopteridine hydrochloride, which is completely hydrated, yields anhydrous 2-aminopteridine (**18**) with alkali.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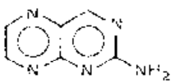
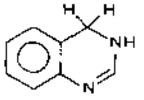
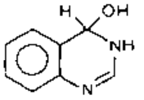

(18)

Some quantitative effects of covalent hydration on experimental results are worth noting [49]. Addition of water across a $-C=N-$ bond disrupts conjugation and is expected to produce electronic spectral shifts to shorter wavelengths (though not necessarily).



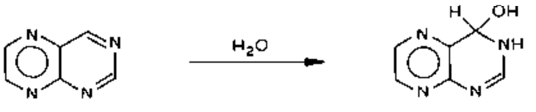
3,4-dihydroquinazoline
λ = 291 nm (log ε 3.76)

and



3,4-dihydro-4-hydroxyquinazoline
λ = 265 nm (log ε 3.97)

Compare, for example, with pteridine where a 20 nm spectral shift to longer wavelength has been observed upon hydration [62]. An important and distinguishing property observable by the NMR method is that the hydration reaction converts an unsaturated carbon atom into a saturated one so that the signal for any proton bonded to this carbon undergoes a considerable upfield shift (caution being exercised that such a shift(s) is not due to other causes). Table 1 depicts NMR data for 8-azapurines. It is evident from the data that hydration of the cationic species leads to upfield shifts of both the H(6) and H(2) protons. Similar upfield shifts are expected for both the



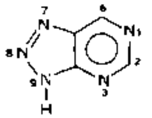
pteridine

3,4-dihydro-4-hydroxy
pteridine

(1)

TABLE 1

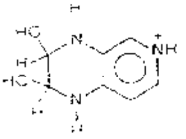
NMR data [a] upon covalent hydration of



8-Azapurine	Solvent	Species	δ (ppm)	
			H(6)	H(2)
Unsubstituted	D_2O	Anhydrous neutral	9.68	9.20
	DCl	Hydrated cation	6.81	8.54
	CF_3COOH	Anhydrous cation	10.31	9.60
6-Methyl	DCl	Anhydrous cation		9.46
7-Methyl	D_2O	Anhydrous neutral	9.87	9.44
	DCl	Hydrated cation	7.05	8.68
	CF_3COOH	Anhydrous cation	10.55	9.87

[a] From J.W. Bunting and D.D. Perrin, J. Chem. Soc. B, (1966) 433.

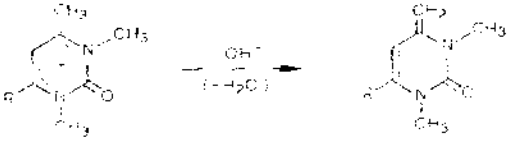
C(6) and C(2) ^{13}C signals. This has been demonstrated for the hydrate of 1,4,6-triazanaphthalene (**19**) wherein the C(2) and C(3) sp^3 carbon signals occur at ca. 73 ppm (downfield from TMS); the sp^2 carbon signals are generally found at > 100 ppm [63].



(19)

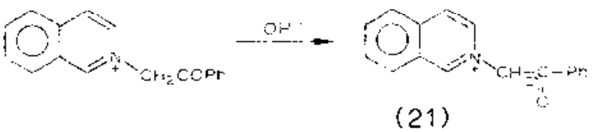
C. PSEUDOBASES IN HETEROCYCLES [61,64]

The concept of pseudobase formation by heteroaromatic cations is intimately related to the covalent hydration of heteroaromatic molecules [26,27,49] and to Meisenheimer complex formation [65]. All these reactions involve the formation of σ-complexes by nucleophilic addition to electron-deficient aromatic species. pH-dependent electronic spectra of a heteroaromatic cation which contains no readily ionizable protons are usually attributed to pseudobase formation. However, such spectral changes may also result from the formation of an anhydrobase (**20**) [66], or a ylid (**21**) as



(20)

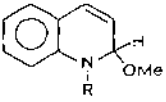
(2)



(21)

(3)

in reactions (2) and (3), respectively, or formation of ion pairs. The former two phenomena can readily be distinguished from pseudobase formation by PMR spectral data by the appearance of vinylic protons in the case of (**20**). Analogous to the discussion on covalent hydrates of heterocycles, pseudobase formation from an unsaturated heterocyclic cation causes significant changes in the ^{1}H NMR spectrum; saturation of the C through pseudobase formation results in an upfield shift of ca. 4 ppm for the signal of the proton bonded to that carbon. Neighbouring protons also undergo an upfield shift (but lesser), particularly if pseudobase formation results in a large disruption of the aromatic character of the ring. In contrast to covalent hydration, however, where water addition occurs across the polarized —C=N— bond, nucleophilic addition in pseudobase formation can occur at position α or γ to the nitrogen heteroatom in a six-membered ring; NMR spectra can distinguish between the two locations on the basis of coupling constants and chemical shifts as in the case of the two quinolines (**22**) and (**23**) in which (**22**) appears to be the predominant species [67,68]. ^{13}C NMR spectroscopy, while being a potentially useful technique for assignment of pseudobase structure, has not been widely used [61] (but see e.g. ref. 63).



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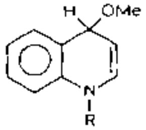
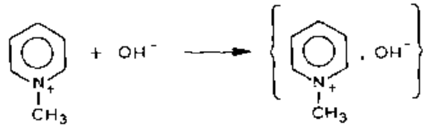


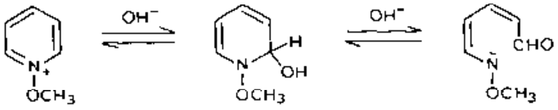
(23)

No spectral evidence exists to indicate pseudobase formation by the *N*-methylpyridinium cation (**24**) even in the most basic aqueous solutions attainable. Both NMR and IR spectroscopy reveal an ionic *N*-methylpyridinium hydroxide (**25**) [69]. In contrast, the *N*-methoxypyridinium cation (**26**) forms a pseudobase which upon further reaction with OH^- leads to ring opening (reaction 5) [70,71]. It is interesting to note that the UV spectra of the *N*-methylquinolinium (**27**) and *N*-methylisoquinolinium (**28**) cations are



(24) (25)

(4)



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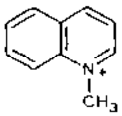

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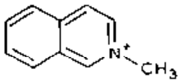
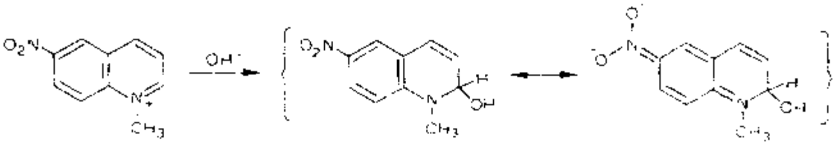


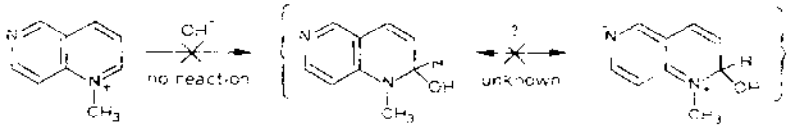
(28)

pH independent below pH 14; further reaction with OH^- in more basic solution leads to irreversible reactions.

Resonance stabilization of the pseudobase also appears to be important in pseudobase formation. Specifically, the 1-methyl-6-nitroquinolinium cation (**29**) forms the pseudobase (**30**) which is resonance stabilized; but the analogous 1-methyl-1,6-naphthyridinium cation (**31**) forms no pseudobase [61].



(29) (30) (6)

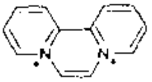
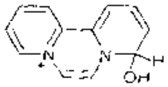
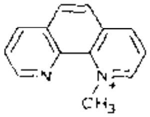
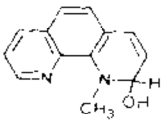
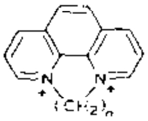
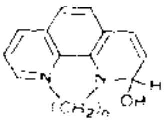


(31) (7)

The complicated nature of the rapid spectral changes observed in basic

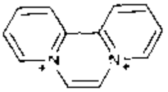
TABLE 2

pK_{R^+} - values of some pseudobases [a]

Q^+	QOH		pK_{R^+}
			9.9 [b]
			14
		$n = 2$ $n = 3$	9.54 9.17

[a] From ref. 64. [b] Pseudobase structure not definitely established.

solutions for the dication (**32**) has been rationalized [72] in terms of the formation of a monopseudobase by OH^- addition at C(2) or C(4) of one of the pyridinium rings, and a pseudobase (**33**) in more basic solutions by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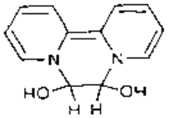


(33)

addition of two OH^- in the pyrazinium ring of (**32**) [61].

Another important parameter in the chemistry of pseudobases of heterocycles is pK_{R^+} where pK_{R^+} has its usual meaning [73] and K_{R^+} refers to the equilibrium expressed by reaction (8) [64]. Some of the pK_{R^+} values of relevant bipyridinium and phenanthrolinium analogs are presented in Table 2.

$$Q^+ + H_2O \rightleftharpoons QOH + H^+ \qquad (8)$$

D. COVALENT HYDRATION AND PSEUDOBASE FORMATION IN TRANSITION METAL COMPLEXES

This section is devoted to a brief review and discussion of some of the work which has led to much of the controversies evident in the recent literature (from ca. 1973 to the present) but is by no means intended to be exhaustive. The past work is classified in terms of the type of metal complexes. To begin, we deal with the platinum(II) and palladium(II) complexes; studies on these have led to disagreements between various workers in the interpretation of spectral results.

(i) The $M(NN)_2^{2+}$ complexes (M = Pt, Pd)

In one of the early articles on "equilibria in complexes of heterocyclic ligands", Gillard and Lyons [11] suggest that the large changes in the electronic spectra (cf. Fig. 1) which occur on addition of base to $Pt(bpy)_2^{2+}$ can be attributed to the equilibrium (9) which involves nucleophilic attack by hydroxide ion on the C(6) carbon of the bpy ligand. These spectral changes are reversed on acidification as are the changes observed for $Pt(phen)_2^{2+}$ [74]. Hydrolysis of the complexes was said to be slow; however, no kinetics were reported [11]. While these spectral changes occur with OH^-, they apparently do not with Cl^- [11]; this was taken [11] to preclude 5-coordinate structures for the product of reaction (9). The nature of the pseudobases (**36**) and (**37**) was confirmed [11] by the ^1H NMR spectra

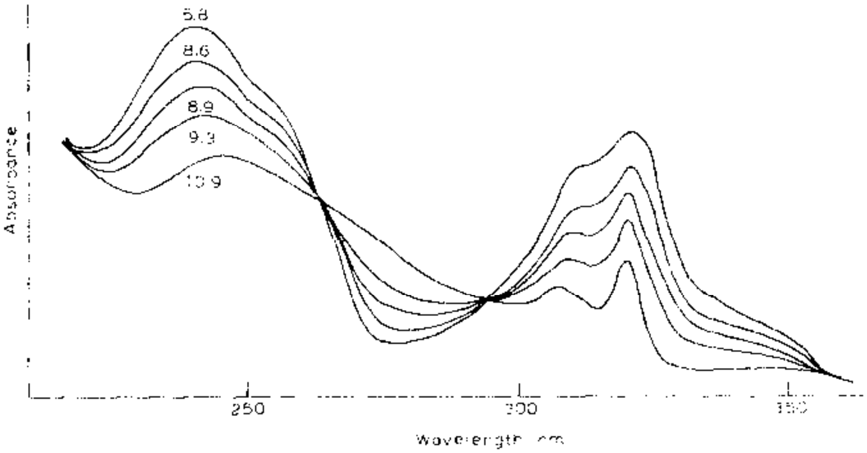
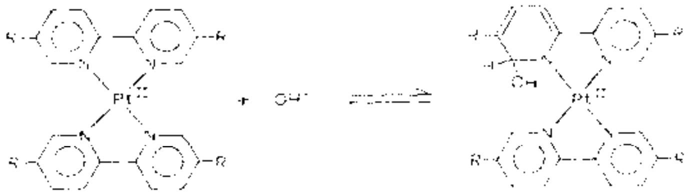


Fig. 1. Electronic spectrum of $Pt(bpy)_2^{2+}$ in aqueous solution as a function of pH. Reprinted with permission from ref. 11.

shown in Fig. 2. Apparently, on addition of base, only the signals H(6) and H(6′) at τ 1.01 ppm [75] suffer loss of intensity accompanied by the growth of a new signal at highest field (Fig. 2b). The spectra a and b in Fig. 2 are reversed on neutralization [11], and show no specific H–D exchange of any aromatic H with the solvent D_2O. Figure 3 shows an analogous behaviour by $Pt(phen)_2^{2+}$ [74]. For $Pt(5,5'\text{-}Me_2bpy)_2^{2+}$, spectra in Fig. 2c and 2d indicate that addition of base in D_2O leads to inequivalence of the CH_3 groups for the pseudobase (**37**). The NMR spectra of $Pt(bpy)_2^{2+}$ in neutral D_2O medium indicate [74] a possible tetrahedrally distorted configuration [76]. Gillard and co-workers [75] also note that acidification of $Pt(bpy)(OH)_2$ with $HClO_4$ or tetrafluoroboric acid (to pH ca. 2) yields electronic spectral changes arising from equilibrium (10). The lowest energy band (MLCT) shifts substantially to higher energy [74].



(**34**) R = H bpy
(**35**) R = CH_3 5,5′-Me_2bpy

(**36**) R = H
(**37**) R = CH_3

(9)

$$Pt(bpy)(OH)_2 \underset{OH^-}{\overset{H^+}{\rightleftharpoons}} Pt(bpy)(OH_2)OH^- \qquad (10)$$

The following possibilities were ruled out [74] in favour of attack by hydroxide on the aromatic ring at C(6) or C(6′) of bpy, or C(2) or C(9) of phen: (a) opening of a chelate ring by rupture of a platinum–nitrogen bond: attack by OH^- at Pt(II) or at Pd(II) is slow (but see below) and while it causes gradual hydrolysis of the complexes it is unlikely to be responsible for the rapid changes of the spectra; (b) attack by OH^- at the metal to give a

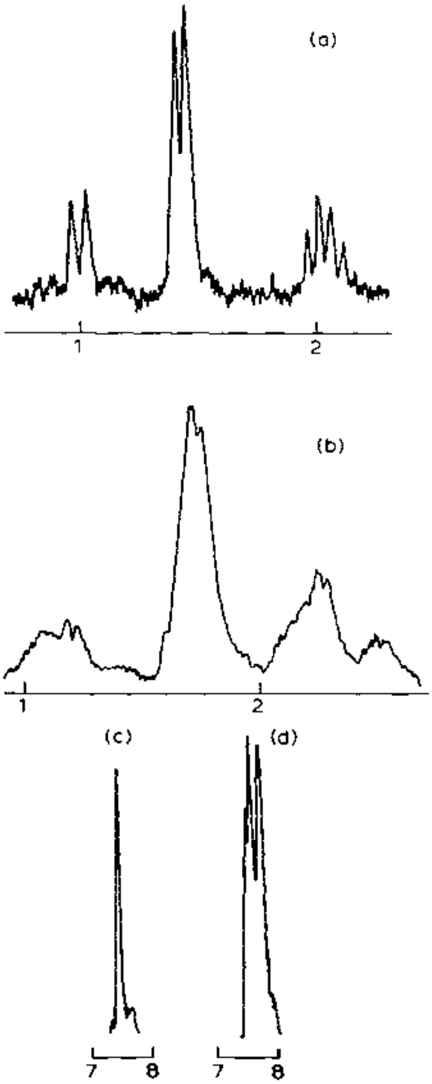


Fig. 2. 100 MHz ^1H NMR spectra of: (a) $Pt(bpy)_2^{2+}$ in neutral D_2O; (b) $Pt(bpy)_2^{2+}$ in alkaline D_2O; (c) methyl resonance signal of $Pt(5,5'\text{-}Me_2bpy)_2^{2+}$ in alkaline D_2O. Reprinted with permission from ref. 11.

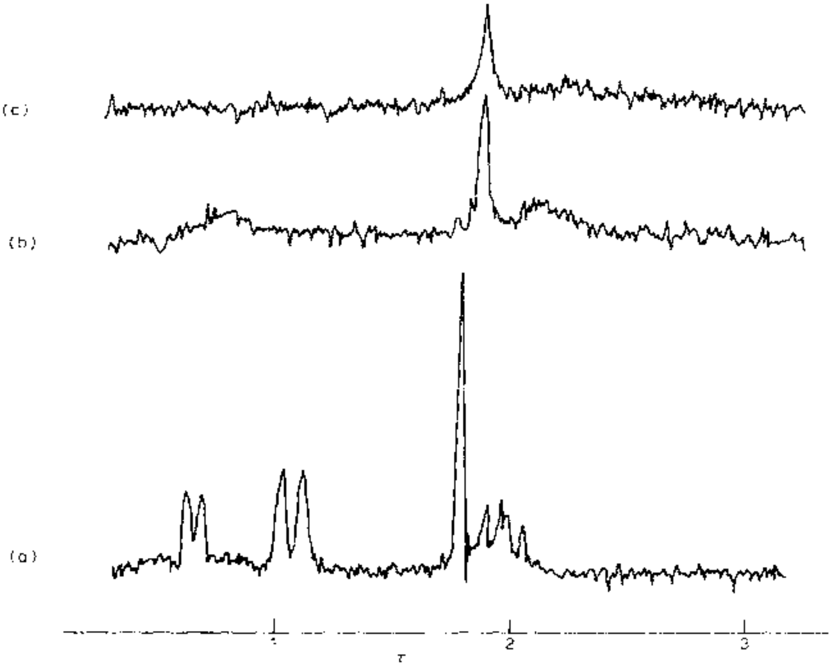
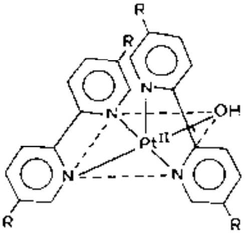


Fig. 3. ^{1}H NMR spectrum of [Pt(phen)$_2$]Cl$_2$ in neutral solution of (a) pD 7.2, and (b and c) successive spectra in alkaline solutions to pD 9.5. Reprinted with permission from ref. 74.

5-coordinate complex; the spectroscopic changes are apparently specific for hydroxide, neither Cl^- nor CN^- (but see below) producing shifts of this type; (c) formation of a conjugate base by abstraction of a proton from coordinated phenanthrolines or bypyridines owing to lack of H D exchange in alkaline D_2O.

Inspection of Fig. 1 reveals that the electronic spectral changes are a general decrease in intensity at the higher pHs but hardly show discernible spectral shifts as one might expect [26,61] on covalent hydration or pseudobase formation (see above discussion). The electronic spectral changes are also consistent with 5-coordination upon attack of Pt(II) by OH^- which upon acidification can also "reverse" the changes, and this despite the fact that Cl^- does not show such changes when added to solutions of Pt(bpy)$_2^{2+}$ and Pt(phen)$_2^{2+}$ [11]. This is not inconsistent since Cl^- is a much weaker ligand than OH^- and it is well known that Pt–Cl bonds are naturally labile in Pt(II) complexes. The NMR spectra in Figs. 2 and 3 are more revealing. On addition of base, spectra 2a and 3a change to spectra 2b and 3b which reveal extensive broadening. This broadening is very much reminiscent of stereochemical exchange phenomena [77] observed in many fluxional molecules in which the exchange phenomena scramble all the protons amongst all sites in the fluxional molecules. Formation of a 5-coordinate species $[Pt(bpy)_2OH]^+$ and $[Pt(phen)_2OH]^+$ may occur but upon acidification, the H_2O being a weaker ligand, the compound reverts back to $Pt(bpy)_2^{2+}$ and $Pt(phen)_2^{2+}$, respectively. The supposedly new peak at highest field in Fig. 2b may represent one of the components of a two-site exchange with the other one occurring at lowest field; the doublet at $\tau = 1.01$ ppm in spectrum 2a is still observable in 2b. Broadening in the NMR spectra cannot be rationalized in terms of pseudobase formation. True, if (**36**) and its analogous phen species did exist the structure would be more distorted, the spectra would be expected to be more complex but still show fine structure. The predominant structure for $[Pt(5,5'\text{-}Me_2bpy)_2OH]^+$ (spectrum 2d) may be illustrated by (**38**) (see below) [42]; a structure in which all the methyl groups are symmetry nonequivalent, and so more than one NMR methyl group signal is expected as opposed to the singlet in spectrum 2c for the complex in neutral media where possible distortions from the square plane appear to be inconsequential to the NMR experiment. The general upfield shift of the NMR resonance signals in Figs. 2 and 3 are also consistent with the 5-coordinate nature of $Pt(NN)_2OH^+$ species. Miller and Prince [78] have observed large alterations in the resonance position of H(2) and H(9) protons in $M(phen)_x^{n+}$ complexes (much more so than other protons in the phen ligand) and have attributed such shifts to an interaction between the metal and these non-bonded hydrogens. Some time ago, we [79,80] demonstrated that proton resonances in cationic metal–β-diketonate complexes are downfield from the corresponding resonance signals of neutral metal–β-diketonate species; the downfield shift was attributed to electric field effects arising from the positive charge on the complexes. Conversely, a decrease in positive charge from $Pt(NN)_2^{2+}$ to $Pt(NN)_2OH^+$ is indeed expected to lead to upfield shifts in the resonance signals.



(38)

The additional IR spectral bands observed in the spectra of the solids $[Pt(phen)_2OH]Cl \cdot 1.5\ H_2O$ and $[Pt(phen)_2OH]Br$ relative to their respective parent compounds in the regions 1400–1600 cm^{-1}, 1000–1100 cm^{-1}, and at ca. 830 cm^{-1} [74] can be attributed to the five-coordinate nature of the

$Pt(NN)_2OH^+$ species. Changes in stereochemistry as may occur on addition of OH^- lead to different vibrational selection rules and so to different spectra. The possibility of impurities, also, cannot be overlooked.

In a study on the base hydrolysis of the perchlorate salt of $Pt(bpy)_2^{2+}$, Nord [31] suggests that hydrolysis occurs as depicted in reactions (11)–(13) in which equilibrium K_B is fast as evidenced by the spectral changes [11] illustrated in Fig. 1; $pK_B = 4.76$, k_A (60°C) $= 5.8 \pm 0.2 \times 10^{-}$[illegible] sec^{-1} in 0.01 M HCl, and k_B (60°C) $= 2.3 \pm 0.3 \times 10^{-5}$ sec^{-1} in 0.01 M NaOH. $t_{1/2}$

$$Pt(bpy)_2^{2+} + OH^- \overset{K_B}{\rightleftharpoons} Pt(bpy)_2OH^+ \tag{11}$$

$$Pt(bpy)_2^{2+} \underset{(H_2O)}{\overset{k_A}{\rightleftharpoons}} Pt(bpy)(OH)(H_2O)^+ + bpyH^+ \tag{12}$$

$$Pt(bpy)_2OH^+ + H_2O \xrightarrow{k_B} Pt(bpy)(OH)(H_2O)^+ + bpy \tag{13}$$

(25°C) of $Pt(bpy)_2OH^+$ is 480 h. $Pt(bpy)_2^{2+}$ was considered to contain coordinated water in aqueous solutions and such water being acidic, equi-

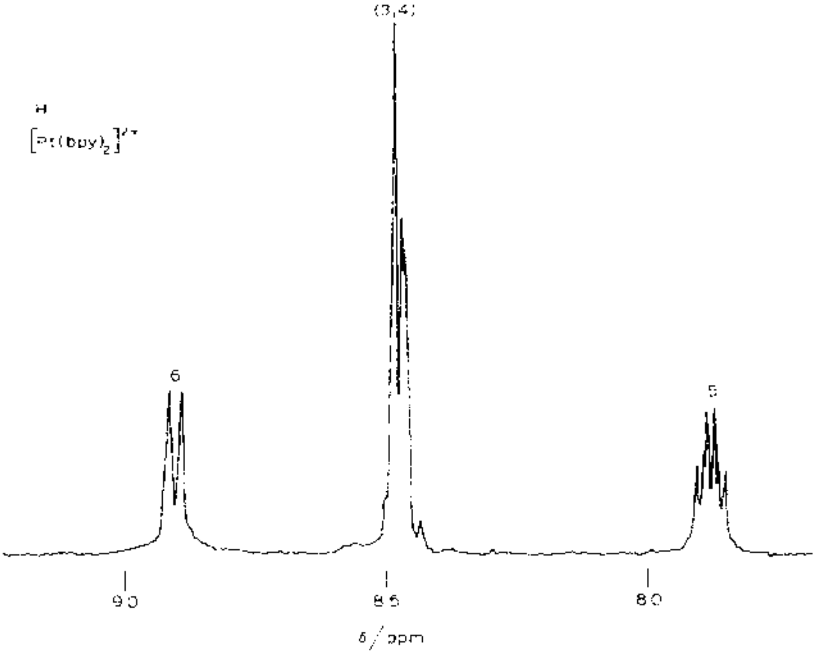


Fig. 4. 270 MHz ^1H NMR spectrum of $Pt(bpy)_2^{2+}$ in D_2O at 300 K. δ values are given relative to acetone (0.1% acetone, 2.17 ppm vs. TMS). Besides a small signal due to water and the reference acetone signals, no additional resonances were observed in the 0–10 ppm range. Reprinted with permission from ref. 30.

librium (11) was taken as equivalent to addition of OH$^-$ to the metal ion. The fact that neither Pt(py)$_4^{2+}$ (py = pyridine) nor Pt(bpy)·py$_2^{2+}$ [81] show pH-dependent spectral behaviour similar to Pt(bpy)$_2^{2+}$ was taken to suggest that distorted square planar coordination is necessary for equilibria such as (11) and that this is a consequence of the steric, and not of the chemical properties of the coordinated bipyridyl ligand [31]. In a later study, Farver et al. [30] report a detailed ^{13}C and ^{1}H NMR study of Pt(bpy)$_2^{2+}$ to establish the nature of the species in alkaline solutions. Potentiometric titration of Pt(bpy)$_2^{2+}$ with base reveals one OH$^-$ in Pt(bpy)$_2$OH$^+$. The ^{1}H and ^{13}C NMR spectra of Pt(bpy)$_2^{2+}$ in neutral D$_2$O at ambient temperature are presented in Figs. 4 and 5, respectively. Figures 6 and 7 illustrate, respectively, the ^{1}H and ^{13}C spectra of the Pt(hpy)$_2$OH$^+$ complex in alkaline D$_2$O media ([OD$^-$] = 0.04–0.05 M). The NMR spectra of the Pt(bpy)$_2$OH$^+$ species are more complex than those of the "parent" complex and reveal that pairs of pyridyl rings from the two bpy ligands are equivalent. Insofar as only 1 mol of OH$^-$ is consumed per mol of complex, this effectively rules out OH$^-$ attack on the bpy ligand, unless the unlikely OH$^-$ exchange between two of

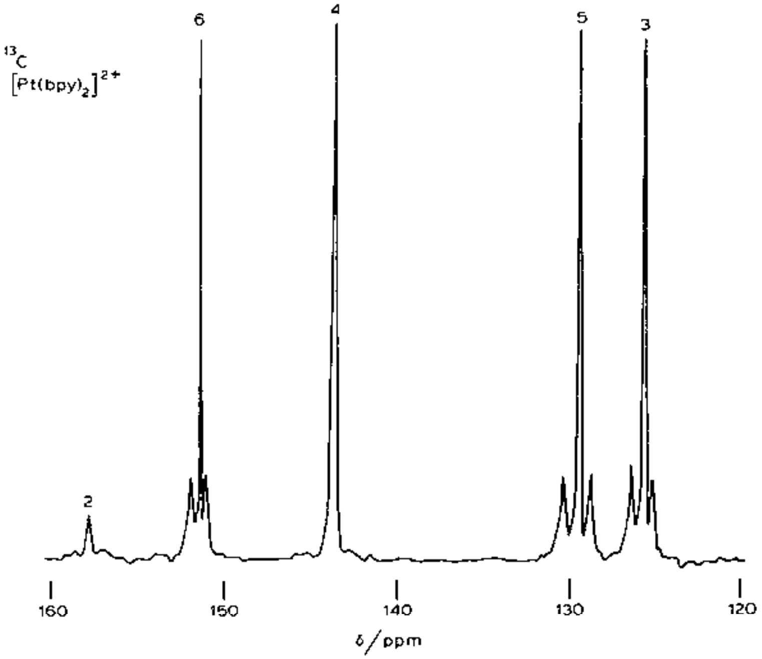


Fig. 5. 22.63 MHz ^{13}C NMR spectrum of Pt(bpy)$_2^{2+}$ in D$_2$O at 300 K. Chemical shifts were measured relative to dioxane (0.25% dioxane, 67.40 ppm vs. TMS). Except for the reference dioxane signal, no other resonances were observed in the range 0–200 ppm. Reprinted with permission from ref. 30.

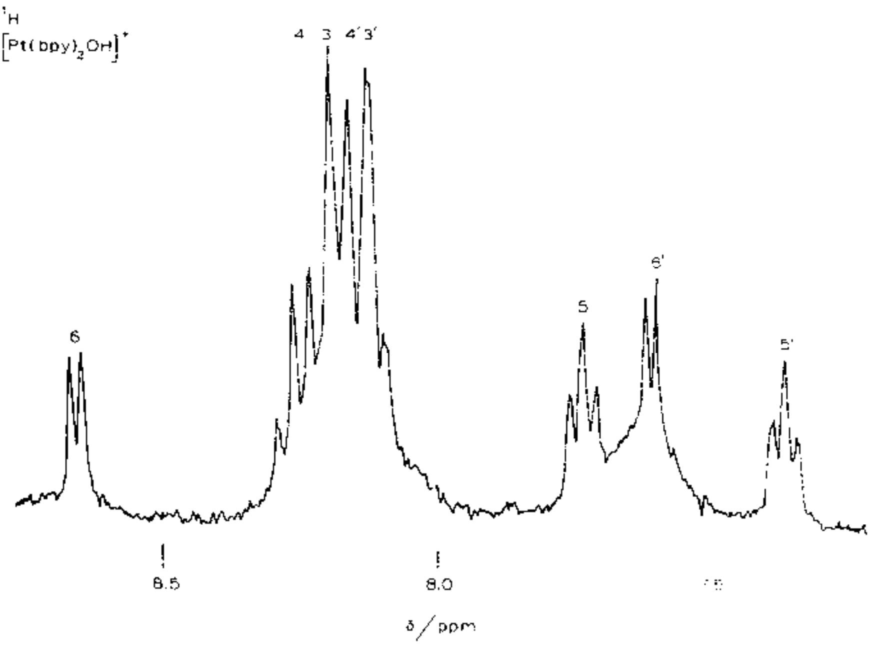


Fig. 6. 270 MHz ^1H NMR spectrum of $Pt(bpy)_2OH^+$ in alkaline D_2O solution; 0.05 M OD^-; 300 K. Chemical shifts given in ppm vs. TMS (reference: acetone). No other peaks apart from those shown here plus the reference signal and a small water signal were observed in the range 0–10 ppm. Reprinted with permission from ref. 30.

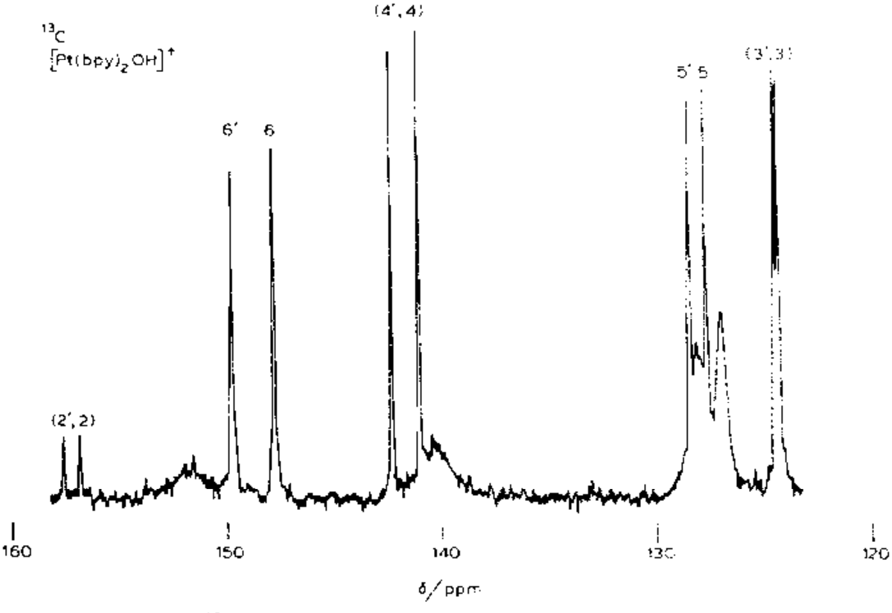
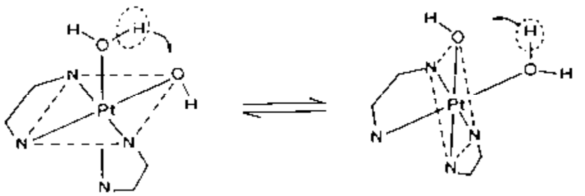


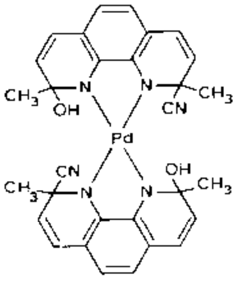
Fig. 7. 67.89 MHz ^{13}C NMR spectrum of $Pt(bpy)_2OH^+$ in alkaline D_2O solution; 0.04 M OD^-; 300 K. Chemical shifts given relative to dioxane (see Fig. 5). Broad bands appear at ca. δ152 and 141 ppm ($W_{1/2}$ = ca. 120 Hz) and at ca. 128 and 127 ppm ($W_{1/2}$ = ca. 40 Hz). Except for the dioxane reference peak, no additional signals are observed in the range 0–200 ppm. Reprinted with permission from ref. 30.

the four aromatic rings is fast on the NMR time-scale [30]. A characteristic feature of the proton NMR spectrum of Fig. 6 is that half of the H(6) protons have shifted upfield (δ of H(6′) = 7.6 ppm; in other bis-bpy–metal complexes δ is 7.8 ppm while for the $Os(bpy)_3^{2+}$ complex δ of H(6) protons is 7.6 ppm [82]). The four broad bands in the $Pt(bpy)_2OH^+$ ^{13}C spectrum are also observed in the kinetically inert *cis*-$Rh(bpy)_2Cl_2^+$ complex [30]. Because chemical exchange is probably slow for this complex, the similarities were attributed [30] to an intramolecular distortion process in the flexible bpy ligands. The NMR data were rationalized in terms of a 5- or 6-coordinated species in alkaline solutions. The proposed [30] structure of $Pt(bpy)_2OH^+$ in alkaline solutions (analogous to **38**) is illustrated in reaction (14). It is also


(14)

noted in this study [30] that CN^- and OH^- give analogous spectral changes in the UV–visible spectrum of $Pt(phen)_2^{2+}$ in contrast to the findings of Gillard and co-workers [74]. Studies of the $Pt(phen)_2CN^+$ cation have shown that the CN^- group is directly coordinated to the platinum both in solution [83] and in the solid state [84]. We will discuss this cation in detail later.

In his 1975 review article, Gillard [6] also draws attention to the fact that $Pd(2,9\text{-}Me_2phen)_2(CN)_2 \cdot 2\ H_2O$ could be formulated as the pseudobase (**39**) and that such a Reissert-type formulation could explain the apparently unusual stoichiometry and stereochemistry of $Pd(oxine)_2(CN)_2 \cdot 2\ H_2O$ (**40**)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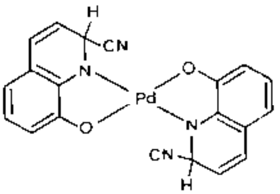
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(oxine ≡ 8-hydroxyquinoline). Recent ^1H NMR and IR spectral studies [78], however, reveal that $Pd(oxine)_2(CN)_2 \cdot 2\ H_2O$ contains two CN^- groups coordinated to Pd(II) and the two oxines are monodentate-bonded to Pd through the nitrogen atoms. NMR studies afforded no evidence of pseudobase in this oxine compound and in the oxinate complex Pt(oxinate)$(CN)_2$; this is in contrast [84] to the purported pseudobase observed in Pd(bpy)$(CN)_2$ [85]. Similar observations were made on the Pd(2,9-Me_2phen)X_2 compound (X = Cl, Br, or I). Also, NMR studies [84] on the nonelectrolyte Pd(2,9-Me_2phen)$_2(CN)_2 \cdot 2\ H_2O$ complex, for which Plowman and Power [86] suggested a six-coordinate *trans* structure, reveal no evidence of either covalent hydration or Reissert-type behaviour. The facts that water is lost from the molecule only at elevated temperatures with accompanying decomposition [86] and that the water molecules are not covalently bonded to the 2,9-Me_2phen ligands or to the Pd atom were explained [84] on the basis that the H_2O molecules are involved in a strong hydrogen-bonding network in the solid state. Plowman and Power [87] have also indicated that complexes of the type Pd(2,9-Me_2phen)$_2X_2$ (X = Cl, Br) exist as the 5-coordinate cations [Pd(2,9-Me_2phen)$_2$X$]^+$ and that such complexes are extensively dissociated. However, under the conditions of the NMR measurements of these Pd(2,9-Me_2phen)$_2X_2$ compounds, no significant dissociation occurs [84]. That covalent hydration in the 2,9-Me_2phen complexes does not occur

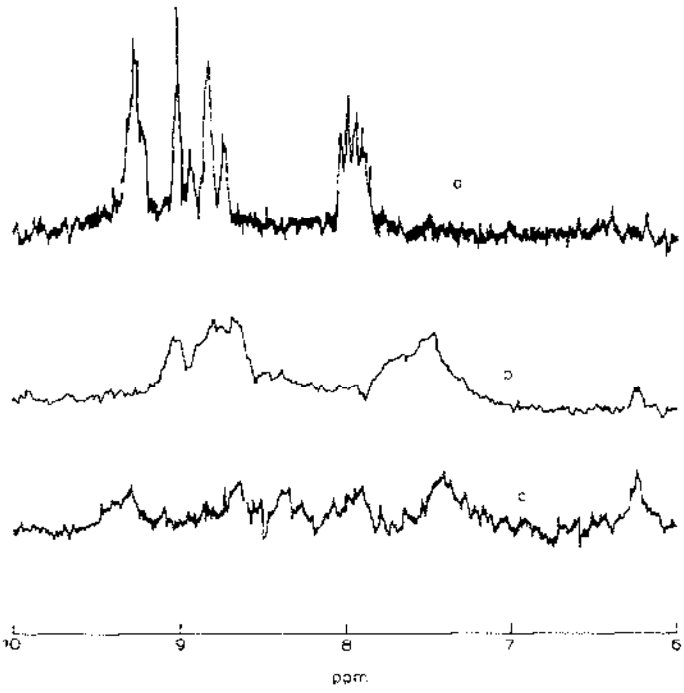


Fig. 8. 90 MHz ^1H NMR spectra of Pt(5-NO_2phen)$_2^{2+}$ in (a) DMSO, (b) DMSO with $[OH^-]$ = ca. 0.1 M, and (c) reaction mixture after 10 min.; temp. ca. 35°C. Reprinted with permission from ref. 88.

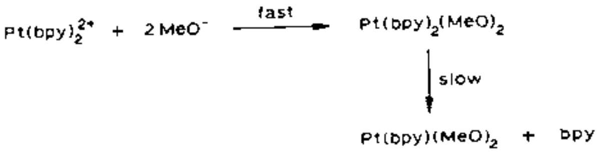
(if it occurs at all) is not surprising in view of the blocking effect of the methyl groups.

The reaction between hydroxide and the cation $\mathrm{Pt(5\text{-}NO_2phen)_2^{2+}}$ has been investigated by ^{1}H NMR spectroscopy; Fig. 8 depicts the 90 MHz NMR spectral changes upon addition of base to a DMSO solution of the cation [88]. The multiplet at 9.27 ppm was assigned to H(2) and H(9) protons while the feature at ca. 7.95 ppm was ascribed to H(3) and H(8); the H(6) singlet is at 9.0 ppm and the doublets of H(4) and H(7) occur at 8.79 and 8.88 ppm, respectively [88]. The spectrum 8b again shows broadening with total loss of fine structure upon addition of $\mathrm{OD^-}$ to the DMSO solution. As we noted earlier, this broadening is consistent with a stereochemical exchange phenomenon in the 5-coordinate species $\mathrm{Pt(5\text{-}NO_2phen)_2OH^+}$, or possibly arises in this case from formation of free radicals [89]. No conclusions can be drawn from spectrum 8c; the feature at 6.24 ppm which Gillard and co-workers suggest to be a new signal is not convincing inasmuch as similar features appear in spectrum 8a. We are also not convinced from these spectra that, "it is evident from the spectrum that the 2- and 9-positions have been attacked and are involved in an equilibrium reaction with $\mathrm{OH^-}$" [88]. In addition, the reversibility in the initially observed electronic spectral variation with pH is also consistent with the equilibrium (15).

$$\mathrm{Pt(5\text{-}NO_2phen)_2^{2+}} \underset{\mathrm{H^+}}{\overset{\mathrm{OH^-}}{\rightleftharpoons}} \mathrm{Pt(5\text{-}NO_2phen)_2OH^+} \qquad (15)$$

The effects of the methoxide base on the $\mathrm{Pt(bpy)_2^{2+}}$ cation have also been reported [88]. The NMR spectral changes upon addition of $\mathrm{MeO^-}$ to a solution of the cation in methanol are illustrated in Fig. 9 as a function of time. Broadening is also evident here and some stereochemical exchange process is likely. Reversibility of the NMR spectral changes upon addition of acid was not possible because of the known dissociation of a bpy ligand under acidic methanolic conditions [88]. Subsequent reaction of the initially formed intermediate (spectra 9c–9e) produce spectra consistent [88] with the presence of free bpy and a product described as $\mathrm{Pt(bpy)(MeO)_2}$ according to reaction (16).

SCHEME 2



$$\begin{tikzcd} \mathrm{Pt(bpy)_2^{2+}} + 2\,\mathrm{MeO^-} \arrow[r, "\text{fast}"] & \mathrm{Pt(bpy)_2(MeO)_2} \arrow[d, "\text{slow}"] \\ & \mathrm{Pt(bpy)(MeO)_2} + \mathrm{bpy} \end{tikzcd} \qquad (16)$$

We agree with this analysis, but whereas Gillard and co-workers suggest that the MeO^- base attacks the bpy ligand, we wish to suggest that $Pt(bpy)_2(MeO)_2$ is probably a five- or six-coordinate species; i.e. the nucleophile attacks Pt(II) and not the ligand, in keeping with observations that 5-coordinate species [42,83] for these types of complexes have been established.

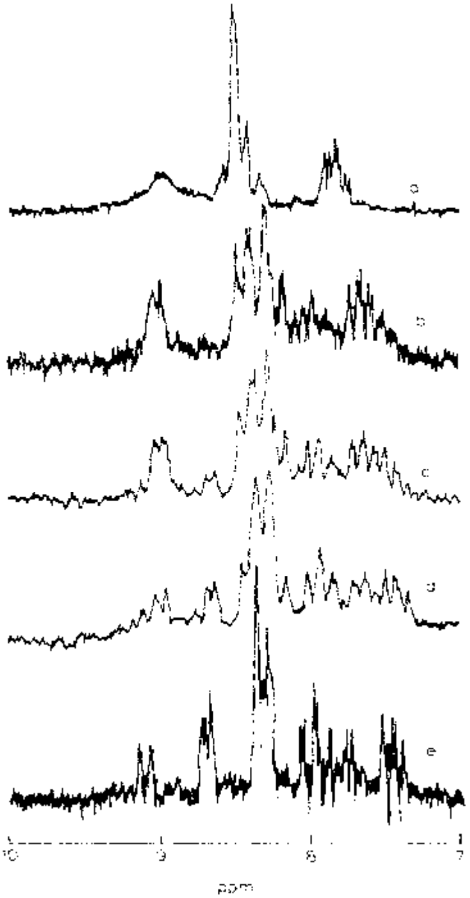


Fig. 9. 90 MHz ^1H NMR spectra of $Pt(bpy)_2^{2+}$ in (a) MeOH, (b) MeOH with $[MeO^-]$ = ca. 0.1 M immediately upon addition of the nucleophile, (c) reaction mixture after 10 min, (d) after 20 min, and (e) at the end of the reaction; temperature ca. 35°C. Reprinted with permission from ref. 88.

A very significant and relevant study on the nature of platinum(II) polypyridyl complexes and in particular $Pt(phen)_2^{2+}$ in solution and in the solid state has recently been reported by Wernberg and Hazell [42]. Conductometric titration of an aqueous solution of $Pt(phen)_2^{2+}$ with aqueous CN^- reveals that a 1 : 1 reaction takes place. The UV-visible spectra of

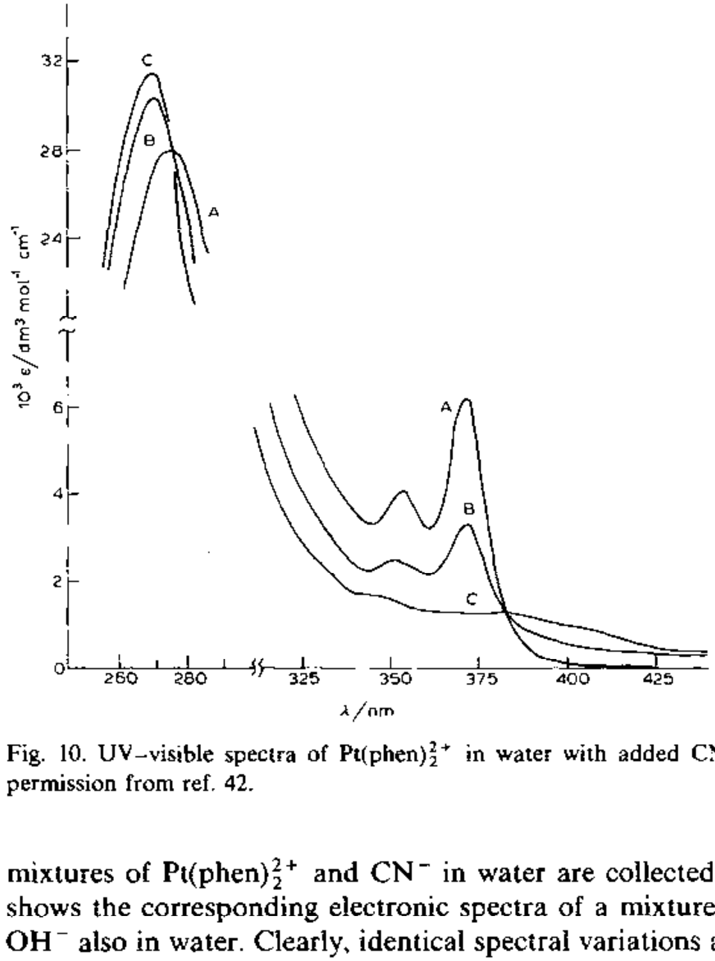


Fig. 10. UV–visible spectra of $\mathrm{Pt(phen)_2^{2+}}$ in water with added $\mathrm{CN^-}$ ion. Reprinted with permission from ref. 42.

mixtures of $\mathrm{Pt(phen)_2^{2+}}$ and $\mathrm{CN^-}$ in water are collected in Fig. 10; Fig. 11 shows the corresponding electronic spectra of a mixture of $\mathrm{Pt(phen)_2^{2+}}$ and $\mathrm{OH^-}$ also in water. Clearly, identical spectral variations are observed for the two systems with isosbestic points at the same wavelengths. This suggests that an addition reaction similar to process (17) ($K_{eq} > 10^6\ \mathrm{M^{-1}}$) also takes

$$\mathrm{Pt(phen)_2^{2+} + CN^- \rightleftharpoons Pt(phen)_2CN^+} \tag{17}$$

place in the mixture of $\mathrm{Pt(phen)_2^{2+}}$ with $\mathrm{OH^-}$ for which K_{eq} = ca. $10^2\ \mathrm{M^{-1}}$ [42]. The proton-decoupled ^{13}C NMR spectra of the $\mathrm{Pt(phen)_2^{2+}{-}CN^-}$ system are presented in Fig. 12. A crystal structural study [42] reveals that $\mathrm{Pt(phen)_2CN^+}$ possesses no elements of symmetry in the solid state; its structure is as depicted by (**41**). The NMR spectra reveal signals corresponding to phenanthroline molecules in which both halves are symmetry- and magnetically-equivalent on the NMR timescale. To the extent that ^{195}Pt satellite signals are observed, rapid dissociation processes are ruled out [42]; it was concluded that the five-coordinate $\mathrm{Pt(phen)_2CN^+}$ cation is fluxional in solution (see above discussion on the 5-coordinate bpy analogue) and

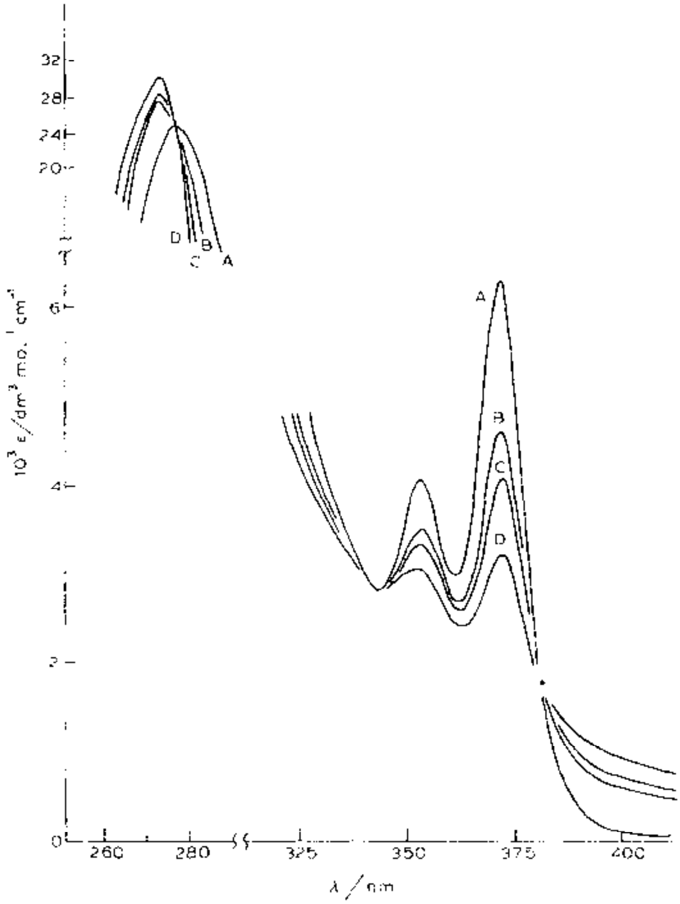
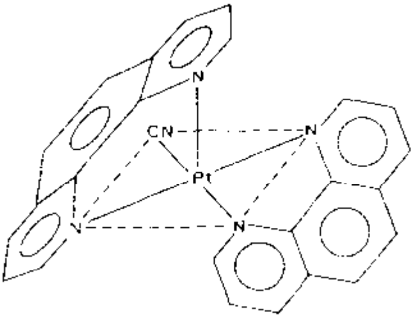


Fig. 11. UV–visible spectra of $Pt(phen)_2^{2+}$ in aqueous solutions with added OH^- ion. Reprinted with permission from ref. 42.



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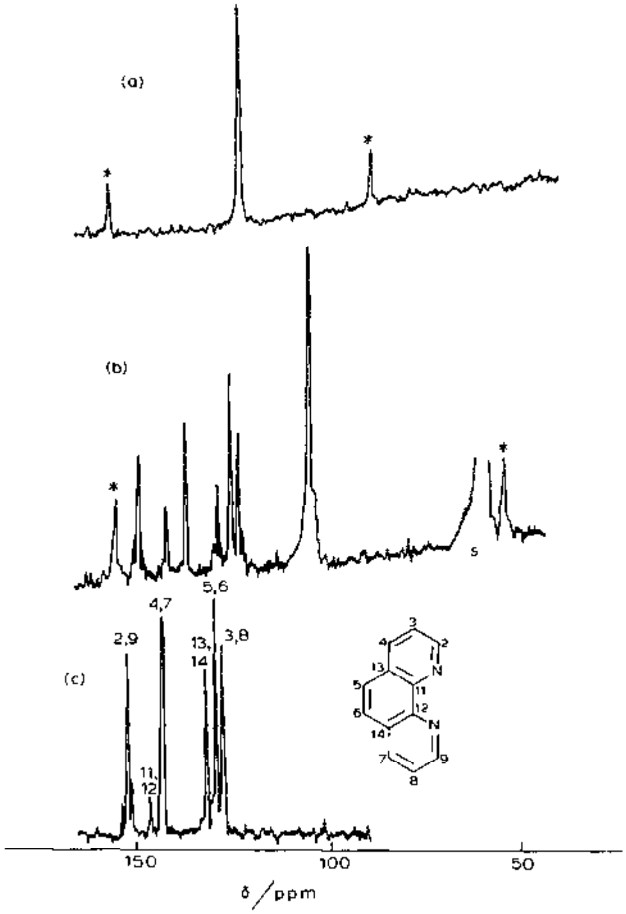


Fig. 12. ^{13}C NMR spectra of (a) $Pt(CN)_4^{2-}$, (b) $Pt(phen)_2CN^+$, and (c) $Pt(phen)_2^{2+}$. Asterisks indicate satellites of the CN signal, and S is the solvent signal. Reprinted with permission from ref. 42.

undergoes a rapid exchange process. Fluxional behaviour is a well-known phenomenon in five-coordinate systems [90] and has been postulated also in ligand-catalyzed isomerization reactions [91,92]. In the exchange process, structure (**41**) is presumably transformed into structures in which all four nitrogens of the phen ligands are in identical positions and this without passing through a structure where both phenanthrolines are in the square plane owing to steric interaction of the H(2) and H(9) hydrogens. It is worth noting here that anomalous kinetic data on the $Pt(terpy)Cl^+$ cation (terpy ≡ 2,2′,2″-terpyridine) have also been interpreted [93] in terms of 5-coordinate geometry. Clearly, neither ^{13}C nor ^{1}H NMR spectral results [42] afford evidence for Gillard's covalent hydrate (or pseudobase) postulate in the reactions and in the behaviour of the $Pt(phen)_2^{2+}$ species.

Recently, Nord and Agarwala [28] have investigated the nature of the $Pt(bpy)(CN)_2$ complex in D_2O/DMSO-d_6 solution using 270 MHz ^1H NMR techniques. The lowest field signal (Fig. 13b) at δ9.23 ppm (vs. TMS) was assigned to the H(6) protons of the bpy ligand (temperature 373 K); upon cooling at 298 K no "new signal" was observed at 6.77 ppm which had been reported by Gillard et al. [85] and assigned to the bpy ligand adduct with OH covalently bound to the C(6) carbon (see Fig. 13A).

We noted earlier that *N*-methylpyridine has not been shown to form pseudobases with OH^-. It is interesting to take note of a recent report by Gillard and Wademan [94] which suggests that hydroxide ion readily adds to

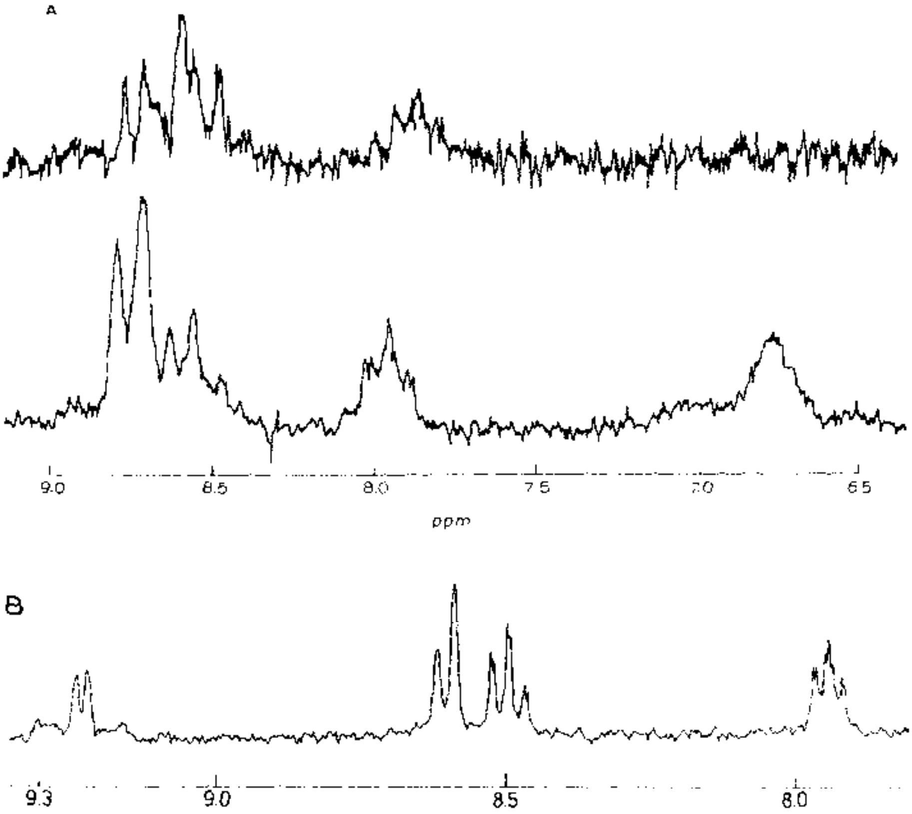


Fig. 13. (A) 100 MHz Fourier transform ^1H NMR spectra $Pt(bpy)(CN)_2$ at 100°C and of $Pt(bpy)(CN)_2 \cdot H_2O$ (lower spectrum). Reprinted with permission from ref. 85. (B) 270 MHz ^1H NMR spectrum (ppm) of $Pt(bpy)(CN)_2$ in D_2O/DMSO-d_6 30/70 (v/v) (temp. 100°C). Reprinted with permission from ref. 28.

the coordinated pyridine or 4-methylpyridine ligand in $Pt(py)_4Cl_2^{2+}$ and $Pt(4\text{-}Mepy)_4Cl_2^{2+}$, respectively. Kinetically inert *trans*-$Pt(py)_4Cl_2^{2+}$, when freshly dissolved in water, gives an acid solution but no Cl^- ions are initially released [94]. The acidic nature of the aqueous solutions was attributed by Gillard to equilibrium (18) (apparent pK_a = ca. 3.4)

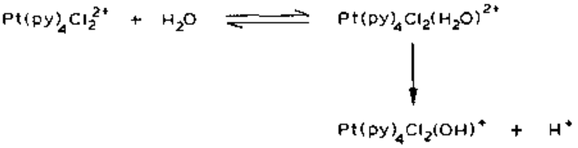
$$Pt(py)_4Cl_2^{2+} + H_2O \rightleftharpoons Pt(py)_3(pyOH)Cl_2^+ + H^+ \tag{18}$$

which involves nucleophilic attack by OH^- ion, followed by much slower release of a Cl^- ion (reaction 19) concomitant with an OH intramolecular

$$Pt(py)_3(pyOH)Cl_2^+ \rightarrow Pt(py)_4Cl(OH)^{2+} + Cl^- \tag{19}$$

shift from the pyOH ligand to the platinum. These observations are also consistent with a model involving 7-coordinate species (reaction 20) necessitating no pseudobase formation. In this, water rapidly adds to the Pt(IV) to form the aquo 7-coordinate species which readily leads to release of H^+ ions. Certainly platinum can, in principle, accommodate a seventh ligand such as water (leading to, albeit, a thermodynamically unstable intermediate). The hydrolysis product is formed by release of a Cl^- ion from the hydroxy species (reaction 21). The intermediacy of a seven-coordinated species was

SCHEME 3



(20)

$$Pt(py)_4Cl_2(OH)^+ \rightarrow Pt(py)_4Cl(OH)^{2+} + Cl^- \tag{21}$$

considered but rejected [94] on grounds that octahedral six-coordination in d^6 coordination cations containing *N*-heterocyclic and halide ligands is much more common than any other, and that, in particular, for platinum(IV) seven-coordination has not been discovered. For that matter, neither do covalent hydrates or pseudobases in *N*-heterocyclic metal complexes appear to have been established. However, we wish to point out that many examples of seven- and eight-coordination in transition metal complexes have been discovered [95] in the last two decades and that Gillard and Wademan's argument [94] is therefore tenuous.

Mønsted and Nord [96] have also refuted the pseudobase of pyridine in $Pt(py)_4Cl_2^{2+}$ noting the possibility that the *trans*-$[Pt(py)_4Cl_2](NO_3)_2 \cdot H_2O$ used [94] may have contained the HNO_3 adduct *trans*-$[Pt(py)_4Cl_2](NO_3)_2 \cdot HNO_3 \cdot 2\ H_2O$, and that 5% of this adduct in an incompletely washed product can account for all the reported [94] data. They also suggest that the work by Grinberg et al. [97] has been misinterpreted by Gillard and Wademan [94]. This work noted that a 10^{-3} M aqueous solution of the pure *trans*-$[Pt(py)_4Cl_2](NO_3)_2$ releases ca. 0.94% of Cl^- and becomes acidic upon standing at room temperature for 20 h; this acidity (pH ca. 5.1) arises [97] from substitution of Cl^- by OH^- [96]. In a rebuttal, Gillard and Wademan [98], quoting from a recent work by Leonora and Evstaf'eva [99] and the work by Grinberg et al. [97], reiterate that a fresh aqueous solution of $[Pt(py)_4Cl_2](NO_3)_2$ is acidic, does not initially contain free Cl^- ion, and that the equilibrium constant ($pK_a = 3.4$) for addition of hydroxide to the cation (equation 18) agrees fairly well with that calculated from the results of ref. 99. Grinberg et al. [97] also attribute the acidity of the aqueous solutions to the presence of an outer-sphere association of type (22) with subsequent

$$[Pt(py)_4Cl_2]^{2+} + OH^- \rightarrow \{[Pt(py)_4Cl_2]OH\}^+ \tag{22}$$

introduction of OH^- into the inner sphere [98]. The analysis of the product obtained from $[Pt(py)_4Cl_2](NO_3)_2$ was given [98] and it was stated that IR, electronic spectral, and thermogravimetric behaviour are characteristic of this product. Recent work by Seddon and co-workers [100] demonstrates that the experimental results reported by Gillard and Wademan [94] are in error: the pK_a of $Pt(py)_4Cl_2^{2+}$ in water is not 3.4 but 7.2 (as originally reported by Grinberg [97]) [101]. In this case, $pK_{R^+} = 6.8$ for the purported

$$Pt(py)_4Cl_2^{2+} + OH^- \rightleftharpoons Pt(py)_3(pyOH)Cl_2^+ \tag{23}$$

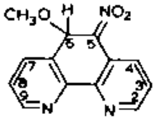
reaction (23) (not 10.6 as reported [94]), and does not compare favourably with values [64] for organic quaternary pyridinium ions.

We noted earlier that the 1-methyl-1,6-naphthyridinium cation (**31**) forms no pseudobase with OH^- ion, the rationalization being that the expected pseudobase is not resonance stabilized [61]. It is worth considering that the supposed pseudobases formed in complexes containing 2,2′-bipyridine or 1,10-phenanthroline (except perhaps 5-NO_2-phenanthroline) ligands possess no resonance stabilization, in contrast to the case for the pseudobase of the 1-methyl-6-nitroquinolinium cation (**30**).

To the extent that experimental data and observations in divalent and trivalent transition metal diimine complexes have been used to support the postulate of covalent hydration and pseudobase formation in these platinum(II) and palladium(II) complexes (and vice versa) we next consider these data and observations.

(ii) Divalent transition metal–polypyridine complexes

It is relevant to begin by considering the reactions of the free polypyridine bases under conditions often analogous to those employed in studying their



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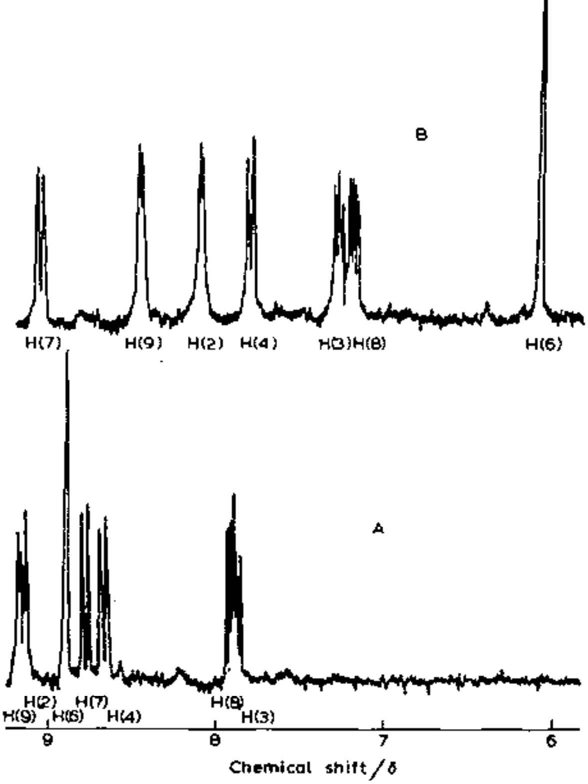
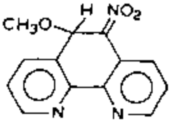


Fig. 14. 220 MHz NMR spectra of 5-NO_2phen in DMSO-d_6 (A) before and (B) after addition of NaOMe. Reprinted with permission from ref. 89.

corresponding metal complexes. One particular polypyridine that has received considerable attention is 5-nitro-1,10-phenanthroline (5-NO_2phen).

Free 5-NO_2phen is readily reduced by borohydride in neutral or alkaline aqueous media and yields, depending on pH and temperature, several products, three of which have been isolated and identified by IR and mass spectra, and by analysis as: 5-amino-1,10-phenanthroline, *N*,*N'*-bis(1,10-phenanthrolin-5-yl)-hydrazine, and 5,5'-azo-1,10-phenanthroline [12]. A rapid reaction follows upon addition of NaOMe to a DMSO solution of 5-NO_2phen as indicated by a change to a red-colored solution typical of Meisenheimer complex formation [89]; 1,10-phenanthroline shows no such reaction under the same conditions. Figure 14 illustrates the changes in the 200 MHz ^{1}H

NMR spectrum associated with the reaction of 5-NO_2phen, the most important of which is loss of the H(6) singlet at ca. 8.9 ppm and the appearance of a singlet resonance of equal intensity at 6.03 ppm; the spectrum being consistent with the Meisenheimer adduct (**42**) [89]. (It would have been interesting to add some CD_3OH to verify that the singlet at 6.03 ppm is not due to this species under those conditions.) A general upfield shift is evident as a result of increased electron density of the ring systems. Binding of the $^-$OMe group at the C(6) rather than the C(5) carbon is evidenced [89] by the long range proton couplings to the C(5) and C(6) signals in the ^{13}C NMR spectrum of the adduct. Also, over a period of a few hours, the DMSO solutions give rise to very broad ^{1}H NMR spectra and display strong ESR signals, indicative of free-radical species (probably beginning by formation of a carbanion) not unusual for nitroaromatics [89,102]. The observation of a Pfeiffer effect in cation–cation systems such as in the *N*-methylphenanthrolinium (**43**) and the *N*-methyl-5-nitrophenanthrolinium cations has also been taken as evidence for the formation of covalent hydrates in these species; covalent hydration occurrence would introduce new chiral centres (e.g. **44**) in such complexes [103]. It is important to note here, however, that other factors [104] may be responsible for such observations, chief among which is formation of ion pairs with OH^- (or other anions) that may enhance interactions between the Pfeiffer-active cation and the environment compound [105] (normally an alkaloid cation).



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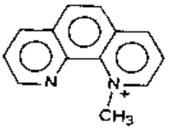

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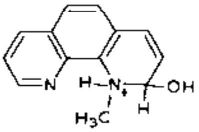
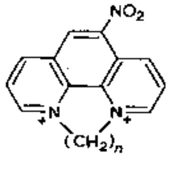


(44)

Successive additions of small amounts of aqueous NaOH to 5-NO_2phen causes (a) an increase in the intensity of the 323 nm band, (b) a decrease in the intensity of the 265 nm band, and (c) the formation of an isosbestic point at 286 nm [106,107]. Such changes are reversed by addition of acid [107]. Burgess and Prince [106] suggest that such observations are consistent with an alkali-dependent equilibrium of two species in which the H(6) proton adjacent to the nitro group is acidic and removed by OH^- ions forming a carbanion. Such acidic aromatic protons have also been demonstrated for

1,3-dinitrobenzene where the H(2) proton undergoes deuterium exchange [108]. Electronic spectral changes analogous to those above have also been observed for alkali nitromethane solutions for which the presence of $CH_2NO_2^-$ has been established [109]. Gillard et al. [107] consider such spectral changes as arising from the formation of the OH^- pseudobase similar to (**42**), with a formation constant of 1.2 ± 0.1 M^{-1}.

Reactions of the quaternized 5-nitrophenanthroline (**45**) and (**46**) with



(45) $n = 2$
(46) $n = 3$

hydroxide ion have been investigated kinetically [110] by stop-flow techniques. Reaction (24) is very rapid even at 0°C and so was studied [110] at

$$(\mathbf{46})^{2+} + OH^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \{(\mathbf{46})OH\}^+ \tag{24}$$

low OH^- concentration (0.005–0.01 M); it is completely reversible upon addition of acid. The data are consistent with the general rate law (25). The relevant kinetic and activation parameters are summarized in Table 3. A

$$k_{obs} = k_1[OH^-] + k_{-1} \tag{25}$$

somewhat different reactivity pattern is observed [110] for the reaction of OH^- with (**45**), the reaction following the rate law (26). Unlike reaction (24),

$$k_{obs} = \frac{k_2 K_{eq}[OH^-]}{1 + K_{eq}[OH^-]} \tag{26}$$

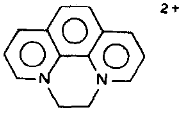
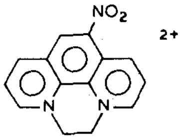
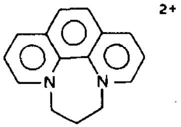
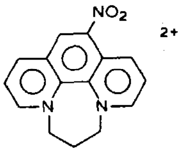
addition of H^+ reverses the reaction only initially; also, extrapolation of absorbance values back to zero time does not give the initial spectrum of the dipositive ion $(\mathbf{45})^{2+}$. Addition of DCl to a D_2O solution of (**45**) causes no changes in the ^1H NMR spectrum relative to that in D_2O alone. These results were taken to mean [110] that the reaction of (**45**) with OH^- is the addition of a second OH^- to a monopositive pseudobase whose rate of formation is too fast to measure (equations 27–29). A possible reason for the differences in kinetic behaviour between the chemically similar heterocycles

$$(\mathbf{45})^{2+} + OH^- \xrightarrow{\text{very fast}} \{(\mathbf{45})OH\}^+ \tag{27}$$

$$\{(\mathbf{45})OH\}^+ + OH^- \overset{K_{eq}}{\rightleftharpoons} \{(\mathbf{45})(OH)_2\}^0 \tag{28}$$

TABLE 3

Kinetic and activation parameters for reaction of *N*-heterocycles and metal–diimine complexes with nucleophiles [a]

Compound	Conditions, nucleophile	k_1 ($M^{-1}\ s^{-1}$)	$\Delta H_1^{\ddagger}$ [b] (kcal mol^{-1})	$\Delta_1^{\ddagger}$ [b] (e.u.)	k_{-1} (s^{-1})	$\Delta H_{-1}^{\ddagger}$ [b] (kcal mol^{-1})	$\Delta S_{-1}^{\ddagger}$ [b] (e.u.)	Ref.
	25°C, $I = 0.2$ M OH^-	5.5×10^5			25			111
	0°C, $I = 0.01$ M OH^-				$k_{obs} = 29.8$	18.1	14.6	110
	25°C, $I = 0.2$ M OH^-	9.4×10^5			14			111
	0°C, $I = 0.01$ M OH^-	5.34×10^3	9.31	7.0	0.34			110
$Fe(5\text{-}NO_2phen)_3^{2+}$	25°C, $I = 0.2$ M OH^-	5.70	16.8	0.8	0.04	21.6	6.9	110
$Ru(5\text{-}NO_2phen)_3^{2+}$	25°C, $I = 0.2$ M OH^-	1.78	17.4	0.3	0.055	18.0	−4.3	110
$Fe(phen)_2(CN)_2$	100°C, $I = 0.1$ M CN^-	1.0			3.0×10^{-4}			112

Fe(5-Clphen)$_2$(CN)$_2$	100°C, $I = 0.10$ M CN$^-$	5.2			5.3×10^{-4}			112
Fe(5-NO$_2$phen)$_3^{2+}$	44.5°C, $I = 0.21$ M CN$^-$	0.26			0.7×10^{-3}			112
Ru(5-NO$_2$phen)$_3^{2+}$	37°C, CN$^-$ $I = 0.50$ M	0.16	12.3	−22.5				113
Ru(5-NO$_2$phen)$_3^{2+}$	37°C, MeO$^-$ Methanol	608	10.6	−10.3	15.1	13.6	−7.2	114
Ru(5-NO$_2$phen)$_3^{2+}$	37°C, EtO$^-$ Ethanol	3190	11.1	−6.9				114
Fe(bipym)$_3^{2+}$	0°C, OH$^-$	24.3	17.3	2.0				115
Fe(bipym)$_3^{2+}$	0°C, CN$^-$	5.0	11.5	−12.8	0.04	18.2	2.0	116
Fe(bipym)$_3^{2+}$	0°C, N$_3^-$	12.0	17.9	12.3	0.05	24.0	24.0	116
Fe(bipy)$_3^{2+}$	25°C, H$_2$O	$k_{obs} = 4.03 \times 10^{-3}$	19.7	−3.4				117
Fe(bipyz)$_3^{2+}$	19°C, OH$^-$	252	7.0	−44.9				117
Fe(box)$_3^{2+}$	18.5°C, OH$^-$	89.9	11.3	−10.3		20.9	15.5	117
Fe(TPT)$_2^{2+}$	0°C, OH$^-$ $I = 1.0$ M	319	17.5	15.4				118
Ru(TPT)$_2^{2+}$	0°C, OH$^-$ $I = 1.0$ M	34.0	10.9	−11.1	0.68	18.2	7.3	118
Co(TPT)$_2^{2+}$	0°C, OH$^-$ $I = 1.0$ M	36.9	9.1	−17.9	0.85	12.8	−11.8	119
Ni(TPT)$_2^{2+}$	0°C, OH$^-$ $I = 1.0$ M	200	12.6	−8.5	~4			119
Cu(TPT)(OH)$_3^-$	0°C, OH$^-$ $I = 1.0$ M	11.4	16.6	7.0				120
Co(TPT)(OH)$_3^-$	0°C, OH$^-$ $I = 1.0$ M	51.0	10.7	−11.3	0.60	12.0	−15.5	120
Ni(TPT)(OH)$_3^-$	0°C, OH$^-$ $I = 1.0$ M	91.6			2.13			120
Cu(TPT)(H$_2$O)$_3^{2+}$	25°C, H$_2$O	$k_{obs} = 1.09 \times 10^{-4}$ s^{-1}	27.3	−12.1				120
Ni(TPT)(H$_2$O)$_3^{2+}$	27.5°C, H$_2$O	$k_{obs} = 14.3 \times 10^{-4}$	11.5	−33.2				120

[a] Except where k_{obs} is noted, kinetic and activation parameters refer to rate expression $k_{obs} = k_1[\text{nucleophile}] + k_{-1}$. [b] Temperature = 25°C.

$$\{(\mathbf{45})(\mathrm{OH})_2\}^0 \rightarrow \text{product} \tag{29}$$

(**45**) and (**46**) is that the site of nucleophilic attack is different in each case [110]. This, however, must be taken cum grano salis. It must also be recognized that the rate expressions (25) and (26) are also kinetically consistent with, (a) formation of a carbanion (removal of the H(6) proton), and (b) with ion-pair formation. No NMR spectral studies were possible for (**45**) and (**46**) due to their low solubility in aqueous media [110]. If the nucleophile were N_3^-, addition of it to a D_2O solution of (**45**) leads to a fast ^1H NMR spectral change where the H(6) singlet is preserved at 9.00 ppm (9.70 ppm in D_2O alone) but the remaining downfield signals are broadened and a new doublet appears at 7.30 ppm [110]. This broadening probably arises from formation of free radicals; however, Gillard et al. [110] suggest that N_3^- initially attacks the heterocycle at the 2 (or 9) position. At longer times, the H(6) singlet shifts upfield to 8.4 ppm. This was taken to indicate that migration of N_3^- to the C(6) site occurs [110]. From the analogous NMR spectral studies of (**46**) in D_2O containing N_3^-, it was inferred that initial attack occurs at 4- (or 7) carbon atom(s), with the final resting position of N_3^- being at the C(6) carbon [110].

Recently, Constable and Seddon [101] found no NMR evidence for reaction of free 2,2′-bipyridine with either sodium hydroxide or sodium methoxide in methanol, water or dimethylsulfoxide under a wide variety of reaction conditions. Evidently, this free base forms no covalent hydrates or pseudobases under these conditions [121].

Treatment of aqueous solutions of $\mathrm{Fe(5\text{-}NO_2phen)_3^{2+}}$ (510 nm, $\log \epsilon = 3.9$) and $\mathrm{Ru(5\text{-}NO_2phen)_3^{2+}}$ (446 nm, $\log \epsilon = 4.08$) with hydroxide ion rapidly leads to formation of an intermediate species (528 nm, $\log \epsilon = 3.8$, and 464 nm, $\log \epsilon = 4.13$, respectively), the rate of production being first order in both the complex ion and OH^- ion in the range $0 < [OH^-] \leqslant 0.05$ [122]. A slower, hydroxide-independent reaction follows that leads to ligand loss. The kinetics of the nucleophilic attack follow equation (25) and were described by reaction (30) where the intermediate was taken [122] as the pseudobase

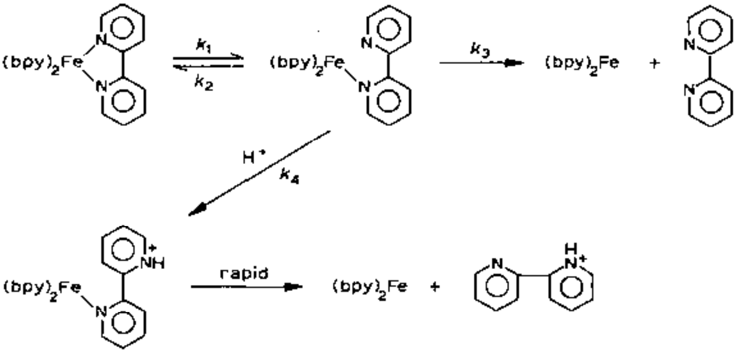
$$\underset{\mathrm{M=Fe,\,Ru}}{\mathrm{M(5\text{-}NO_2phen)_3^{2+}}} + \mathrm{OH^-} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \underset{(\mathbf{47})}{(\mathrm{M(5\text{-}NO_2phen)_2(5\text{-}NO_2phen)\cdot OH})^+} \tag{30}$$

(**47**). Significant upward curvature occurs in the plot of k_{obs} vs. $[OH^-]$ for the ruthenium(II) complex, consistent with the formation of a dihydroxo adduct [122]. The kinetics can also be interpreted in terms of a seven-coordinate species or formation of a ligand carbanion species for (**47**).

Iron(II)-phenanthrolines and -bipyridyls have indeed been the object of many kinetic studies in the last few decades. In aqueous acid solutions, the dissociation of $Fe(phen)_3^{2+}$ is acid independent; for $Fe(bpy)_3^{2+}$ dissociation is acid dependent and has been described by expression (31) and by the reaction sequence (32) [123]. It was noted that in solutions of low acidity,

$$k_{obs} = k_1 \frac{k_3 + k_4[H^+]}{k_2 + k_3 + k_4[H^+]} \tag{31}$$

SCHEME 4



(32)

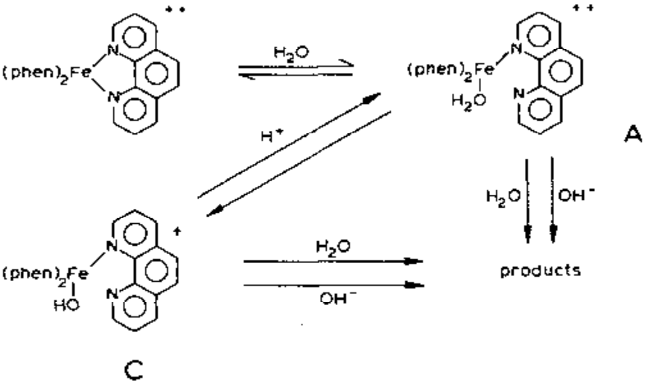
each time a single Fe–N bond breaks the bond reforms ca. 84% of the time and the second bond breaks ca. 16% of the time to lead to complete dissociation. The activation energy for dissociation of $Fe(phen)_3^{2+}$ in 1 M HCl is 32.1 kcal mol^{-1}; for $Fe(bpy)_3^{2+}$, $E_a = 27.4$ kcal mol^{-1} in 1 M HCl and was associated with step k_1. Also, in each case the rate of racemization is greater than the rate of dissociation and it was concluded that an intramolecular process accounts for much of the observed racemization. A mechanism involving rupture of an Fe–N bond was proposed [123] to account for the acid-dependent dissociation and racemization of $Fe(bpy)_3^{2+}$. The effect of added large anions and cations on the rates of dissociation and racemization of $Fe(phen)_3^{2+}$ has also been investigated [124]. Basolo and co-workers [124] point out that the rigid planar structure of phenanthroline lends certain geometrical characteristics to the $M(phen)_3^{2+}$ complex: the complex is not spherical in shape but rather three perpendicular phenanthroline planes jut out from the centre of the complex leaving three major pockets between them. Models show [124] that two water molecules fit rather compactly into each pocket, the whole aggregate now becoming generally spherical and in accord with observations that several phen complexes appear as hexahydrates. Because of the proximity of the water molecules and because they are properly oriented for coordination, it seemed likely [124] that water molecules would immediately occupy any coordination position made vacant by dissociation of phen molecules. The expectation, therefore, was that formation of new aggregates between the complex and the added large ions that loosen up the hydrated arrangement should tend to increase the rate of dissociation; however, if formation of the aggregate leads to removal of water molecules from their close proximity, the rate of dissociation should decrease [124]. These expectations were borne out; when the ion is protonated brucine, a slight increase in k_{diss} and k_{rac} ensues; when the ion is polystyrenesulfonate a large decrease in k_{diss} and k_{rac} is observed [124].

Interaction of hydroxide ion with $Fe(phen)_3^{2+}$ increases the rate of dissociation substantially. Margerum [125] demonstrated that the base-catalyzed dissociation of $Fe(phen)_3^{2+}$ up to $[OH^-] = 4.5$ M follows the rate expression (33).

$$k_{obs} = k_1 + k_2[OH^-] + k_3[OH^-]^2 + k_4[OH^-]^3 \tag{33}$$

At low $[OH^-]$, k_3 and k_4 are not significant and the rate becomes equivalent to (25); viz., $k_{obs} = k_1 + k_2[OH^-]$, where k_1 is the rate constant in neutral or acidic solutions. Two mechanisms were considered [125]: one assumes OH^- ion attack and the other OH^- ion catalysis. In the former, it was necessary to assume some type of unstable reaction intermediates **A** and **C** (Scheme 5) where H_2O or OH^- is associated with $Fe(phen)_3^{2+}$. Although **A** and **C** might be pictured as some type of complex with a coordination number of 7, it was more convenient to represent them with singly-bonded phenanthroline. The introduction of an $[OH^-]^3$ term above 1 M hydroxide could arise [125] from specific salt effects or from activation of a second phen molecule in **C** to form another intermediate **D** having two singly bonded phen molecules followed by a further OH^- attack to give the products. An alternative to nucleophilic attack was offered [125]: it was assumed that $Fe(phen)_3^{2+}$ spontaneously forms an intermediate $\{Fe(phen)_3^{2+}\}^*$ where one phen molecule is only partially bonded to Fe(II). Such a species may then rapidly accept a water molecule or OH^- ion prior to complete dissociation of the phen molecule from Fe(II). The intermediate with hydroxide,

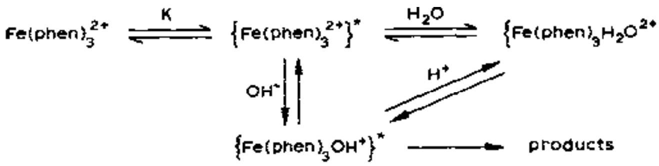
SCHEME 5



(34)

$\{Fe(phen)_3OH^+\}^*$, would lose the partially bonded phen molecule more rapidly than $\{Fe(phen)_3H_2O^{2+}\}^*$ as summarized in reactions (35). To fit this mechanism to the observed data, Margerum [125] assumed formation of additional intermediates, $\{Fe(phen)_3(OH)_2^+\}^*$ and $\{Fe(phen)_3(OH)_3^-\}^*$, with two or three one-ended phen molecules, respectively. An ion-pair mechanism was also considered but discarded on the basis that other ions such as Cl^-, F^-, NO_3^- and ClO_4^- lead to no increase in the dissociation rate; indeed an ion-pair process was not considered possible unless OH^- "forms some unique species with $Fe(phen)_3^{2+}$ in which case it would be bonded to Fe(II) and no longer be a mere ion pair" [125]. The fixed planar structure of the phenanthroline molecule had been earlier used to argue [123] against any tendency for phenanthroline to behave as a monodentate ligand. However, to the extent that 4,5-disubstituted phenanthrenes form optical isomers as a result of non-planarity [126], it is not impossible to have a reaction intermediate with a broken chelate ring [125]. It is worth noting that studies on the dissociation and racemization of Ni(II)-phenanthroline complexes indicate that single bonded phenanthroline intermediates are not possible for an S_N1 mechanism, or else the racemization rates would exceed dissociation rates [127,128]. The alternative for a possible intermediate, as noted earlier, is a seven-coordinate iron(II) complex; this would presumably necessitate changes in the electron configuration of the complex from $d^2d^2d^2$ to $d^2d^1d^1d^1d^1$ which would account [125] for the slowness of its formation.

SCHEME 6



(35)

Both CN^- and N_3^- ions greatly increase the rate of displacement of phenanthroline from $Fe(phen)_3^{2+}$ [128]. Reaction with cyanide ion follows two pathways (reactions 36–39)

$$Fe(phen)_3^{2+} \xrightarrow{k_1} Fe(phen)_2^{2+} + phen \tag{36}$$

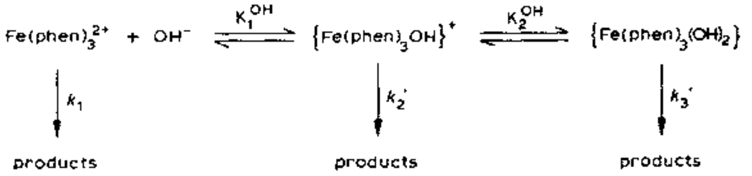
$$Fe(phen)_3^{2+} + 2\,CN^- \xrightarrow{fast} Fe(phen)_2(CN)_2 \tag{37}$$

$$Fe(phen)_3^{2+} + CN^- \xrightarrow{k_2} Fe(phen)_2CN^+ + phen \tag{38}$$

$$Fe(phen)_2CN^+ + CN^- \xrightarrow{fast} Fe(phen)_2(CN)_2 \tag{39}$$

$k_{obs} = k_1 + k_2[CN^-]$ up to 1 M cyanide and E_a is 20 kcal mol^{-1} [128]. Treatment of Fe(phen)$_3^{2+}$ with azide ion first shows rapid 15% loss of Fe(phen)$_3^{2+}$ followed by a slower process. This was thought [127] to be caused by either the formation of an absorbing product or by back reaction of the products; $E_a = 22$ kcal mol^{-1}. The hydroxide ion–iron(II)-phenanthroline system was reexamined [128] for possible mixed OH$^-$–Fe(phen)$_3^{2+}$ complexes. No evidence was found for a stable intermediate. The "unique species between Fe(phen)$_3^{2+}$ and OH$^-$" noted earlier [125] has been suggested [128] to involve interaction between the nucleophile and the antibonding *d* orbitals of the iron on the octahedral face; such an interaction would weaken metal–ligand bonds and result in increased dissociation rates. The nucleophile was viewed as replacing the water molecule in the pockets between the planar phenanthroline molecules to form inner ion pairs. The kinetics of dissociation of Fe(phen)$_3^{2+}$ by hydroxide, cyanide and azide ion were rationalized by equations (40–42) [128].

SCHEME 7



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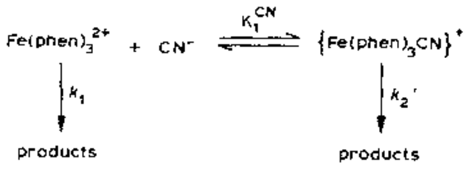
SCHEME 8



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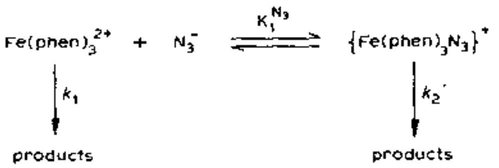
SCHEME 9



(42)

The kinetics of the reaction between several substituted tris(1,10-phenanthroline)iron(II) and hydroxide ion have been investigated by Burgess and Prince [106]. With the exception of the 5-NO$_2$phen complex, the kinetics of dissociation for the unsubstituted and other substituted ferroins (phen, 5-Mephen, 5-Clphen, 5-Phphen, 5,6-Me$_2$phen, 4,7-Me$_2$phen, 3,4,7,8-

Me_4phen, 5-Me-6-NO_2phen) are strikingly similar; $k_{obs} = k_1 + k_2[OH^-]$. This rate expression involves [106] two paths for dissociation, one involving direct participation of hydroxide in the slow step or a pre-equilibrium, and the other not. It is important to note that the values of k_1 for alkali dissociation are nearly equal to those obtained in acid dissociation studies (see Table 4). Such identical values argue against Gillard's proposed mechanism for these substituted (with the exception of 5-NO_2phen) ferroins that k_1 represents the reverse of reaction (43).

$$Fe(NN)_3^{2+} + OH^- \rightleftharpoons Fe(NN)_2(NN \cdot OH)^+ \qquad (43)$$

Differences in the activation energies were ascribed [106] to three factors: changes in σ and π bonding between iron and nitrogen and changes in the electron density around the iron atom, depending on the electron-withdrawing or -donating capacity of the substituents. Greater electron withdrawal by a substituent should make the iron more positive and should facilitate attack by the OH^- ion [106]. This expectation is borne out by the 5-Cl substituent for which the second order rate constant k_2 (forward path of reaction 43) is significantly larger than for $Fe(phen)_3^{2+}$ itself. Increasing methyl substitution increases the activation energy; also, electron-releasing by the methyl groups increases the electron density in the neighbourhood of the iron atom and renders attack by OH^- ion more difficult (compare k_2 values of Table 4). For the 5-methyl-6-nitrophenanthroline ferroin, the activation energy for alkali fission is nearly identical to those for methyl substituted ferroins but the k_2 value is larger by two orders of magnitude. Apparently, the NO_2

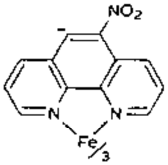
TABLE 4

Comparison of rate constants for alkali and acid dissociation, and activation energies for alkali dissociation of substituted ferroins, $Fe(NN)_3^{3+}$, at 25°C [a]

NN	k_1 (min^{-1}) (alkali)	k_1 (min^{-1}) (acid)	E_a (kcal mol^{-1})	k_2 (M^{-1} min^{-1}) (alkali)
phen	0.004	0.0044	23.6	0.65
5-Mephen	0.010 [b]	0.0113 [b]	24.1	0.238
5-Clphen	0.010	0.0143	23.9	3.03
5-Phphen	0.005	0.0048	23.9	0.302
5,6-Me_2phen	0.0033 [b]	0.0035 [b]	26.2	0.030
4,7-Me_2phen	0.006 [b]	0.0065 [b]	26.6	0.043
3,4,7,8-Me_4phen	0.028 [b]	0.034 [b]	27.1	0.0313
5-Me-6-NO_2phen	0.040 [c]	0.020 [c]	26.6	5.2
5-NO_2phen			20.2	5.6

[a] Ref. 106. [b] 35.0°C. [c] 20.0°C.

group has no activating effect [106], probably due to non-coplanarity with the phenanthroline rings. The 5-NO_2phen ferroin is exceptional [106]; the rate decreases slightly with increasing [OH^-] in strongly alkaline media. Also, the initial absorbance values for the kinetic runs decreased with increase in hydroxide ion concentration. These spectral variations implicate a rapidly established equilibrium with a species that is less reactive than $Fe(5\text{-}NO_2phen)_3^{2+}$. This species (**47**) was described [106] as one in which a



(47)

proton is lost from the 6 position adjacent to the NO_2 group. The exceptional results for the 5-NO_2phen complex are apparently not due to the nitro group nor to proton loss from any position other than 6 [106], in keeping with the lability of protons *ortho* to nitro groups in *m*-dinitrobenzene [108]. The low activation energy is consistent [106] with the electron withdrawing properties of the nitro group, thus encouraging nucleophilic hydroxide attack at the iron atom.

Recently, the rates of racemization and dissociation of ferroin, $Fe(phen)_3^{2+}$, have been measured [129] in water, methanol, acetone, formamide, *N,N*-dimethylformamide, acetonitrile and acetic acid, and also in mixtures of water with methanol, acetone, formamide and *N,N*-dimethylformamide. Racemization rates were also determined in mixtures of water with glycerol and ethylene glycol [129]. In all cases, dissociation is slower than racemization. Ion association (with ClO_4^-) has a retarding effect on the rate of racemization. The order of dissociation rates in pure solvent was observed to be: *N,N*-dimethylformamide > formamide > water > methanol > acetone > acetonitrile > acetic acid. For dimethylformamide, methanol and acetone, the rates are in the same order as the solvent's ability to act as a ligand, the latter ability being judged on the basis of stability constants of complexes where the solvents act as ligands [129]. Presumably, organic solvents act to lower the activation barrier to dissociation of a phenanthroline ligand, but a strongly coordinating ligand must be present to replace the dissociated ligand. Hence, in mixed solvents, a maximum in the rate is observed when there is water to fill the vacated coordination sites and an organic solvent to solvate the leaving ligand [129].

The observation that the "exciton" band in the circular dichroism spectrum of $Fe(phen)_2(CN)_2$ disappears in acid solutions led Gillard et al. [130] to suggest that not only may the cyanide groups be protonated in acidic

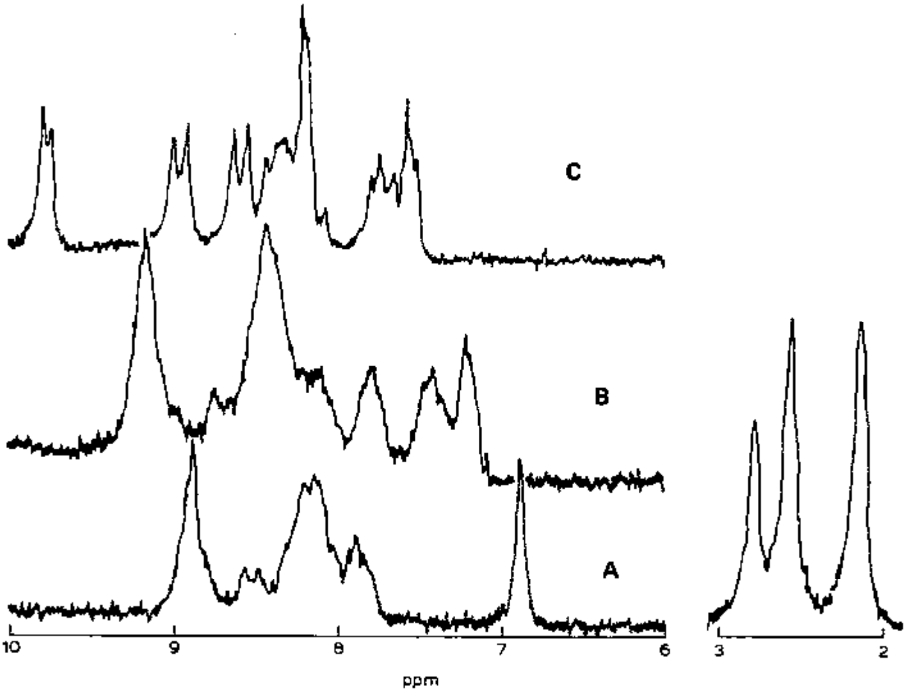
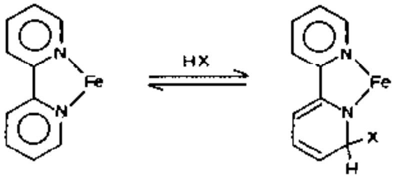


Fig. 15. 90 MHz ^{1}H NMR spectra of Fe(NN)$_2$(CN)$_2$ complexes in 50/50(v/v) D_2O/D_2SO_4: NN = 5,5′-Me$_2$bpy (A), bpy (B), and phen (C). Reprinted with permission from ref. 130.

solution but that the phen ligand itself may have undergone some reaction. The nature of the complexes Fe(NN)$_2$(CN)$_2$ and Fe(NN)(CN)$_4^{2-}$ (NN = phen, bpy, and 5,5′-Me$_2$bpy) were investigated in various solvents and in acid media by ^{1}H NMR spectroscopy. The NMR spectra in D_2SO_4 reveal that the geometry of Fe(phen)$_2$(CN)$_2$ is such that the two halves of the phen ligand are neither spatially nor magnetically equivalent; it is not possible to ascertain from the spectrum whether the ligands had been attacked [130]. The NMR spectrum of Fe(5,5′-Me$_2$bpy)$_2$(CN)$_2$ in D_2SO_4 solutions is illustrated in Fig. 15; the areas of the peaks for the methyl groups could not be rationalized [130] in terms of a single new compound being the sole product of the reaction with acid. They were explained, as indeed was also the broadening of all signals, as arising from an equilibrium situation. Both H_2SO_4 and HCl may act in a way similar to H_2O and HCN to give rise to the equilibrium (44). The non-equivalence could also arise [130] from proto-



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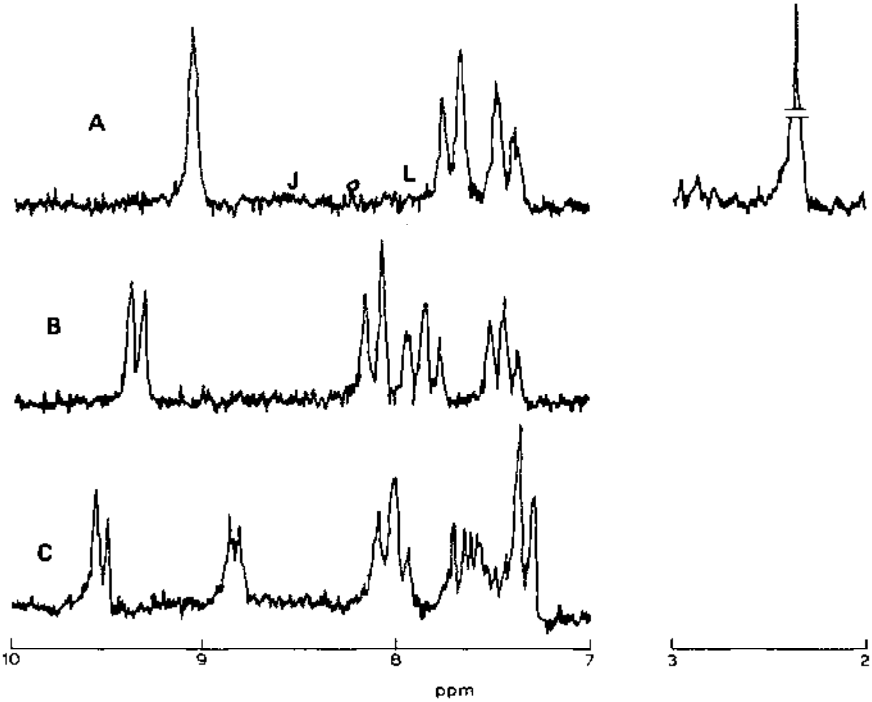
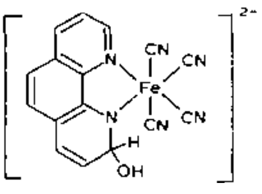


Fig. 16. 90 MHz ^1H NMR spectra of $Fe(NN)(CN)_4^{2-}$ complexes in D_2O; NN = 5,5-Me_2bpy (A), bpy (B), and phen (C). Reprinted with permission from ref. 130.

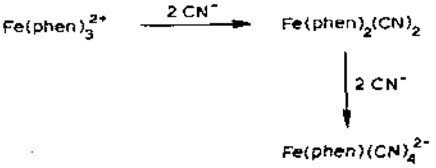
nation of only one cyano group as well as from the cleavage of an iron–nitrogen bond by strong acid, a reaction often invoked, as seen earlier, to explain kinetic data obtained during reactions of strong acids with tris-complexes of Fe(II) with diimine ligands. Both of these explanations were considered unlikely [130] but are not to be excluded. NMR spectra of $Fe(NN)(CN)_4^{2-}$ in D_2O for NN = phen, bpy, and 5,5′-Me_2bpy are presented in Figure 16 [130]; the NMR spectra of the last two display the two-fold symmetry expected of the diimine ligand molecule while the former shows an unexpected corresponding inequivalence. This inequivalence was attributed to the covalent hydrate (**48**).



(48)

The kinetics of reaction (45) of $Fe(phen)_3^{2+}$ with cyanide have recently

SCHEME 10



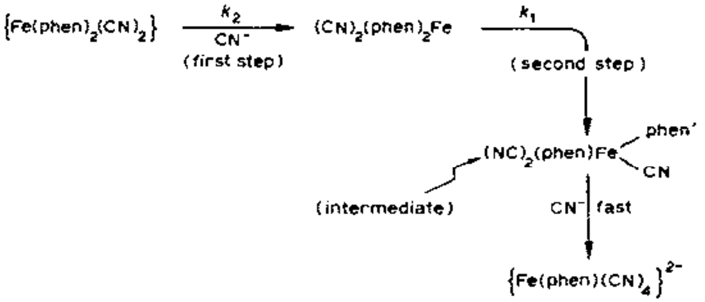
(45)

been re-examined by Burgess and Haines [112] in light of the possibility of "pseudobases" [6] in these types of complexes; for the first stage of reaction (45), $k_{obs} = k_1 + k_2[CN^-]$ with k_2 being the dominant term. In this study [112] kinetic results for the reactions of $Fe(NN)_2(CN)_2$ (NN = bpy, phen, or 5-Clphen) with cyanide are reported. The k_1 and k_2 of equations (46) are

$$\begin{array}{ll} k_{obs} = k_2[CN^-] & k_{obs} = k_1 \\ \text{(first step)} & \text{(second step)} \end{array} \qquad (46)$$

associated with the reaction mechanism (47) for NN = phen and 5-Clphen.

SCHEME 11



(47)

In the reactions of the complexes, the second step is in both cases sufficiently slower than the first that the reactions are kinetically distinguishable [112]. The second order k_2 value of equation (46) for the phen complex reaction is lower (1.0 M^{-1} s^{-1}) than that for the 5-Clphen complex reaction (5.2 M^{-1} s^{-1}; 100°C), as expected (see above); k_1 values for transfer of cyanide from ligand to metal are 3.0×10^{-4} and 5.3×10^{-4} s^{-1}, respectively. If such transfer occurs, we would expect cyanide transfer to be slower for the 5-Clphen case, since presumably the cyanide would be held more strongly in 5-Clphen than in the phen. The very low sensitivity of the rate constant k_{obs} for the second stage of the $Fe(bpy)_2(CN)_2 + 2\ CN^-$ reaction to solvent variation (k_1 = ca. 3.0–3.4×10^{-4} s^{-1}) was also taken [112] to demonstrate the intramolecular nature of this process. While this argument is well taken, the kinetic data do not preclude intermediates of a nature different from that shown in reaction (47). It is notworthy that for the reaction of $\mathrm{Fe(bpy)_2(CN)_2}$, the activation energy is unusually high [112] (ca. 47 kcal $\mathrm{mol^{-1}}$) and $\Delta S^{\neq}$ = ca. +56 e.u., which is also rather high. These values are difficult to explain, particularly insofar as they are meant to represent activation parameters for the intramolecular transfer of cyanide to form a Fe–CN bond coupled to breaking a Fe–N(bpy) bond (cf. Table 3).

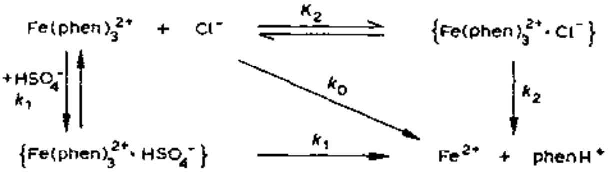
Reaction of $\mathrm{Fe(5\text{-}NO_2phen)_3^{2+}}$ with cyanide to prepare $\mathrm{Fe(5\text{-}NO_2phen)_2(CN)_2}$ according to the method of Schilt [23] gives a product containing three $\mathrm{5\text{-}NO_2phen}$ ligands and two cyanide ions per iron atom, thus presenting three possibilities: $\mathrm{[Fe(5\text{-}NO_2phen)_3](CN)_2}$, $\mathrm{[Fe(5\text{-}NO_2phen)_2(5\text{-}NO_2phen \cdot CN)](CN)}$, and $\mathrm{[Fe(5\text{-}NO_2phen)(5\text{-}NO_2phen \cdot CN)_2]}$ [112]. The first of these was discarded on the basis of expected solubility and UV–visible spectra. The IR spectrum of the red product is consistent [112] with the third formulation on the basis of $\nu(\mathrm{C \equiv N})$ at 2190–2200 $\mathrm{cm^{-1}}$, close to the range (2220–2240 $\mathrm{cm^{-1}}$) where aliphatic nitriles are expected; ionic cyanide has $\nu(\mathrm{C \equiv N})$ at 2070–2100 $\mathrm{cm^{-1}}$. The fingerprint region, 665–805 $\mathrm{cm^{-1}}$, of the proposed formulation is different [112] from those of $\mathrm{Fe(5\text{-}NO_2phen)_3^{2+}}$ and $\mathrm{Fe(5\text{-}NO_2phen)_2(CN)_2}$. Unfortunately, the obvious conductivity measurements were not done [112,113,131] on the red product, even in solvents where the compound might be soluble. The nature of the species formed between the analogous $\mathrm{Ru(5\text{-}NO_2phen)_3^{2+}}$ and cyanide was also suggested to be $\mathrm{Ru(5\text{-}NO_2phen \cdot CN)_2(5\text{-}NO_2phen)}$ from IR spectral observations [113,131].

The $\nu(\mathrm{C \equiv N})$ position in an IR spectrum deserves comment. There are several metal cyanide compounds for which $\nu(\mathrm{C \equiv N})$ also occurs in the upper part of the 2250–2040 $\mathrm{cm^{-1}}$ frequency range: $\mathrm{Hg(CN)_2}$, 2194 $\mathrm{cm^{-1}}$; $\mathrm{Ir(CN)_6^{3-}}$, 2185 $\mathrm{cm^{-1}}$; $\mathrm{Rh(CN)_6^{3-}}$, 2166 $\mathrm{cm^{-1}}$; AuCN, 2239 $\mathrm{cm^{-1}}$; CuCN, 2172 $\mathrm{cm^{-1}}$; AgCN, 2178 $\mathrm{cm^{-1}}$; $\mathrm{Fe(CN)_5NO^{2-}}$, 2152 $\mathrm{cm^{-1}}$ [132]. In some cases, as in $\mathrm{Fe(phen)_2(CN)_2^+}$ and $\mathrm{Fe(bpy)_2(CN)_2^+}$ complexes [133], the $\nu(\mathrm{C \equiv N})$ are barely discernible above the noise [134]. According to El-Sayed and Sheline [135], the $\mathrm{C \equiv N}$ stretching frequencies of cyano complexes depend on several factors such as, (1) electronegativity, (2) the oxidation number and (3) the coordination number of the metal. It is evident then that while a $\nu(\mathrm{C \equiv N})$ at 2190–2200 $\mathrm{cm^{-1}}$ is a reasonable argument for a cyano group bonded to a $\mathrm{5\text{-}NO_2phen}$ ring, such frequencies reflect the nature of the covalent bond of CN to another atom and therefore IR data do not preclude other possibilities for the intermediates.

The postulated intermediate $\mathrm{Fe(5\text{-}NO_2phen \cdot CN)_2(5\text{-}NO_2phen)}$ reacts further with cyanide and hydroxide nucleophiles. Pseudo-first-order kinetics are observed in 30% methanol solutions; $k_{\mathrm{obs}} = k_1 + k_2[\mathrm{nucleophile}]$ for which k_1 values for the two reactions are nearly identical [112]. A common dissociative rate-determining step was inferred. Values of k_2 for the cyanide and hydroxide reactions are 0.26 and 0.033 $M^{-1}\ s^{-1}$ (44.5°C), respectively, consistent with the better nucleophilic character of cyanide [112]. That the k_1 values above are greater than k_{obs} values (0.7–$0.8 \times 10^{-3}\ s^{-1}$) observed for the disappearance of $Fe(5\text{-}NO_2phenCN)_2(5\text{-}NO_2phen)$ in H_2SO_4 solutions were taken [112] to indicate that these latter values reflect dissociation of the complex while k_1 values reflect rapid intramolecular cyanide transfer from ligand to iron.

A preliminary report appeared recently on the acid solvolysis of $Fe(phen)_3^{2+}$ in dimethylsulfoxide, catalyzed by chloride ion via ion-pair formation [136]. The kinetics of the acid (H_2SO_4) solvolysis of this complex in DMSO is first order in complex and loss of the first ligand is rate-determining; k_{obs} at 25°C = $1.07 \times 10^3\ s^{-1}$, an order of magnitude larger than in water [137], $\Delta H^* = 26.6$ kcal mol^{-1}, $\Delta S^* = 17.1$ e.u. while in water $\Delta H^* = 29.3$ kcal mol^{-1} and $\Delta S^* = 20.7$ e.u. [136]. Addition of chloride ion produces a dramatic increase in the rate of solvolysis (by nearly a factor of 50 for 0.05 M Cl^-). For ca. 0.1 M chloride, the reaction is first order in both complex and chloride ion; it was thought possible that Cl^- was involved in a bimolecular reaction at the ligand or at the metal centre [136]. However, a plot of k_{obs} vs. $[Cl^-]$ is not linear, and, moreover, increases in concentration of H_2SO_4 acid for constant $[Cl^-]$ causes a decrease in k_{obs}. These observations were quantitatively interpreted in terms of competitive ion-pairing between Cl^-, HSO_4^- and $Fe(phen)_3^{2+}$ as depicted in the reaction sequence (48);

SCHEME 12



(48)

$$k_{obs} = \frac{k_0 + k_1K_1[HSO_4^-] + k_2K_2[Cl^-]}{1 + K_1[HSO_4^-] + K_2[Cl^-]} \tag{49}$$

$K_1 = 180 \pm 90\ M^{-1}$, $K_2 = 50 \pm 27\ M^{-1}$ and $k_2 = 0.58 \pm 0.02\ s^{-1}$.

Gillard [138] has seriously questioned the early acid solvolysis work of Twigg and co-workers [136] in DMSO: ".... the results, although undoubtedly correct, are incomplete and therefore naively interpreted, and why, in any case, the whole study... is irrelevant to reactions in water".

Apparently, in DMSO, $Fe(phen)_3^{2+}$ reacts rapidly with Cl^-, in the absence of acid, the reaction being taken to be the anation reaction (50)

$$Fe(phen)_3^{2+} + 2\ Cl^- \overset{K}{\rightleftharpoons} cis\text{-}Fe(phen)_2Cl_2 + phen \qquad (50)$$

to give $Fe(phen)_2Cl_2$; $K = 227\ M^{-1}$ [138]. The rate of loss of complex refers not only to acid solvolysis but also to anation in DMSO; in water, anation is of no significance [138].

Recently, a more complete report has appeared [139] on the kinetics of acid solvolysis in DMSO for $Fe(phen)_3^{2+}$ as well as for $Fe(5\text{-}NO_2phen)_3^{2+}$ and $Fe(bpy)_3^{2+}$ complexes. Unlike the behaviour in aqueous solutions, the dependence of k_{obs} on [acid] is similar for these three complexes. It was concluded that species containing unidentate protonated bpy are not formed to a significant extent during the acid solvolysis of $Fe(bpy)_3^{2+}$ in DMSO [139]. The relevant kinetic data and activation parameters are collected in Table 5. The enhanced reactivity in DMSO was ascribed to the smaller enthalpies of activation; entropies of activation are similar in both solvents. While solvation effects are no doubt important, participation of ion pairs is also possible [139]. In addition, the enhanced reactivity (about one order of magnitude for $[H^+] = 0.2$–0.8 M) of the $5\text{-}NO_2phen$ complex over the unsubstituted phen complex was attributed [139] to the greater sensitivity of the former to solvent effects. It had previously been noted [140] that addition of salts to methanol solutions of $Fe(bpy)_3^{2+}$ and $Fe(phen)_3^{2+}$ increases the rate of acid solvolysis of these complexes and it was suggested that this results from the formation of reactive ion pairs. The small dependence of k_{obs} on $[H_2SO_4]$ for the acid solvolysis of both the above bpy and phen complexes in DMSO is consistent [139] with the formation of hydrogen sulfate ion pairs with these $Fe(NN)_3^{2+}$ complexes and which are (somewhat)

TABLE 5

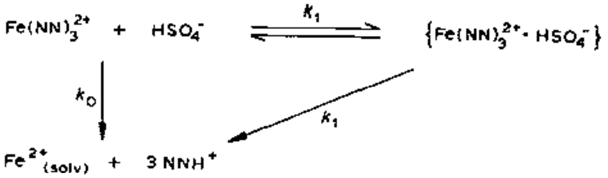
Kinetic data and activation parameters for acid solvolysis of $Fe(NN)_3^{2+}$ in water and DMSO [a]

Parameters	NN					
	phen		bpy		$5\text{-}NO_2phen$	
	H_2O	DMSO	H_2O	DMSO	H_2O	DMSO
10^4k (s^{-1})	0.7	10.7	2.0	12.7	4.9	15.6
$\Delta H^{\neq}$ (kcal mol^{-1})	29.3	26.6	27.2	26.3	28.0	25.7
$\Delta S^{\neq}$ (e.u.)	20.8	17.1	15.7	16.3	20.2	19.3

[a] Temperature, 25°C; from ref. 139.

more reactive than the complexes (reaction sequence 51). The value of K_1 was estimated to be 220 ± 90 M^{-1} (phen), 230 ± 60 M^{-1} (bpy), and 110 ± 70 M^{-1} (5-NO_2phen). The k_{obs} data for acid solvolysis of $Fe(phen)_3^{2+}$ in DMSO in the presence of Cl^- at 25°C was fitted with the following parameters for equation (49): $k_2 = 0.58\ s^{-1}$, $K_1 = 183\ M^{-1}$, $K_2 = 53\ M^{-1}$, $k_0 = 0.77 \times 10^{-3}\ s^{-1}$, and $k_1 = 1.10 \times 10^{-3}\ s^{-1}$. The relevant activation parameters for the k_2 path of (48) are $\Delta H^* = 22.7$ kcal mol^{-1} and $\Delta S^* = 16.3$ e.u. [139]. Interestingly, K_1 and K_2 are somewhat larger than expected for an ion pair formed between a +2 and a −1 ion; the Fuoss equation [141] predicts K_{ip} = ca. 32 M^{-1} for two ions separated by a distance of 5.7 Å (shortest Cu–Cl distance in $Cu(phen)_3(ClO_4)_2$ [142]), but if the anion gets as close to the metal ion as ca. 3 Å [143] the corresponding K_{ip} = ca. 240 M^{-1} [139]. Gillard's proposal [6] of initial attack of a nucleophile on a coordinated heterocyclic ring was also considered, inasmuch as the kinetics are consistent with such a proposal but now K_1 and K_2 of (48) represent formation constants of the "pseudobase" [139]. Such a possibility was not believed likely [139] because, (a) ClO_4^- and HSO_4^- ions accelerate the rate of acid-catalyzed decomposition and these ions are not known to attack activated carbon atoms in organic molecules; (b) where Cl^- is concerned, the formation constant of the "pseudobase" intermediate is large enough for it to be detected by NMR spectroscopy and no such spectral variations were observed [139].

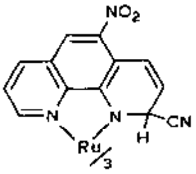
SCHEME 13



(51)

$$k_{obs} = \frac{k_0 + k_1 K_1[HSO_4^-]}{1 + K_1[HSO_4^-]} \qquad (52)$$

The UV–visible spectroscopic changes that occur upon addition of cyanide ion to an aqueous solution of $[Ru(5\text{-}NO_2phen)_3](NO_3)_2$ are reversible upon



(49)

acidification, and are analogous to those associated with the addition of hydroxide ion to a solution of the same complex [113]. Such changes in absorbance during kinetic runs were taken as resulting from formation of the monocyano adduct (**49**); the kinetics of the reaction are consistent with the formation of this adduct, depicted in reactions 53 and 54, and for which $k_{obs} = k_2[CN^-]$ under conditions of low hydroxide concentration [113]. This

$$Ru(5\text{-}NO_2phen)_3^{2+} + CN^- \xrightarrow{k_2} Ru(5\text{-}NO_2phen)_2(5\text{-}NO_2phen \cdot CN)^+ \qquad (53)$$

$$Ru(5\text{-}NO_2phen)_2(5\text{-}NO_2phen \cdot CN)^+ \underset{\substack{CN^- \\ \text{(in excess)}}}{\leftrightarrows}$$

$$Ru(5\text{-}NO_2phen \cdot CN)_2(5\text{-}NO_2phen) \qquad (54)$$

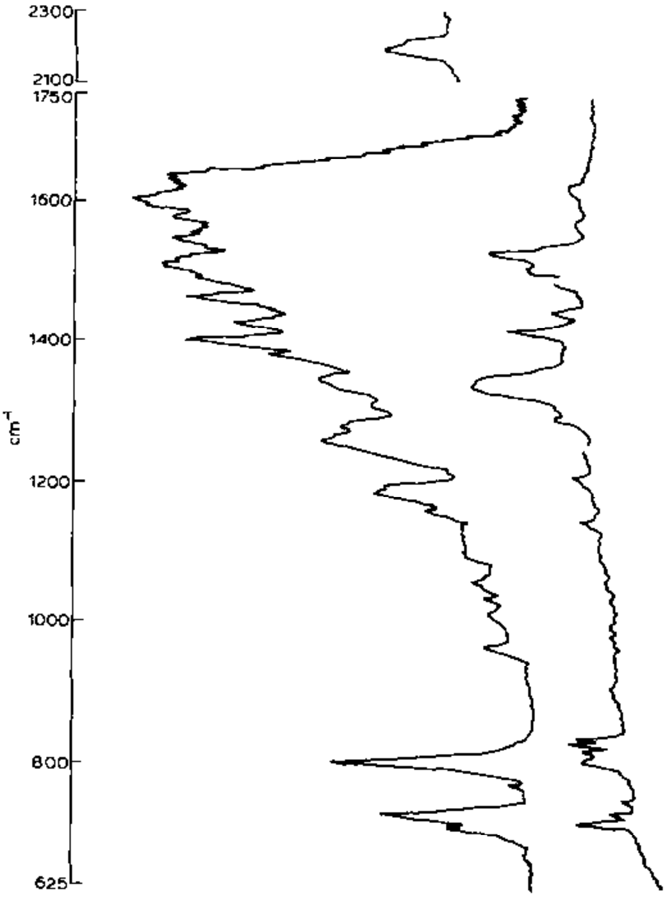


Fig. 17. IR spectra (KBr discs) of $[Ru(5\text{-}NO_2phen)_3](NO_3)_2 \cdot 4\ H_2O$ (left) and $Ru(5\text{-}NO_2phen \cdot CN)_2$ (right). Reprinted with permission from ref. 113.

is in contrast to reactions of the iron(II) analogs where ligand loss occurs. The nature of the dicyano adduct of reaction (54) was deduced from comparing the IR spectrum (Fig. 17) of $[Ru(5\text{-}NO_2phen)_3](NO_3)_2 \cdot 4\ H_2O$ with that of $Ru(5\text{-}NO_2phen \cdot CN)_2(5\text{-}NO_2phen)$, both as KBr discs. The CN stretch at 2198 cm^{-1} along with the large number of new bands in the 1650–1150 cm^{-1} region and the changes in the aromatic bands at ca. 665 and 805 cm^{-1} were taken [113] to indicate that the reaction between cyanide ion and $Ru(5\text{-}NO_2phen)_3^{2+}$ involves attack at the ligand. Notwithstanding the comments made earlier about IR CN stretching frequencies, this comparison must be regarded as tenuous. The comparison was made between spectra of two solids, one of which contains NO_3^- and H_2O molecules, and while differences are evident in Fig. 17, the complexity of the spectrum assigned to the dicyano adducts precludes any conclusions about the nature of such a species. When comparing IR spectra of solids, site symmetry effects can often complicate the spectrum rendering assignments difficult [132]. Unfortunately, this dicyano adduct was too insoluble in all solvents for its nature to be examined by NMR techniques. The second-order rate constant k_2 (reaction 53) for the CN^- reaction is 0.16 $M^{-1}\ s^{-1}$ (37°C), two orders of magnitude smaller than that reported [122] for the analogous reaction with OH^- (18.7 $M^{-1}\ s^{-1}$) [113]. Such a large difference is not expected [113] for attack at the metal; OH^- ion has been shown [144] to react faster than CN^- in addition at various organic cations.

The reactions of OH^-, CN^-, MeO^-, or EtO^- with Δ-(−)-$Ru(5\text{-}NO_2phen)_3^{2+}$ in solutions have been investigated by CD spectroscopic methods [131]. The results support [131] earlier findings that these reactions proceed through the formation of pseudobases with the ligand. The initial CD spectral changes in all reactions are reversible by addition of HCl to the solution up to ca. 5 h, but over a longer period, further reaction takes place with MeO^- and OH^- to give other species. The initial reactions with CN^- and EtO^- appear to be reversible indefinitely [131]. The diminution of the Cotton effects in the "exciton" region (see Fig. 18) has been suggested [6] as arising from a modification of the long-axis-polarized transitions of the ligand; one such possibility being changes in the nature of the ligand as might occur upon formation of pseudobases [131]. Also, increases in the CD spectra in the visible metal-to-ligand charge transfer region (see Fig. 19) might arise from new chiralities resulting from, also, formation of pseudobases, with alkoxide being a striking example [131]. Be that as it may, it is known that new chiralities may be formed by distortion of the phenanthroline plane (see above for the substituted phenanthrene case) as might occur in the formation of tight ion pairs (or possibly a loose seven-coordinate species) within the pockets of the metal complex with such nucleophiles; also, the possibility of ligand carbanions cannot be overlooked.

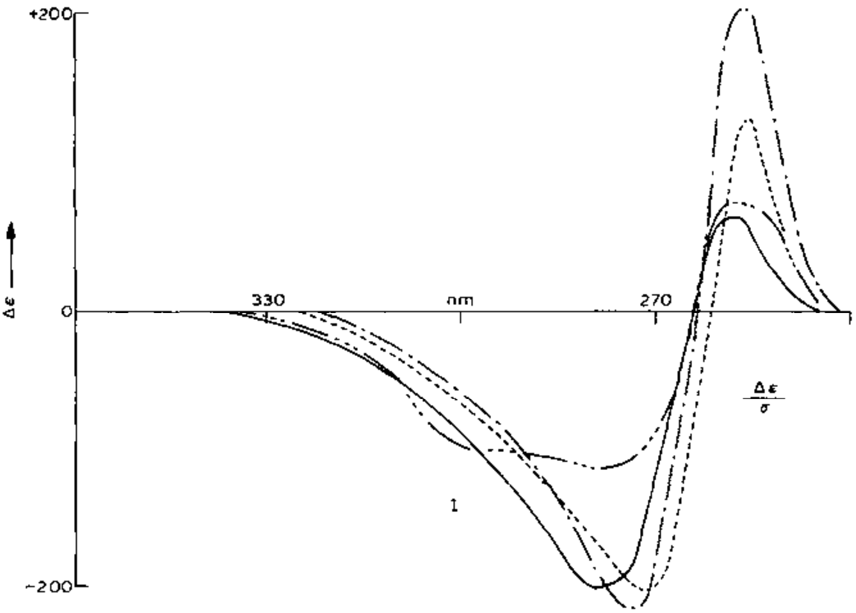


Fig. 18. Circular dichroism spectra in the "exciton" region of Ru(5-NO_2phen)$_3^{2+}$ in 0.001 M aqueous OH^- (——), in 0.05 M aqueous CN^- (······), in 0.001 M methanolic MeO^- (–·–·–), and in 0.001 M ethanolic EtO^- (–·····–····–) solutions. The vertical bar represents the error magnitude. Reprinted with permission from ref. 131.

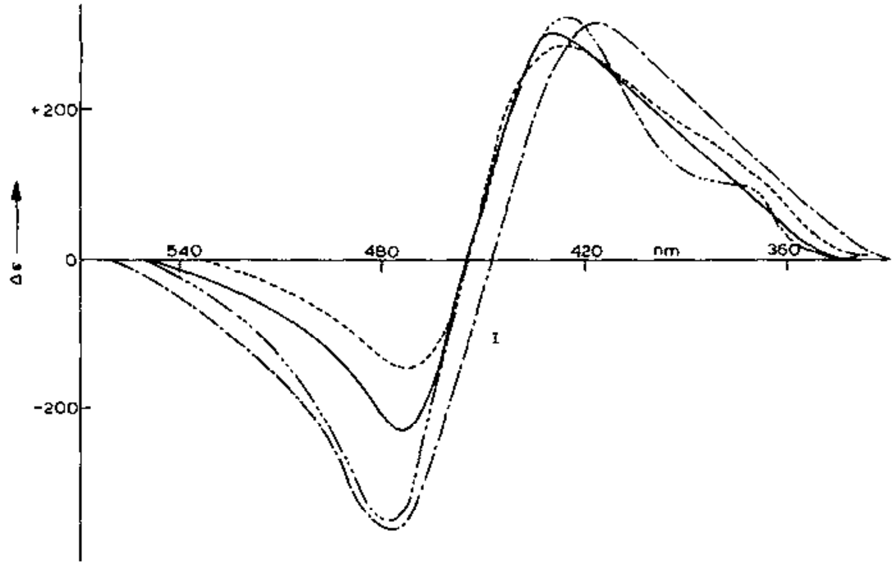
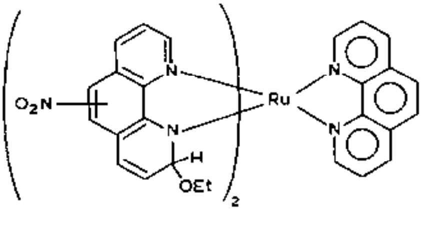


Fig. 19. Circular dichroism spectra in the visible region of Ru(5-NO_2phen)$_3^{2+}$ in 0.01 M aqueous OH^- (——), in 0.05 M aqueous CN^- (······), in 0.001 M methanolic MeO^- (–·–·–), and in 0.001 M ethanolic EtO^- (–·····–····–) solutions. The vertical bar represents the error magnitude. Reprinted with permission from ref. 131.

The reactions of Ru(5-NO_2phen)$_3^{2+}$ with alkoxide ion (MeO^- and EtO^-) have been examined in detail using a variety of spectroscopic techniques, and the diethoxy adduct has been isolated and characterized by C, H, N analyses and by IR spectroscopy [114]. The kinetics were followed [114] by stopped-flow spectrophotometric techniques employing a strong visible light source provided by a Bausch and Lomb high-intensity monochromator. The likelihood of a photochemical reaction under such irradiation source must be queried inasmuch as pseudobases have been reported [145] for excited quaternized pyridine under such conditions, and one must question whether this whole area of covalent hydrates and pseudobase is not in most cases due to photochemical reactions. This notwithstanding, the reactions of Ru(5-NO_2phen)$_3^{2+}$ with MeO^- and EtO^- show UV–visible spectral changes which are reversible not only by addition of dilute acid, but dilution of the reaction mixtures with diethylether affords 100% recovery of [Ru(5-NO_2phen)$_3$]Cl_2 [114]. NMR studies of this complex in deuterated methanol in the presence of d_3-MeO^- were also reported [114]. A striking feature of the NMR spectrum is the complete disappearance of the H(2) proton resonance at 8.96 ppm and the appearance of a new high-field proton signal at 6.48 ppm. This change was attributed to the addition of a MeO^- ion to the 2-position of the 5-NO_2phen ligand, and to the extent that the signals are quantitatively transposed it seems that all three ligands have undergone attack to yield the MeO^- analog of structure (**49**) [114]. Burgess and Prince [106] postulate that, in base, 5-nitrophenanthroline, both as a ligand and as the free base, loses the H(6) proton; however, Gillard et al. [114] find in the present case that the H(6) signal is retained. Also, no deuterium exchange was observed on repeated reversal with acid and base in the reaction with OH^- ions [11,74,122]. The 220 MHz NMR spectra of both Ru(5-NO_2phen)$_3^{2+}$ and Fe(5-NO_2phen)$_3^{2+}$ in dimethylsulfoxide in the presence of excess NaOMe have been reported [89]. Addition of MeO^- to the DMSO solutions of these two complexes reveals a general broadening in the NMR spectra ascribed to the presence of free radicals (ESR) [89], probably a ligand anion radical; a singlet at 6.38 ppm is discernible in the broadened spectrum and is close to that predicted for the H(6) signal in the coordinated Meisenheimer species. The IR spectrum of the proposed diethoxy adduct (**50**) isolated from the



(50)

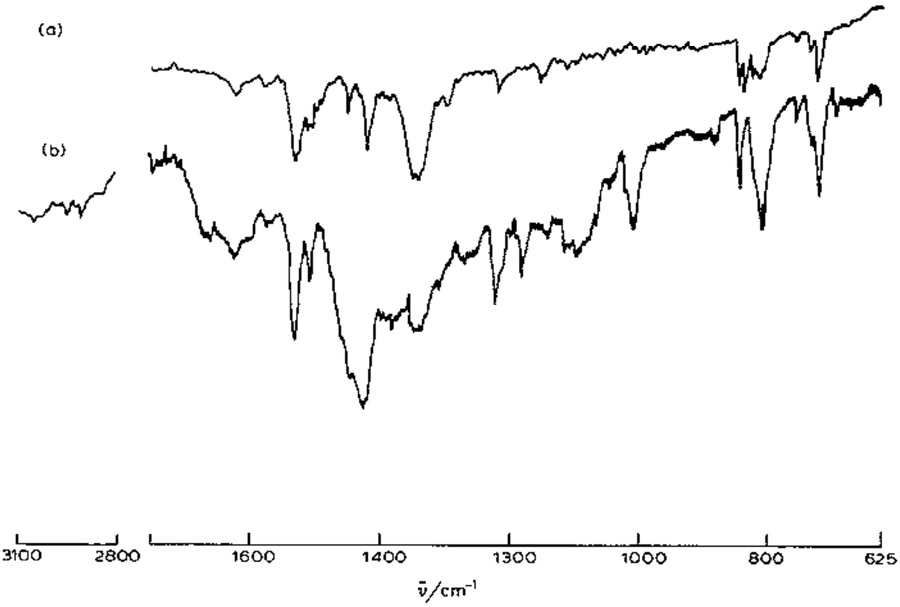


Fig. 20. IR spectra (KBr discs) of (a) $[Ru(5\text{-}NO_2phen)_3]Cl_2 \cdot 6\ H_2O$ and (b) the diethoxy adduct (**50**). Reprinted with permission from ref. 114.

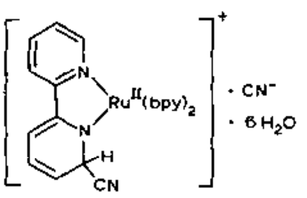
reaction between $Ru(5\text{-}NO_2phen)_3^{2+}$ and EtO^- is illustrated in Fig. 20 and is compared with the spectrum of $[Ru(5\text{-}NO_2phen)_3]Cl_2 \cdot 6\ H_2O$ (in KBr discs) [114]. The nature of this adduct was deduced from the new bands present in the IR spectrum, some of which were assigned to aliphatic C–H and aromatic ether stretching frequencies together with the changes in the aromatic band at ca. 665 cm^{-1}. That these IR spectral observations indicate a reaction between $Ru(5\text{-}NO_2phen)_3^{2+}$ and EtO^- involving attack at the ligand are not convincing; in fact, we see no spectral change at 665 cm^{-1} in Fig. 20.

The kinetics of reaction (55) have been studied;

$$Ru(5\text{-}NO_2phen)_3^{2+} + MeO^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Ru(5\text{-}NO_2phen \cdot MeO)(5\text{-}NO_2phen)_2^+ \quad (55)$$

$k_{obs} = k_1[MeO^-] + k_{-1}$ [114]. For the analogous reaction with EtO^-, $k_{obs} = k_1[EtO^-]$ such that the reverse of reaction (55) is not significant except on addition of diethyl ether [114]. Based on the k_1 rates, the order of nucleophilicity towards $Ru(5\text{-}NO_2phen)_3^{2+}$ decreases in the order $EtO^- > MeO^- \gg OH^- \gg CN^-$ (3.7×10^4: 7.5×10^3: 1.2×10^2 : 1). In contrast, Burgess [146] concludes from his studies on displacement of the $5\text{-}NO_2phen$ ligand in $Fe(5\text{-}NO_2phen)_3^{2+}$ by OH^- and CN^- that attack by the nucleophile occurs at the metal.

The isolation of a number of intermediates found during the reaction of cyanide with $Fe(phen)_3^{2+}$, $Fe(5\text{-}NO_2phen)_3^{2+}$, $Ru(phen)_3^{2+}$ and $Ru(bpy)_3^{2+}$, all of which contain cyanide added to the ligand [147], has been reported. The species with the formulation $Fe(phen)_3(CN)_2 \cdot H_2O$, $Fe(5\text{-}NO_2phen)_3(CN)_2 \cdot 2\ H_2O$, $Ru(phen)_3(CN)_2 \cdot 6\ H_2O$, and $Ru(bpy)_3(CN)_2 \cdot 6\ H_2O$ were investigated by IR spectroscopy as Nujol mulls or as KBr discs. The most prominent feature of the IR spectra is the CN stretching frequencies. The $Ru(bpy)_3(CN)_2 \cdot 6\ H_2O$, $Ru(phen)_3(CN)_2 \cdot 6\ H_2O$, and $Fe(5\text{-}NO_2phen)_3(CN)_2 \cdot 6\ H_2O$ compounds (see **51** and **52**) each have a characteristic ionic cyanide stretching frequency [132] at 2083, 2080 and 2082 cm^{-1}, respectively in Nujol mull [147]. In addition, another CN stretching band is observed at, respectively, 2172, 2170 and 2205 cm^{-1}. That the ligand is indeed involved in the reaction, and that the isolated intermediate species do not have metal-coordinated cyanide groups is evident [147] from the changes in the "fingerprint" regions of the spectra, ca. 700–950 cm^{-1}. In the case of $Fe(phen)_3(CN)_2 \cdot H_2O$, two sharp ionic cyanide stretching frequencies are observed at 2090 and 2082 cm^{-1} (Nujol); in addition, a weak absorption is found at 2183 cm^{-1} (Nujol) and 2184 cm^{-1} (KBr discs) [147]. This species is present predominantly as the dication with two ionic cyanide counter ions, but a small amount of pseudobase is also present [147]. It is significant that the proposed [147] intermediates (**51**) and (**52**) could be isolated only from the most concentrated aqueous cyanide solutions; that is, when equilibria K_1 and K_2 (reaction 56) are driven appreciably to the right. For $Fe(phen)_3^{2+}$,



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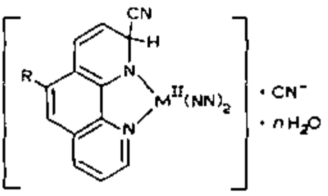


(a) R = H, M = Ru, n = 6
(b) R = NO2, M = Fe, n = 2

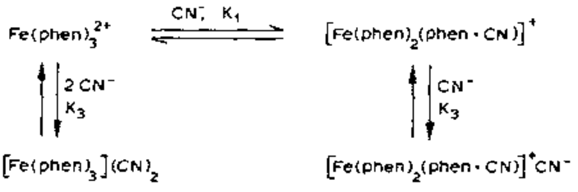
(52)

$$M(NN)_3^{2+} + \overset{CN^-,K_1}{\rightleftharpoons} \{M(NN)_2(NN)\cdot CN)\}^+$$

$$+ \overset{CN^-,K_2}{\rightleftharpoons} [M(NN)_2(NN \cdot CN)]^+CN^- \qquad (56)$$

reaction sequence (57), $K_3 > K_1$ [148]. Obviously, in dilute cyanide solutions, the concentration of species such as (**53**) is very small [147]. Similar equilibria in the reactions [148,149] of $Fe(phen)_3^{3+}$, $Fe(phen)_3^{2+}$, and $Fe(bpy)_3^{3+}$ with OH^- and H_2O were also shown to be small in magnitude (see later).

SCHEME 14

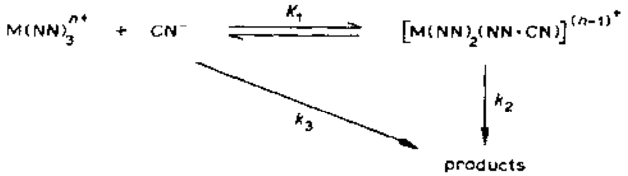


(53)

(57)

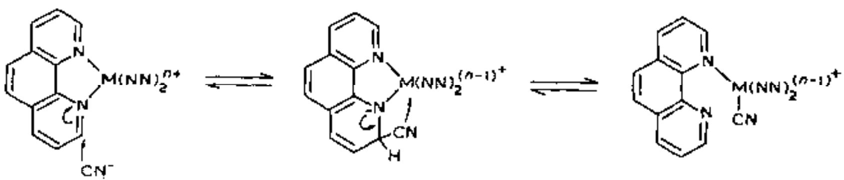
Analogous results were reported for Ni(phen)$_3^{2+}$ [150]. A reaction sequence (58) for attack by CN$^-$ at these and similar species has been proposed [147], for which k_{obs} is given by equation (59); for $K_1[CN^-] \ll 1$, $k_{obs} = k_3 + k'[CN^-]$ where k' is a composite rate constant [148]. It has been suggested [6] that upon attack at the ligand, the nucleophile CN$^-$ is involved in an intramolecular shift as illustrated in the equilibria (60) for a metal–phenanthroline system. While (60) was considered satisfactory for bipyridyl complexes, the rigid structural nature of the phen ligand was thought [147] to render difficult accommodation of the species having monodentate phen; rather, it was proposed that dissociation of the ligand follows reaction (61), or equivalent.

SCHEME 15



(58)

$$k_{obs} = \frac{k_3}{(1 + K_1[CN^-])} + \frac{k_2 K_1 [CN^-]}{(1 + K_1[CN^-])} \qquad (59)$$



(60)

$$M(NN)_2(NN{-}CN)^{(n-1)+} \rightarrow (M(NN)_2(CN))^{(n-1)+} + NN \qquad (61)$$

With regard to pseudobases formed between the cyanide ion and Ru(bpy)$_3^{2+}$ (see above), it is noteworthy that Constable and Seddon [101] found no evidence for reaction of either free bpy or Ru(bpy)$_3^{2+}$ with either sodium hydroxide or sodium methoxide in methanol, water or dimethylsulfoxide, under a wide variety of reaction conditions. However, when Ru(bpy)$_3^{2+}$ reacts with NaOCD$_3$ in (CD$_3$)$_2$SO/CD$_3$OD solution pronounced changes are observed in the ^{1}H NMR spectrum of the complex. Under similar reaction conditions, free bpy is unreactive [101]. The 3,3′-bpy proton signals in Ru(bpy)$_3^{2+}$ occur at lowest field (Fig. 21) but after 24 h at 35°C, these proton signals disappear while the signals for the 5,5′- and 6,6′-protons remain essentially unchanged. These observations indicate that complete exchange of the 3,3′-protons for deuterium occurs. Chemical analysis of the product showed Ru(bpy-3,3′-d_2)$_3^{2+}$ and not Ru(bpy-3,3′-(OCD$_3$)$_2$)$_3^{2+}$. The lability of the H(3) and H(3′) protons towards H–D exchange was interpreted [101] in terms of a decreased pK_a generated as a result of the high steric

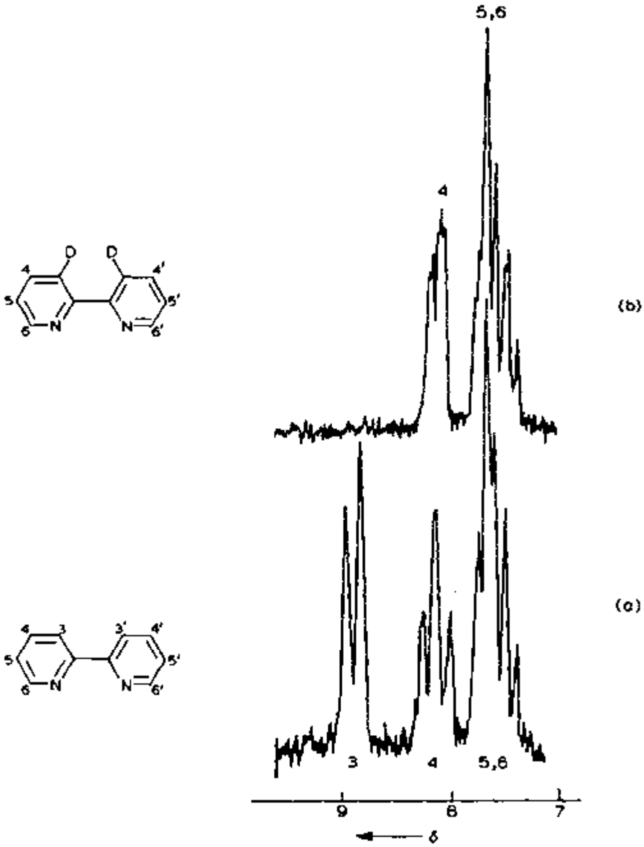


Fig. 21. 60 MHz ^{1}H NMR spectra of Ru(bpy)$_3^{2+}$ in (CD$_3$)$_2$SO (a) immediately after addition of NaOCD$_3$ in CD$_3$OD and (b) 24 hrs later (35°C). Reprinted with permission from ref. 101.

strain [151] on these protons. No other protons undergo H–D exchange. These results were taken [101] as strong evidence in favour of a mechanism involving initial deprotonation of the complex (carbanion), rather than one involving Gillard's [6] pseudobase formation. Of importance, $Ru(phen)_3^{2+}$, which possesses no positions of steric strain, and $Ru(4,4'\text{-}Me_2bpy)_3^{2+}$, in which the 3,3′-positions are shielded to nucleophilic attack by the 4,4′-methyl groups, show no reaction under conditions in which $Ru(bpy)_3^{2+}$ undergoes H–D exchange [101]. Constable and Seddon [101] conclude that the MeO^- nucleophile occupies a special position in $(CH_3)_2SO$ being sufficiently basic to deprotonate the coordinated ligand, but not basic enough to generate significant amounts of the highly reactive [152] $[CH_2SOCH_3]^-$. Reactions

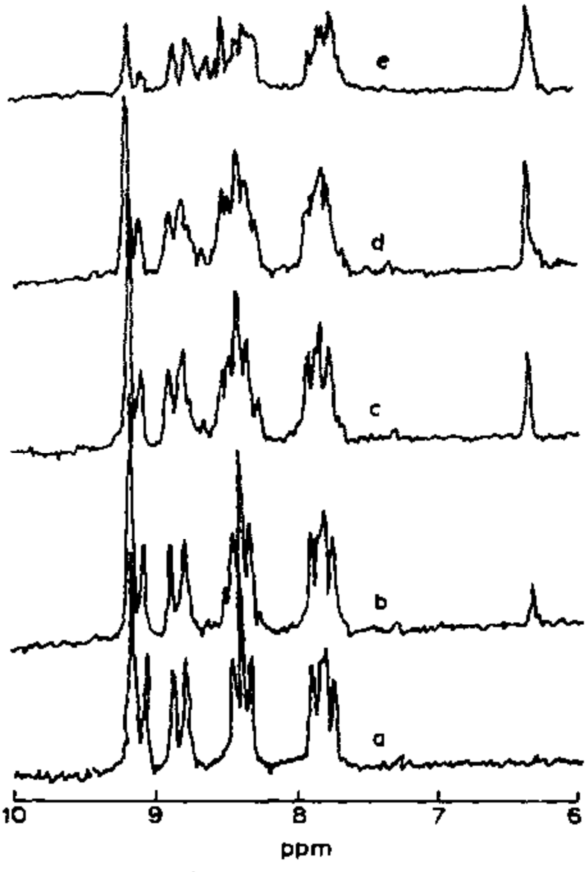
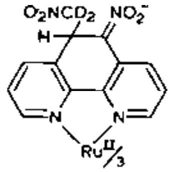


Fig. 22. 90 MHz ^1H NMR spectra of the reaction of $Ru(5\text{-}NO_2phen)_3^{2+}$ in CD_3NO_2/d_5-pyridine (5 : 1, v/v) as a function of time: (a) $t = 0$, (b) $t = 20$ min, (c) $t = 55$ min, (d) $t = 115$ min, (e) $t = 400$ min; temperature = 35°C. For (e) the spectral amplitude is 1/2×. Reprinted with permission from ref. 153.

with the more basic nucleophiles $CH(CH_3)_2O^-$ or $C(CH_3)_3O^-$ in $(CD_3)_2SO$ lead to complete decomposition of $Ru(bpy)_3^{2+}$ owing to the formation of the $[CD_2SOCD_3]^-$ anion [101].

When d_5-pyridine is added to solutions of $Ru(5\text{-}NO_2phen)_3^{2+}$ and $Ru(5\text{-}NO_2phen)(bpy)_2^{2+}$ in d_3-nitromethane solutions, thus generating $CD_2NO_2^-$, addition of the anion to the ligand occurs [153]; this is illustrated in the NMR spectra of Fig. 22 for the former complex. The H(6) proton signal occurs at 9.18 ppm but with time the H(6) singlet is quantitatively replaced by a new upfield singlet at 6.33 ppm [153]. Analogous behaviour was observed for the mixed complex. These observations were interpreted [153] in terms of the presence of species (**54**).



(54)

Variations in the kinetics of attack of OH^- at the ligand in a series of tris-complexes of 5-nitrophenanthroline are shown in Table 6 [154]. For the Co(II), Cu(II) and Ni(II) complexes, the final products of the reaction are the aquated metal ions; however, prior to this reaction an equilibrium step (reaction 62) occurs ascribed [154] to pseudobase formation. The reverse k_{-1}

$$M(5\text{-}NO_2phen)_3^{2+} + OH^- \xrightarrow{k_1} M(5\text{-}NO_2phen)_2(5\text{-}NO_2phen \cdot OH)^+ \qquad (62)$$

step is not important here [154]. Evidently, the variations in k_1 arise from variations in the entropies of activation. Gillard and co-workers [154] noted, "One order of magnitude is almost enough to embrace the rates of all

TABLE 6

Rate constants and activation parameters for pseudobase formation at 25°C and $I = 1.0$ M [a]

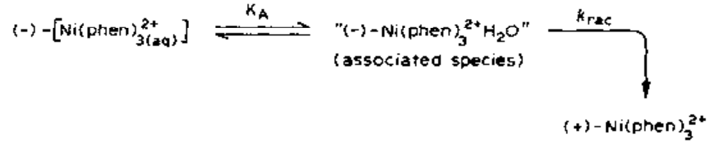
Complex	k_1 ($M^{-1}\ s^{-1}$)	ΔH_1^* (kcal mol^{-1})	ΔS_1^* (e.u.)	ΔG_1^* (kcal mol^{-1}) [c]
$Co(5\text{-}NO_2phen)_3^{2+}$	0.23 (1.0) [b]	9.8	−30.0	18.7
$Ni(5\text{-}NO_2phen)_3^{2+}$	9.75 (3.3) [b]	16.0	−6.5	17.9
$Cu(5\text{-}NO_2phen)_3^{2+}$	1.03 (4.5) [b]	14.9	−10.8	18.1
$Fe(5\text{-}NO_2phen)_3^{2+}$	4.25 (18.5) [b]	16.8	0.8	16.6
$Ru(5\text{-}NO_2phen)_3^{2+}$	1.18 (5.1) [b]	17.4	0.3	17.0

[a] Ref. 154. [b] Normalized rates. [c] Calculated from ΔH_1^* and ΔS_1^*.

complexes at 298 K. It thus appears that variation of the metal in isostruct ural complexes has little effect on rates of reaction.". Contrary to thes conclusions, we wish to point out that the changes in k_1 are significan (albeit small) and would not have been expected if OH^- attacked the ligan in complexes as similar as those of Table 6. Important variations are als noted for $\Delta H_1^{\neq}$ values and most significant for $\Delta S_1^{\neq}$. Changes in the latte parameter were ascribed [154] to the importance of solvation effects. How ever, we fail to understand why in such complexes as related as those liste in Table 6 solvation should be so different, particularly if $\Delta S_1^{\neq}$ refers to th k_1 step of reaction (62) and if attack occurred at the ligand. These variation in $\Delta H_1^{\neq}$ and $\Delta S_1^{\neq}$ probably result from variations in the nature of the meta and would be expected if nucleophilic attack occurred at the metal.

In a study of the racemization reaction of (−)-$[Ni(phen)_3]^{2+}$ in 1,2-dichloroethane containing various amounts of water, Fujiwara and Yamamot [155] suggested that the first step was the rapid formation of a, "(−)-$[Ni(phen)_3]^{2+}$–H_2O associated species" (reaction 63); $K_A = 8$ and $k_{rac} = 1 \times$

SCHEME 16

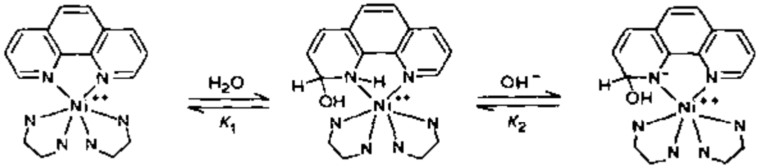


(63)

10^{-6} s^{-1}. It has also been suggested [156] that dissociation (reaction 64) in

$$Ni(phen)_3^{2+} \xrightarrow{H_2O} Ni(phen)_2(H_2O)_2^{2+} + phen \tag{64}$$

aqueous solution involves participation of water. In addition, rates of racemization and dissociation in aqueous solution have been found to be pH dependent as have the analogous rates for $Ni(bpy)_3^{2+}$ [157] and the mixed complexes [158–160] $Ni(bpy)(phen)_2^{2+}$ and $Ni(bpy)_2(phen)^{2+}$. Recently, Gillard and Williams [150] have investigated in detail the pH-dependent racemization of (−)-$Ni(phen)_3^{2+}$. The following observations were made: (1) the intensity of the $\pi \rightarrow \pi^*$ transition in the electronic spectrum diminishes upon changing the solvent from H_2O to 0.25 M H_2SO_4 to dichloroethane; (2) there is a growth of a new band in the spectrum at 365 nm in anhydrous dichloroethane; (3) on acidification of the aqueous solution of (−)-$Ni(phen)_3^{2+}$ there is an accompanying increase in the magnitude of the Cotton effects associated with the long axis polarized $\pi \rightarrow \pi^*$ transition region of the spectrum; (4) there is diminution of the Cotton effects in the "exciton" bands when water is present in solution indicating that the long axis polarized transitions of the phen molecules have been markedly modified; (5) there are changes in the CD spectrum in the visible region arising from the presence of new chiralities in the molecule; (6) there are some differences in the IR spectral region 3000–3400 cm^{-1} and at ca. 1600 cm^{-1}. The spectral observations were attributed [150] to formation of the covalent hydrate (**56**) or pseudobase (**57**) in reaction (65). The comment was also



(55) (56) (57) (65)

made [150], "we have now demonstrated the existence of a covalent hydrate of (−)-$Ni(phen)_3^{2+}$ in aqueous solution and also in water-saturated 1,2-dichloroethane, and the variation of k_{diss} and k_{rac} with pH may be explained by the equilibria established between (**55**), (**56**) and (**57**)." Unfortunately, the above observations are also consistent with the associated species described as a seven-coordinate intermediate species, and thus covalent hydration is not demonstrated. Whatever the nature of the species, k_{rac} and k_{diss} are pH independent in the pH range 0–12; they are suppressed at pH < 0 and enhanced at pH > 12. In very acidic solutions, K_1 favours (**55**) due to the lowering of the activity of water, a_{H_2O} (see also next section). Despite the rationalization [150] for $k_{rac} > k_{diss}$ [159] in terms of covalent hydrate and pseudobase, our suggested seven-coordinated species can easily drive the racemization reaction to its conclusion by twist processes as these require passage through some trigonal prismatic intermediate; such species can also provide a path towards dissociation by weakening metal–nitrogen bonds in the seven-coordinate geometry.

In analogous studies, the rate of racemization of $Fe(phen)_3^{2+}$ has been examined in very acidic aqueous media up to 11.0 M HCl [149]; k_{rac} decreases with increase in $[H^+]$ and reaches a limiting value at a_{H_2O} = ca. 0.5. Basolo and co-workers [161] suggest that decreases in k_{rac} result from decrease in a_{H_2O}. Gillard et al. [149] explain the variations in k_{rac} in terms of a shift in equilibrium between the iron(II) analogs of (**55**) and (**56**) towards the unsolvated (**55**) species.

Striking variations in the redox potentials of several transition metal complexes of polypyridine compounds have been noted by many workers [162]. Schilt [10] attributes these phenomena to ion pair formation. Gillard and Williams [163], on the contrary, taking $Fe(phen)_3^{2+}$ as an example, attribute these changes in redox potentials to the existence of covalently hydrated metal complexes of phen and bpy and their related pseudobases.

NMR spectral changes are observed upon addition of alkali to a neutral aqueous solution of Ru(bpy)$_2$(py)$_2^{2+}$; these changes are reversible on acidification and no loss of pyridine is observed [164]. The spectrum in alkali is typical of a chemically exchanging system, where the equilibrium constant is small, and where the adduct has the hydroxide ion attached at the C(6) carbon of bpy [164]; in this position, the hydroxide could subsequently

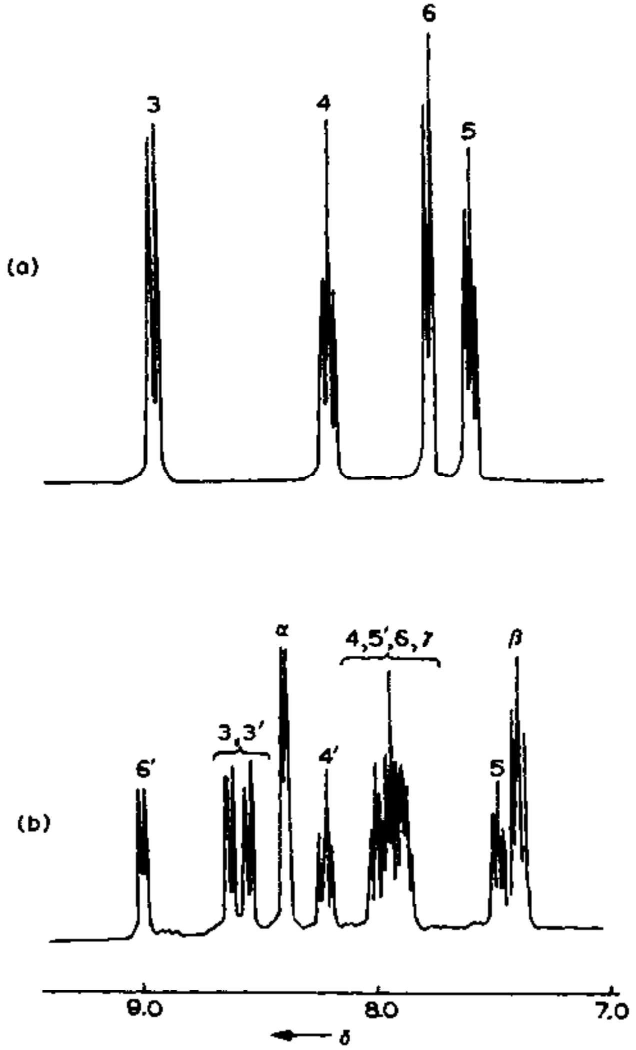


Fig. 23. 300 MHz ^{1}H NMR spectra of (a) Ru(bpy)$_3^{2+}$ and (b) Ru(bpy)$_2$(py)$_2$ in (CD$_3$)SO. In (b) the primed ring is *trans* to bpy, whilst the unprimed ring is trans to py. The α, β, and γ signals are due to H$_{2,6}$, H$_{3,5}$ and H$_4$ protons on pyridine respectively. Reprinted with permission from ref. 101.

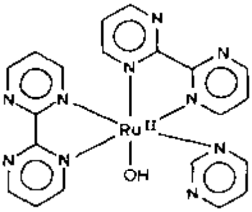
displace a pyridine in a concerted fashion. It was also reported that in *o*-dichlorobenzene, attack by cyanide ion upon $Ru(bpy)_2(py)_2^{2+}$ is rapid and shows second order kinetics [165] suggestive of a Reissert adduct as intermediate. Analogous claims have been made [164] regarding pseudobase formation when aqueous solutions of compounds of the type $Ru(NN)_2(L)_2^{2+}$ (NN = phen, bpy, 5-NO_2phen, or 5,5′-Me_2bpy; L = py or 4-Mepy) are treated with such nucleophiles as OH^-, RO^- and CN^- ions. The 300 MHz ^1H NMR spectrum of a solution of $Ru(bpy)_2(py)_2^{2+}$ in $(CD_3)_2SO$ is illustrated in Fig. 23; the features attributable to the bpy and py ligand were readily identified by comparison with the spectrum of $Ru(bpy)_3^{2+}$ in the same solvent [101]. Contrary to observations by Gillard and Hughes [164], upon addition of NaOD in D_2O to the $(CD_3)_2SO$ solution of $Ru(bpy)_2(py)_2^{2+}$ no significant changes are observed [101] in the ^1H NMR spectrum, and a brown solid slowly separates from solution. Constable and Seddon [101] conclude that any changes which may have been originally observed [164]

$$Ru(bpy)_2(py)_2^{2+} + L' \rightleftharpoons Ru(bpy)_2(py)L'^{2+} + py \qquad (66)$$

could only be attributed to the facile reaction (66), a reaction well documented for $Ru(phen)_2(py)_2^{2+}$ [166].

In an attempt to obtain more detailed information and a better understanding of the reactions of transition metal complexes with phenanthroline and bipyridyl ligands, Gillard et al. [115] investigated species containing more reactive diazine moieties, such as 2,2′-bipyrimidine, 3,3′-bipyridazine, 4,4′-bipyrimidine, 2,2′-bipyrazine, and ferrozine. These free diazines are in some cases known to form covalent hydrates and pseudobases (see Sections B and C). For example, pyrimidines readily add nucleophiles [167,168], especially in the quaternized or condensed state and are sometimes decomposed by subsequent ring opening [169–171]. Quaternized pyrazines and pyridazines also form covalent hydrates and pseudobases in aqueous solution [172]. Reissert reactions [173,174] (with CN^-) and similar nucleophilic additions to mono- and diazines have been studied extensively [175,176]. Insofar as studies [115] on complexes of these diazines may shed light into covalent hydration in metal complexes of diimine ligands, we also review these. It is useful to point out that complexes of these diazines contain an additional position which the nucleophile(s) can attack; this is of course the metal ion.

Reaction of OH^-, N_3^- and SCN^- with iron(II) and ruthenium(II) complexes of 2,2′-bipyrimidine together with the kinetic results for the reaction of $Fe(bipym)_3^{2+}$ with OH^- [115] and with CN^- and N_3^- [116] in aqueous solutions have been reported. No apparent reaction occurs at room temperature during five days when $Ru(bipym)_3^{2+}$ is allowed to stand in aqueous solution containing OH^-, N_3^-, or CN^- [115]. A reaction does occur at higher temperature. NMR evidence reveals that during the reaction between Ru(bipym)$_3^{2+}$ and NaOD in D_2O, one of the bipym ligands is cleaved at the 2-position to give a product (**58**) having a coordinated pyrimidine ring; the liberated pyrimidine undergoes complete hydrolysis. Clearly, attack occurs at the 2-position of the ligand. The iron(II) analogue was found to be kinetically more labile than Ru(bipym)$_3^{2+}$ [115]; however, if less than a stoichiometric amount of NaOD is added to a D_2O solution of Fe(bipym)$_3^{2+}$, dissociation is not immediately observed. The NMR spectra show a broadening of the ligand resonances, which was ascribed to the presence of a rapidly exchanging high-spin intermediate proposed [115] to be the species (**59**). The NMR data do not preclude a fluxional seven-coordinate species, however, and additional evidence is required for the high-spin species proposal. Addition of N_3^- instead of OD^- leads to analogous NMR observations along with an electronic spectral red shift in the visible region [115]. Kinetic studies give $k_{obs} = k_1[OH^-]$ for reaction (67) (k_{-1} was negligible). Where the nucleophiles are CN^- and N_3^- an initial pre-equilibrium (equivalent to 67) was observed [116] with the former nucleophile producing the Schilt compound Fe(bipym)$_2$(CN)$_2$ as the reaction product; $k_{obs} = k_{OH}[OH^-] + k_1[CN^- \text{ or } N_3^-] + k_{-1}$.



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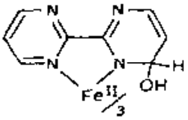

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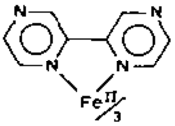
$$\text{Fe(bipym)}_3^{2+} + \text{OH}^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{Fe(bipym)}_2(\text{bipym}\cdot\text{OH})^+ \qquad (67)$$

The reactions of tris(2,2′-bipyrazine)iron(II), Fe(bipyz)$_3^{2+}$ (**60**) and tris[2,2′-bis(5,6-dihydro-4-H-1,3-oxazine]iron(II), Fe(box)$_3^{2+}$ (**61**) ions have also been studied, and the kinetics have been reported [117]. No free bipyrazine could be isolated from an aqueous solution of Fe(bipyz)$_3^{2+}$ (reactions 68 and 69), but in the presence of alkali, both free bipyrazine and $Fe(OH)_3 \cdot n\ H_2O$ form (reactions 70–72) though the yield of free ligand is



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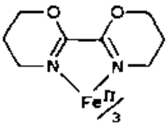

(61)

not quantitative. The interesting possibility remains that the nucleophile

$$\mathrm{Fe(bipyz)_3^{2+} + H_2O \rightleftarrows Fe(bipyz)_2(bipyz \cdot H_2O)^{2+}} \tag{68}$$

$$\mathrm{Fe(bipyz)_2(bipyz \cdot H_2O)^{2+} \xrightarrow{H_2O} Fe(OH)_3 \cdot \mathit{n}\, H_2O + ligand\ dec.\ products} \tag{69}$$

reacts first with the metal leading to dissociation, followed by attack of the

$$\mathrm{Fe(bipyz)_3^{2+} + OH^- \rightleftharpoons Fe(bipyz)_2(bipyz \cdot OH)^{+}} \tag{70}$$

$$\mathrm{Fe(bipyz)_2(bipyz \cdot OH)^{+} \underset{H_2O}{\xrightarrow{OH^-}} Fe(OH)_3 \cdot \mathit{n}\, H_2O + ligand\ dec.\ products} \tag{71}$$

$$\mathrm{Fe(bipyz)_2(bipyz \cdot OH)^{+} \underset{H_2O}{\xrightarrow{OH^-}} Fe(OH)_3 \cdot \mathit{n}\, H_2O + 3\ bipyrazine} \tag{72}$$

nucleophile onto the free ligand to yield the ligand decomposition products.

The anomalous kinetic behaviour of the bipyridazine complex (**62**), Fe(bipyd)$_3^{2+}$, has been investigated by Williams and co-workers [177]. The kinetic

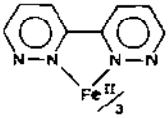

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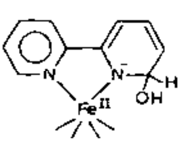
TABLE 7

Kinetic results of some tris-(diimine)iron(II) complexes

Complex	k_{H_2O} (s^{-1})	k_{OH} (M^{-1} s^{-1})
Fe(phen)$_3^{2+}$ [a]	7.1×10^{-5}	6.0×10^{-3}
Fe(bpy)$_3^{2+}$ [b]	1×10^{-4}	2.9×10^{-3}
Fe(bipym)$_3^{2+}$ [c]	Not measured	386
Fe(bipyz)$_3^{2+}$ [d]	4×10^{-3}	328
Fe(bipyd)$_3^{2+}$ [e]	Negligible	3.3×10^{-5}

[a] D.W. Margerum, J. Am. Chem. Soc., 79 (1957) 2728. [b] G. Nord, Acta Chem. Scand., 27 (1973) 743. [c] R.D. Gillard, R.J. Lancashire and P.A. Williams, Transition Met. Chem., 4 (1979) 115. [d] R.D. Gillard, D.W. Knight and P.A. Williams, Transition Met. Chem., 4 (1979) 375. [e] R.D. Gillard, D.W. Knight and P.A. Williams, Transition Met. Chem., 5 (1980) 321.

results of this and related complexes are summarized in Table 7. The second-order rate constant involving the nucleophile OH^- varies by nearly seven orders of magnitude for the complexes listed in Table 7. Direct attack by H_2O or OH^- at the iron(II) centre was considered unlikely [177] on the basis that accessibility of the metal centre is comparable for all these complexes and that variations in rates of dissociation are expected to depend on the differences in the iron–nitrogen bond strengths which, to a first approximation, can be related [177] to the first pK_b values of the free ligands. On the basis of pK_b values alone, the expected order of dissociation is [177]: $Fe(bipyz)_3^{2+}$ > $Fe(bipym)_3^{2+}$ > $Fe(bipyd)_3^{2+}$ > $Fe(bpy)_3^{2+}$ ~ $Fe(phen)_3^{2+}$, which is clearly not the case. Rather, it was suggested [177] that attack at the ligand occurs and that the observed variations in the second order rates can easily be explained by noting that the nucleophile may attack the ligand at different positions (see **63**–**65**) and the OH^--intramolecular shift, k_i, to the metal centre path (reaction 73) is not available to species (**64**) and (**65**). (We doubt that (**65**) has any existence in this case owing to the distortions the ligand would incur.) The inductive effects of the N atoms in the ligands [178], the importance of the k_i path, and the greater reactivity of diazines versus monoazines lead to the observations of Table 7: $Fe(bipym)_3^{2+}$ > $Fe(bipyz)_3^{2+}$ > $Fe(bpy)_3^{2+}$ ~ $Fe(phen)_3^{2+}$ > $Fe(bipyd)_3^{2+}$ [177].



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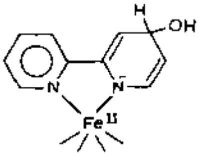

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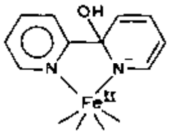

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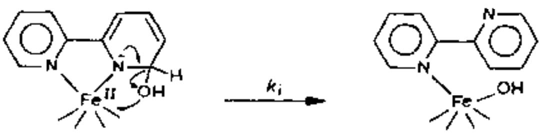

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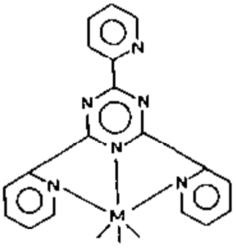
Despite the conclusions of Williams and co-workers [177] and the plausibility of the above arguments, a few points can be raised concerning direct nucleophilic attack at the metal centre. First, use of pK_b values to rationalize trends of bond strengths and thus reactivity of complexes is highly tenuous even to a first approximation. pK_b values refer to reactions such as (74) and

$$B + H^+ \overset{K_b}{\rightleftharpoons} BH^+ \qquad (74)$$

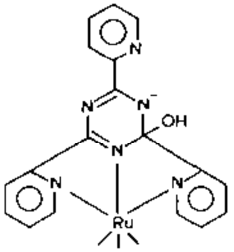
it is well known that these values are very much dependent on solution medium. Also, other factors dictate bond strengths among which are the electronic structures of the metal centres, the availability of vacant π-type orbitals on the ligands and/or metal centre, and, not least, substituents on the ligands. It was noted earlier that N atoms in heterocycles have an inductive effect comparable to a NO_2 group and as such are expected to greatly affect the iron–nitrogen bond strengths in the iron(II) species of Table 7; these bond strengths are not known. While the inductive effects of these N atoms in the 2,2′-bipyrimidine, 2,2′-bipyrazine, and 3,3′-bipyridazine complexes on the charge at the metal centre have not been reported [178] it is expected that the electrophilic character of the metal centre will be increased. We would also expect complexes of iron–diazines to be more reactive towards dissociation than those of the monoazines. The anomalous and very small value of $k_{OH^-} = 3.3 \times 10^{-5}$ M^{-1} s^{-1} for the bipyridazine complex (**60**) can be rationalized by noting that a barrier exists for direct nucleophilic attack of the iron(II) centre; the metal must be accessible to the nucleophile for reaction but the electron pairs in the non-bonded nitrogen atoms of bipyridazine effectively inhibit the reaction with the incoming nucleophiles by closing the so-called interligand pockets. We deduce that direct attack at the metal is also plausible and cannot be precluded by the kinetic data of Table 7.

The kinetics of reactions of hydroxide ion and water with the bis-[2,4,6-tris(2-pyridyl)-1,3,5-triazine], (TPT), complexes (**66**) of Fe(II) and Ru(II) [179,180] and Co(II) and Ni(II) [181] along with the triaquo-mono TPT complexes of Cu(II), Ni(II) and Co(II) [182] have been investigated by Gillard's school. Although $Ru(phen)_3^{2+}$ and $Ru(bpy)_3^{2+}$ are unreactive towards base, $Ru(TPT)_3^{2+}$ undergoes [180] a reversible reaction with aqueous hydroxide ion (UV–visible spectral evidence); at $[OH^-] > 5$ M, complete dissociation of the complex occurs to yield pure, solid TPT quantitatively [180]. NMR spectral results in D_2O and in NaOD—D_2O solutions reveal that (a) the symmetry of the two halves of the TPT ligand is lost, (b) shifts occur in all of the resonance signals, and (c) some broadening of the spectrum also occurs. This was taken [180] to mean that the ligand has been



(66)

attacked by OH^-. However, no new resonance signal is observed in the region ca. 6–6.5 ppm as observed in other complexes such as in the $Ru(5\text{-}NO_2phen)_3^{2+}$—$MeO^-$ (6.48 ppm) [183] system for example (see discussion in this section). Apparently, species (**67**) and/or (**68**) are formed [180],



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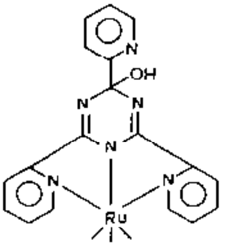

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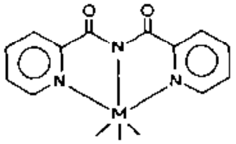

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though not demonstrated; also hydrolysis of TPT is not observed in $Ru(TPT)_2^{2+}$ in contrast to $M(TPT)(OH_2)_3^{2+}$ [M = Cu(II), Co(II), Pd(II) and Pt(II)] which hydrolyze to give [184] the carboximidate complex (**69**). Lerner and Lippard [184–186] have noted that hydrolysis of TPT does not take place with all metals. The kinetics of aquation of $Ru(TPT)_2^{2+}$ and $Fe(TPT)_2^{2+}$ follow the rate law $k_{obs} = k_1[OH^-] + k_{-1}$; for the latter complex k_{-1} is not significant [179]. Nucleophilic OH^- attack at the ligand was suggested [179] despite the lack of hydrolysis of the ligands; Margerum [125,187] on the other hand, suggests that attack occurs at the metal centre. The reactions of $Ni(TPT)_2^{2+}$ and $Co(TPT)_2^{2+}$ with aqueous hydroxide ion involve [182] the formation of pseudobase species prior to dissociation of a ligand molecule; the $M(TPT)(H_2O)_3^{2+}$ and $M(TPT)(OH)_3^-$ species formed react further with hydroxide to yield carboximidate compounds (see below). The kinetics of "pseudobase" formation have been studied [182].

Studies of the reaction of $Cu(TPT)(H_2O)_3^{2+}$ and $Ni(TPT)(H_2O)_3^{2+}$ with water suggest [181] that the formation of covalent hydrates is important in understanding these systems. The $Co(TPT)(OH)_3^-$ compound and its Ni(II) analogue are attacked by OH^- initially to form a pseudobase species and in the case of Ni(II), the ligand hydrolyzes to give a compound related to the carboximidate species formed when OH^- reacts with the Cu(II) analogue [181]. In this case also, the formation of a pseudobase involving attack of OH^- at the triazine ring in the ligand is significant [181]. Of particular interest in this regard, a recent X-ray structural study [188] of the tetrachloroaqua[2,4,6-tris(2-pyridyl)-1,3,5-triazine]dicobalt(II) monohydrate complex was quoted [181] as clearly demonstrating the initial stages of the formation of a covalent hydrate in the solid state based on the fact that the "lattice" water is [188] (a) within the Van der Waals' contact limit of the triazine ring and (b) directly above one of the central C—N bonds; the triazine ring is puckered considerably. It is important to point out that the "lattice" water is associated [188] with the coordinated water molecule (O–O distance 2.59 Å [188]; hydrogen bonding O—H ··· O is 2.72 Å [189]), with two Cl atoms and with the triazine ring; association with the triazine ring may involve hydrogen bonding between the lattice water and the ring nitrogen atoms (O—N distance 2.97 Å [188]; hydrogen bonding O–H ··· N is ca. 2.78 Å [189]), and may have nothing to do with initial stages of covalent hydrate formation. In a recent X-ray crystal structural study, we have observed [36] that the two lattice water molecules in the complex $[Cr(bpy)_2(H_2O)Cl](ClO_4)\cdot 2\ H_2O$ are tightly associated with the bound water (O—O distances, 2.64 and 2.67 Å).

Some of the relevant kinetic and activation data are collected in Table 3 for some of the systems discussed heretofore. Because of the varied experimental conditions used in the kinetic studies, it is difficult to make an overall comparison of the k_1 values. For a bimolecular reaction, the entropy of activation ΔS_1^* is expected to be negative as observed in most cases; for the first order process, ΔS_{-1}^* is expected to be positive as found. Where this expectation was not found, ΔS^* values have been interpreted as anomalous and may indicate that solvation of the transition state is significant in such reactions. The ΔH_1^* values are more revealing. Curiously, for reaction of TPT complexes of Fe(II), Ru(II), Co(II) and Ni(II) with OH^- ions, where experimental conditions were kept constant, ΔH_1^* ranges from ca. 9 to ca. 18 kcal mol^{-1} and ΔS_1^* from ca. −18 to ca. +15 e.u. If nucleophilic attack occurred at the ligand, expectations are that activation parameters be nearly identical. That they are not suggests to us that attack may occur at the metal, despite the implicit contentions [177,190] that differences in these parameters could be attributed to attack at different ligand sites.

(iii) Trivalent transition metal–polypyridine complexes

Reactions of iron(III) and osmium(III) complexes with 1,10-phenanthroline, 2,2′-bipyridine, and methyl substituted derivatives of these have been studied in aqueous solutions by Nord and Wernberg [190]. These trivalent metal complexes are reduced in basic media (reaction 75) with no net ligand

$$4\ M(NN)_3^{3+} + 4\ OH^- \rightarrow 4\ M(NN)_3^{2+} + O_2 + 2\ H_2O \qquad (75)$$

$M = Fe, Os$

dissociation under the experimental conditions used; rate = k_{obs}[complex]

[OH$^-$]. The phen complexes react faster than the corresponding bpy analogs, and iron(III) species react faster than the analogous osmium(III). Accurate enthalpy of activation data indicate that the reduction process does not proceed via reaction (76); $\Delta H^{\neq}$ (see Table 8) values are smaller than ΔH^0 (24.4 ± 3.6 kcal mol^{-1} for bpy and 26.0 ± 3.6 kcal mol^{-1} for phen) calculated for the previously postulated [191] rate-determining step k_1 for this reaction. Consideration of stopped-flow, potentiometric, and NMR data, together with those from pulse radiolysis [192] and chemiluminescence [193] studies for these and similar reactions led Nord and Wernberg to postulate that the first-formed product in reaction (75) is a highly reactive precursor complex and they formulated this as the pseudobase $M(NN)_2(NN \cdot OH)^{2+}$. No D/H exchange occurs when $Fe(phen)_3^{3+}$ is treated with OD^- in D_2O as evidenced from NMR spectra of the reduced product; this is consistent with recent observations [101] on $Ru(phen)_3^{2+}$ by Constable and Seddon. The proposed mechanism [190] is illustrated in the reaction sequence (77), and the relevant kinetic data and activation parameters are collected in Table 8. Interestingly, both $Fe(bpy)_3^{3+}$ [194] and $Os(bpy)_3^{3+}$ [195] are reduced by SCN^- and I^-; $k_{obs} = k_1[\text{nucleophile}] + k_2[\text{nucleophile}]^2$. These nucleophiles form no "pseudobases" and thus another intermediate precursor complex

$$Fe(bpy)_3^{3+} + OH^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Fe(bpy)_3^{2+} + \cdot\ddot{O}H \tag{76}$$

TABLE 8

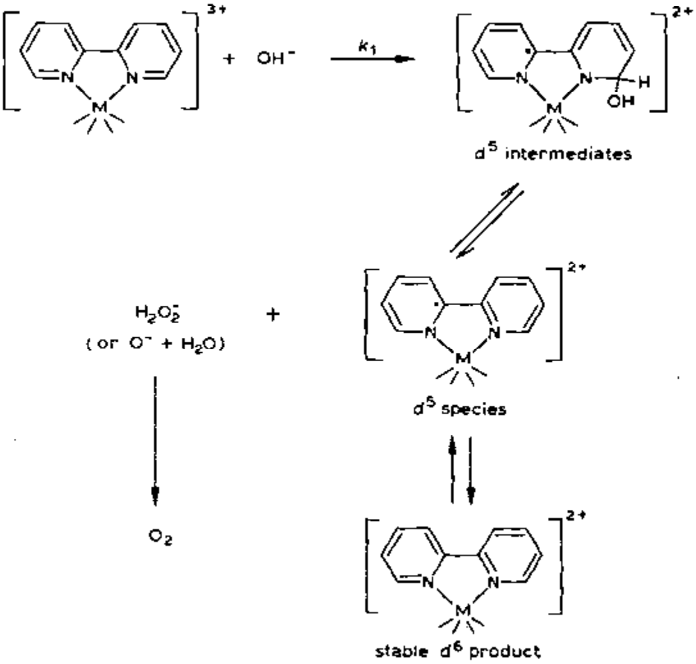
Kinetic data and activation parameters (25°C) for reduction of $M(NN)_3^{3+}$ complexes in basic aqueous media [a]

Complex	k_1 ($M^{-1}\,s^{-1}$)	$\Delta H^{\neq}$ (kcal mol^{-1})	$\Delta S^{\neq}$ (e.u.)	$\Delta G^{\neq}$ (kcal mol^{-1})
$Fe(phen)_3^{3+}$	210 ± 1	11.1 ± 0.2	10.0 ± 0.7	13.83 ± 0.04
$Fe(5\text{-}Mephen)_3^{3+}$	95 ± 1			14.33 ± 0.09
$Fe(5,6\text{-}Me_2phen)_3^{3+}$	58 ± 1	9.1 ± 0.1	18.6 ± 0.5	14.62 ± 0.07
$Fe(4,7\text{-}Me_2phen)_3^{3+}$	17 ± 1	10.3 ± 0.1	17.1 ± 0.5	15.34 ± 0.02
$Fe(3,4,7,8\text{-}Me_4phen)_3^{3+}$	8.5 ± 2.7	15.0 ± 1.9	2.9 ± 0.5	15.76 ± 0.48
$Fe(bpy)_3^{3+}$	7.9	14.9 ± 0.2	4.1 ± 0.7	15.81
$Fe(4,4'\text{-}Me_2bpy)_3^{3+}$	0.8 ± 1.1	12.9 ± 1.4	14.3 ± 4.8	17.15 ± 0.05
$Os(phen)_3^{3+}$	80 ± 1	11.9 ± 1.2	8.4 ± 3.8	14.45 ± 0.05
$Os(5\text{-}Mephen)_3^{3+}$	46 ± 1	8.6 ± 1.0	19.1 ± 3.8	14.76 ± 0.05
$Os(bpy)_3^{3+}$	2 ± 1	15.6 ± 0.4	3.1 ± 4.8	16.53 ± 0.07
$Os(4,4'\text{-}Me_2bpy)_3^{3+}$	0.2 ± 1.1	15.3 ± 0.4	11.0 ± 1.2	18.13 ± 0.07

[a] [OH$^-$] = 0.005 – 0.075M; ionic strength is 1.0 M (NaCl + NaOH); ref. 190.

must be postulated. The possibility of a seven-coordinate intermediate species was also considered but discarded on the grounds that such species have only been reported for spin-free iron(III) and that the increased rates of reduction of the phen complexes over those of bpy complexes would then be inexplicable [190]. This is now a moot point. Seven-coordination is now well established for most of the transition metals (except Rh, Pd, Pt, Ag and Au) [95,196]. Recent studies [197] on outer-sphere complexes between metal polypyridyl complexes and several different anions (e.g. ClO_4, Cl^-, etc....) indicate that tight ion-pairs exist for such species. It is also clear that where the anion is OH^-, tight ion-pairs can also form and reduction of $M(NN)_3^{3+}$

SCHEME 17



(77)

could in principle proceed according to reaction (78). The larger rates of reduction for the phen over the bpy complexes may arise from the greater stability [197] of the phen outer-sphere complexes and the nature of such ion

SCHEME 18

$$\begin{tikzcd} M(NN)_3^{3+} + OH^- \arrow[r, shift left] & \{M(NN)_3^{3+}, OH^-\} \arrow[l, shift left] \arrow[r, shift left] & \{M(NN)_3^{2+}, \cdot OH\} \arrow[l, shift left] \arrow[d] \\ & & \text{reduction products} \end{tikzcd} \qquad (78)$$

pairs within the { } cage. Interaction of the anions with the π-electronic systems in iron–phen and iron–bpy systems tends to favour the phen systems [197]. No pseudobase needs be invoked though it is not precluded by the kinetic data.

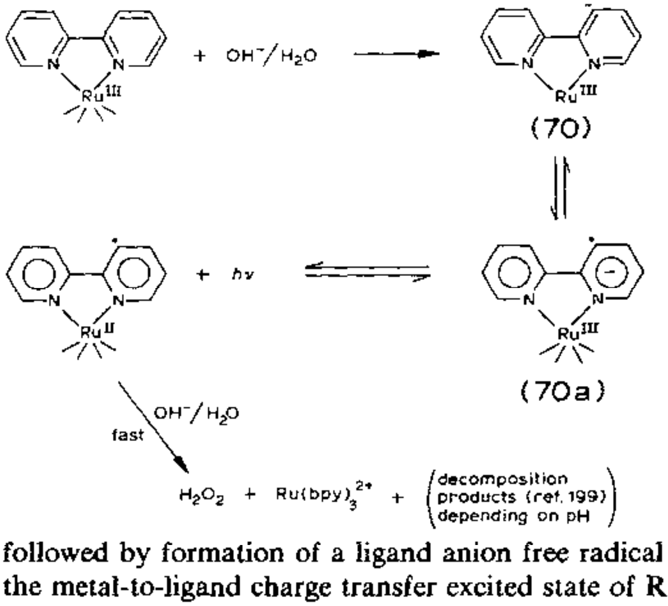
The oxidation of some tris-bpy and tris-phen osmium(II) complexes by Tl(III) in aqueous acid has been reported [198]. In such media $TlOH^{2+}$ also exists; oxidation proceeds according to reactions (79) and (80) where the nature of $Os(NN)_3OH^{2+}$ is

$$Tl^{3+} + Os(NN)_3^{2+} \xrightarrow{k_0} Tl^{2+} + Os(NN)_3^{3+} \tag{79}$$

$$TlOH^{2+} + Os(NN)_3^{2+} \xrightarrow{k_1} Tl^{2+} + Os(NN)_3OH^{2+} \tag{80}$$

described as analogous to the pseudobase species [190] suggested in the above reduction reaction (77). Creutz and Sutin [199] have proposed similar species in the reduction of $Ru(bpy)_3^{3+}$ in neutral and basic aqueous media. In the case of bpy complexes, however, an additional pathway opens up. No doubt the 3,3′ protons in the bpy ligand are much more acidic for $Ru(bpy)_3^{3+}$ than for the corresponding ruthenium(II) complexes (see ref. 101). Thus, even in aqueous media a species like the carbanion (**70**) may form

SCHEME 19



(81)

followed by formation of a ligand anion free radical (**70a**) that is similar to the metal-to-ligand charge transfer excited state of $Ru(bpy)_3^{2+}$.

Pedersen and Nord [200] have recently re-examined the reduction of $Fe(bpy)_3^{3+}$ in basic media in greater detail. From a study of the reaction stoichiometry, they found that O_2 evolution occurs only when $Fe(bpy)_3^{3+}$ is partly dissociated; that is, when the reactant solutions contain OH^- coordinated to Fe(III). Interestingly, when solid $[Fe(bpy)_3](ClO_4)_3$ is dissolved in 0.1 M NaOH, or when $Os(bpy)_3^{3+}$ is the reactant, no O_2 is produced [200]. In the latter case, an osmium species with an oxidation state > 3 was suggested, while in the former an oxidized NN ligand and O_2 are the stable products. Reduction of $Fe(bpy)_3^{3+}$ occurs faster ($t_{1/2} < 1$ s) than the subsequent dissociation and re-oxidation of $Fe(bpy)_3^{2+}$ ($t_{1/2} \geqslant 15$ min) [200]. Two important features emerged from these new studies [200]: (a) the step where the O—O bond is formed involves oxygen atom transfer to an OH^- coordinated to iron(III), and (b) the O_2 evolution reaction "can no longer be used as evidence for the occurrence of reversible nucleophilic attack (pseudobase formation) on coordinated polypyridyl ligands". The possibility that such suggestions also apply to the analogous $Ru(bpy)_3^{3+}/OH^-$ system cannot be overlooked, inasmuch as Creutz and Sutin [199] have also reported such oxidized ligand species.

In this context, Gillard et al. [148,201,202] have studied the dependence of the rate of racemization and dissociation of iron(III)—phenanthroline and —bipyridyl complexes upon "covalent hydrate formation". The generally accepted mechanism [203] (reaction sequence 82) for the dissociation of bipyridyl complexes in aqueous acid predicts that k_{diss} will increase with increased $[H^+]$ and reach a limiting rate as illustrated by eqn. (83), or (84) [137] if the k_{-3} step is also included. Figure 24 depicts the dependence of the rate of dissociation of $Fe(bpy)_3^{3+}$ on $[H_2SO_4]$ or a_{H_2O}; a maximum in k_{diss} is attained at ca. 3 M H_2SO_4 after which the rate of dissociation falls to zero

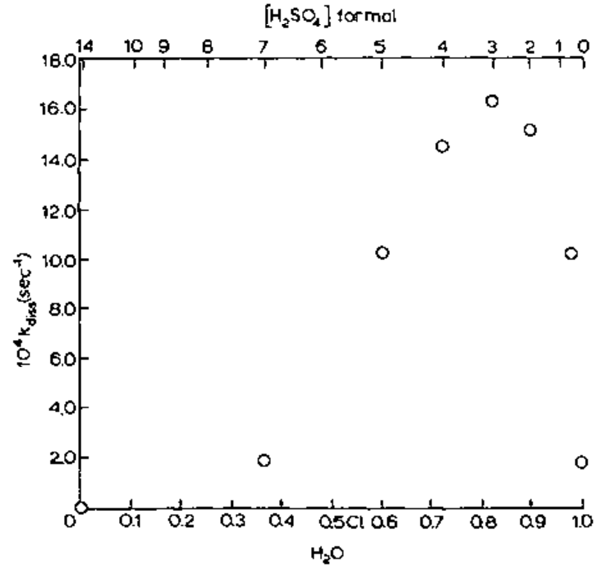
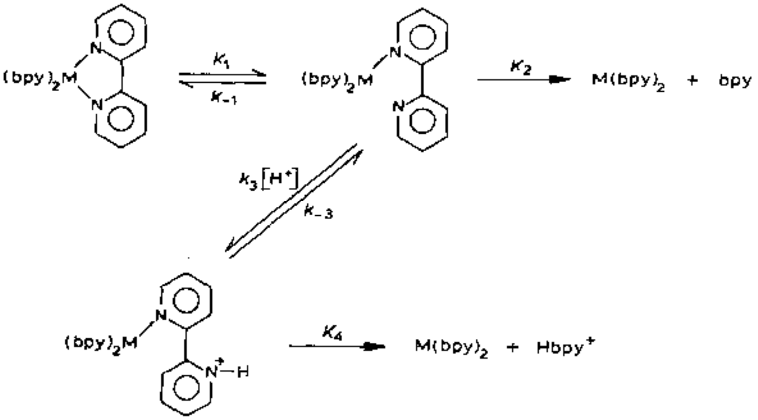


Fig. 24. Rate of dissociation at 31.4°C of $Fe(bpy)_3^{3+}$ as a function of $[H_2SO_4]$ and a_{H_2O}. Reprinted with permission from ref. 148.

with increasing acid concentration [148]. The rate of racemization of optically active $Fe(bpy)_3^{3+}$ is zero in concentrated H_2SO_4 [148].

SCHEME 20



(82)

$$k_{obs} = \frac{k_1(k_2 + k_3[H^+])}{k_{-1} + k_2 + k_3[H^+]} \tag{83}$$

$$k_{obs} = \frac{k_1(k_2 + K_3k_4[H^+])}{k_{-1} + k_2 + K_3k_4[H^+]} \tag{84}$$

In addition, no dissociation of $Ni(bpy)_3^{2+}$ occurs in concentrated H_2SO_4 [204]. These observations were interpreted [201] on the basis that both

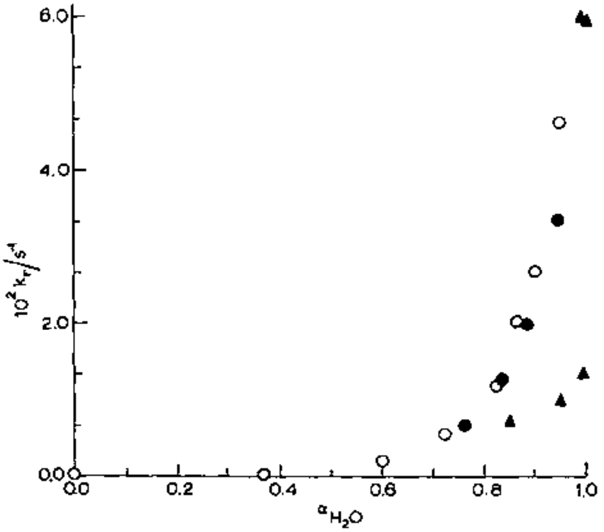


Fig. 25. Racemization of $Fe(phen)_3^{3+}$ in acid solution: ○, H_2SO_4; ●, HNO_3; ▲, HCl. Reprinted with permission from ref. 201.

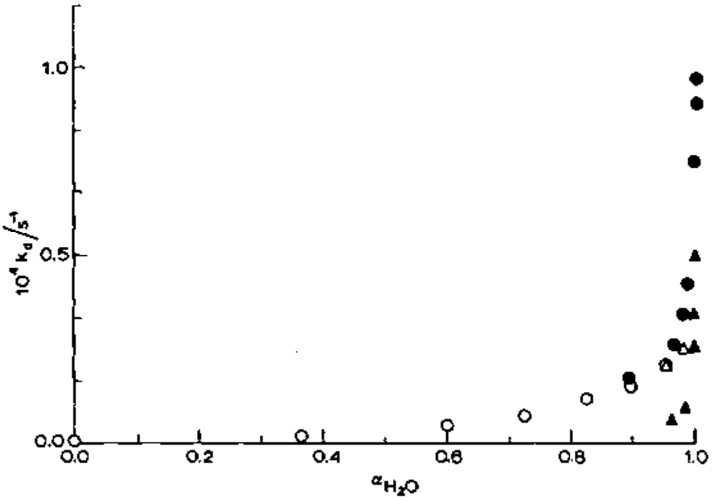
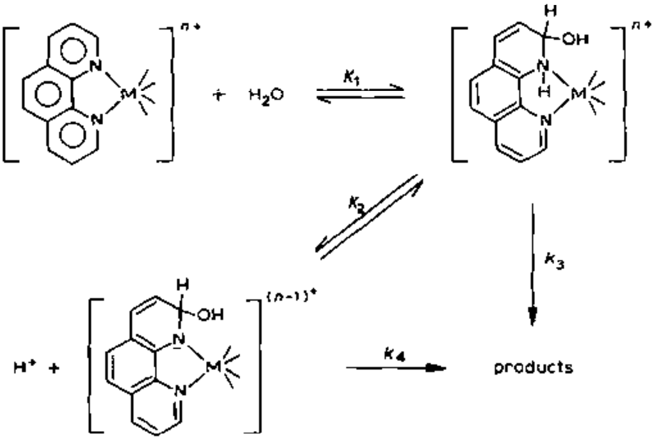


Fig. 26. Dissociation of $Fe(phen)_3^{3+}$ in acid solution: ○, H_2SO_4; Δ, HNO_3; ●, H_2SO_4; ▲, HNO_3. Reprinted with permission from ref. 201.

dissociation and racemization of $Fe(bpy)_3^{3+}$ is preceded by formation of a covalent hydrate species $Fe(bpy)_2(bpy \cdot H_2O)^{3+}$. The dependences of the rates of racemization and dissociation of $Fe(phen)_3^{3+}$ on the activity of water, a_{H_2O}, are shown in Figs. 25 and 26, respectively [201]. It is clear that both k_{rac} and k_{diss} decrease to zero in concentrated acid. In this case also, the observations were treated employing covalent hydrates as in the reaction

SCHEME 21



(85)

where

$$k_{\mathrm{obs}} = \frac{k_3K_1[\mathrm{H_2O}] + k_4K_1K_2[\mathrm{H_2O}][\mathrm{H^+}]^{-1}}{1 + K_1[\mathrm{H_2O}] + K_1K_2[\mathrm{H_2O}][\mathrm{H^+}]^{-1}} \tag{86}$$

sequence (85); the pseudobase species is more reactive than the covalent hydrate [201]. Kinetically, all of the above observations can also be rationalized through a species in which water attacks the metal centre directly. Here also, in concentrated acid solutions, where $a_{\mathrm{H_2O}} = 0$, the rates of dissociation and racemization are expected to fall to zero.

The kinetics of reaction of the tris(5-X-1,10-phenanthroline)iron(III) cations (X = Br or Cl) have been investigated in detail in 0–100% sulphuric acid solutions [202]. Relationships between the rates of reactions and the activity of water were examined; no net dissociation reaction is observed without water present, that is when $a_{\mathrm{H_2O}} = 0$ [202]. The dissociation rate/activity of water profile parallels those depicted in Figs. 25 and 26 for $\mathrm{Fe(phen)_3^{3+}}$. The reactions have been interpreted [202] in terms of covalent hydrate and pseudobase formation. Evidence supportive [202] of this conclusion is collected in Table 9 which summarizes observed rate constants (k_{obs}) for acid aquation of iron(II) and iron(III) tris-complexes of substituted

TABLE 9

Observed first-order rate constants for acid aquation of iron(II) and iron(III) tris complexes of substituted phenanthrolines together with second order rate constants for nucleophilic attack at the iron(II) complexes for comparison [a]

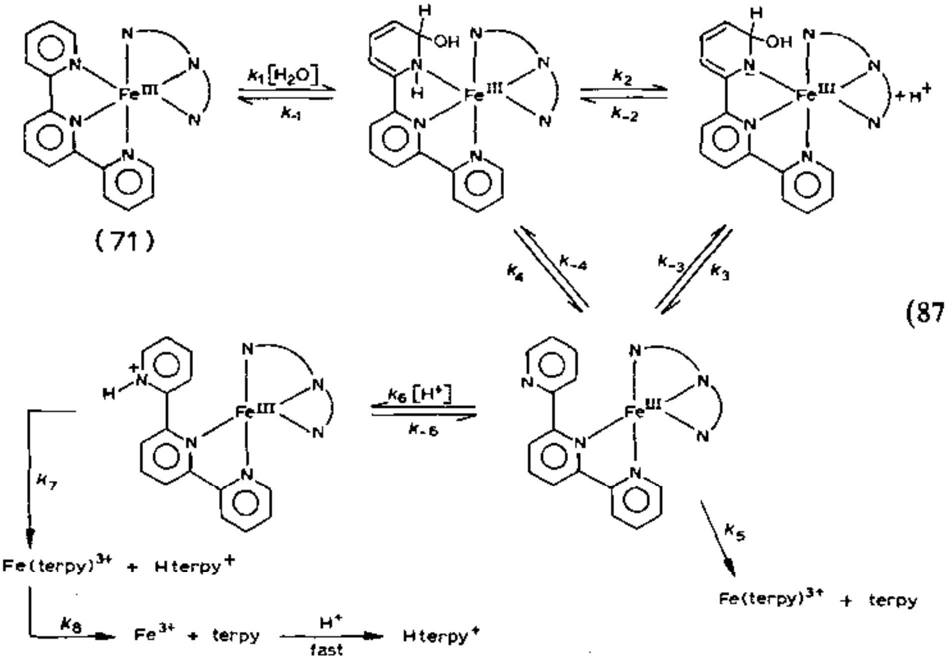
Substituent	Iron(II) 10^4k_{obs} ($\mathrm{s^{-1}}$)	Iron(III) 10^4k_{obs} ($\mathrm{s^{-1}}$)	Iron(II) $k_2[\mathrm{OH^-}]$ ($\mathrm{M^{-1}\,s^{-1}}$)	Iron(II) $k_2[\mathrm{CN^-}]$ ($\mathrm{M^{-1}\,s^{-1}}$)
5-Me-6-$\mathrm{NO_2}$	32		0.38	
5-$\mathrm{NO_2}$	23	200	0.29	0.51
4,7-$\mathrm{(OH)_2}$	17		Stable	
3-$\mathrm{SO_3^-}$			0.20	0.042
5-Br		20.9		
5-Cl	12	22 (16.8)	0.18	0.10
5-$\mathrm{SO_3^-}$			0.066	0.017
5-Ph	4.0		0.018	
(None)	3.8	1.2	0.039	0.034
5-Me	1.9		0.015	0.016
4,7-$\mathrm{Me_2}$	1.1	0.13	0.0029	0.006
3,4,7,8-$\mathrm{Me_4}$	5.7		0.0023	0.007
5,6-$\mathrm{Me_2}$	0.6		0.0021	0.0042

[a] Ref. 202.

phenanthrolines together with second-order rate constants (k_2[OH$^-$] and k_2[CN$^-$]) for nucleophilic attack at the iron(II) complexes for comparison [202]. These data were suggested [202] to demonstrate that the processes of covalent hydration and pseudobase formation in substituted phenanthroline complexes are dependent upon the nature of the substituent; in general, the more electron-withdrawing the substituent, the more favoured the process. Unfortunately also, the electrophilicity of the iron(II) or iron(III) metal centre and thus dependences of rates for direct attack at the metal core is expected to vary in the same direction as those noted in Table 9. Besides the electron-withdrawing or -donating factor of the substituents, an additional factor that decreases the rates of dissociation for these iron complexes, in the case of the methylated phen species, is the ability of these methyl groups to partially block the interligand pockets, thus inhibiting direct attack (see discussion below on the analogous chromium(III) complexes).

For the iron(III)—terpyridyl cation (**71**), the dissociation reaction profile in acid media closely resembles that observed for the dissociation of $\mathrm{Fe(bpy)_3^{2+}}$ [148] in aqueous H_2SO_4 and parallels that of $\mathrm{Fe(phen)_3^{3+}}$ [201] (Fig. 26) in that there is no observable reaction when $a_{\mathrm{H_2O}} = 0$ [205]. Burgess and Twigg [206] have interpreted their dissociation kinetic data (to ca. 7 M H_2SO_4) of $\mathrm{Fe(terpy)_2^{2+}}$ (terpy = 2,2′,2″-terpyridine) in terms of successive Fe—N bond rupture. In the corresponding iron(III) species, Gillard and

SCHEME 22



(87)

where

$$k_{\text{obs}}=\frac{\left(K_1k_4a_{\text{H}_2\text{O}}+K_1K_2k_3a_{\text{H}_2\text{O}}/[\text{H}^+]\right)\left(k_5+k_6[\text{H}^+]\right)}{\left(1+K_1a_{\text{H}_2\text{O}}+K_1K_2a_{\text{H}_2\text{O}}/[\text{H}^+]\right)\left(k_3+k_{-4}+k_5+k_6[\text{H}^+]\right)} \tag{88}$$

and

$K_1=k_1/k_{-1}$; $K_2=k_2/k_{-2}$

co-workers [205] begin the dissociation process (reaction sequence 87) with covalent hydrate and pseudobase formation at the C-6 position of the terpyridyl ligand followed by bond rupture to explain the dependence of the dissociation rate on the activity of water in H_2SO_4 media (range $0 < a_{H_2O} < 1$ or 12 M $\geqslant [H_2SO_4] \geqslant 0$ M). That k_{obs} is 0 when a_{H_2O} is 0 was taken [205] as evidence that water is an essential ingredient in the dissociation kinetics in the iron polypyridyl species. While this is true, we wish to point out, however, that an associative pathway, where the nucleophile H_2O attacks the metal directly, is kinetically indistinguishable from the path involving covalent hydrate formation. It needs to be emphasized also that the importance of water proves neither of these two mechanisms. Relevant to this discussion are Van Meter and Neumann's dissociation and racemization studies [129] on $Fe(phen)_3^{2+}$ in various solvents. It was shown that the order of dissociation rates in pure solvent is: DMF > formamide > H_2O > CH_3OH > acetone > CH_3CN > CH_3COOH; for DMF, formamide, CH_3OH and acetone, the rates vary in the same order as the solvent's ability to act as a ligand [129]. Hence it is not surprising that no observable dissociation reaction occurs when $a_{H_2O}=0$ for the iron(III)–terpyridyl complex. Gillard et al. [202] also stated, "the configurational strain of the ligand in $Fe(terpy)_2^{3+}$ may well indeed favour covalent hydration of the ligand and for this complex the concentration in solution of such species may be larger than is the case with complexes of substituted phenanthrolines". In the corresponding chromium(III)–terpyridyl cation, our crystal structural studies [34,37] reveal that the lattice water molecule in $[Cr(terpy)_2](ClO_4)_3 \cdot H_2O$ is nowhere near a carbon atom that might be construed as "the initial stages of covalent hydration". Rather, the chromium(III) core is exposed to solvent molecules in solution and we suggested [37] that Cr(III) can be regarded as being essentially hydrated in aqueous solutions. Similar conclusions were reached [207] for $Fe(phen)_3^{2+}$ from apparent molar volumes studies in such solvents as formamide, DMSO and DMF; these solvent molecules can occupy the space between the phen ligands in much the same way that ClO_4^- ions do in solids.

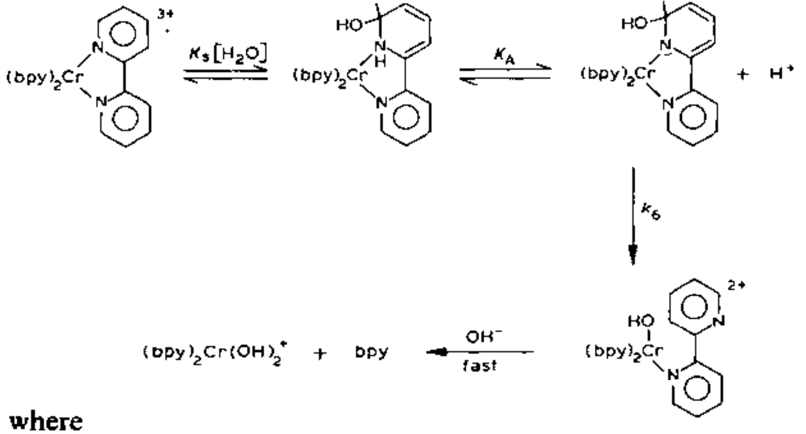
The reactions of $Ru(bpy)_3^{3+}$, $Ru(phen)_3^{3+}$ and $Ru(bpy)_2(CN)_2$ in aqueous solution have been followed; neither $Ru(bpy)_3^{3+}$ nor $Ru(phen)_3^{3+}$ racemizes or dissociates in aqueous solutions [208]. The CN groups in $Ru(bpy)_2(CN)_2$ react in aqueous solution to yield $Ru(bpy)_2(H_2O)_2^{3+}$. Orange solutions of $Ru(bpy)_3^{2+}$ are oxidized by Ce(IV) or Cl_2 to yield green solutions of the Ru(III) species, which gives a purple solution if maintained under Cl_2. In 100% H_2SO_4 the change to a purple compound does not occur [208], but where $a_{H_2O} \neq 0$ and under a Cl_2 atmosphere, a purple compound was isolated with the formulation $Ru(bpy)_3(ClO_4)_3 \cdot H_2O$. Electronic and circular dichroism spectral evidence, along with IR data reveal [208] that the compound does not contain the six-coordinate $Ru(bpy)_3^{3+}$ cation. Dissolution of this purple product in water gives an orange solution for which the ^1H NMR spectrum indicates that it corresponds to an authentic sample of $Ru(bpy)_3^{2+}$ [208]. However, in CF_3CO_2D the purple compound has a distinct NMR spectrum. Indeed, the purple product is equivalent to neither $Ru(bpy)_3^{3+}$ nor $Ru(bpy)_3^{2+}$ but is derived from the former and easily reacts under very mild conditions to give the latter. Two stereochemistries were considered for the purple species [208]: one involving a structure containing a unidentate bpy ligand, analogous to the one suggested for an iridium(III) compound [209] (see below for a discussion on such a compound) and to those proposed [210,211] in reactions involving $Ru(bpy)_3^{2+}$ for which attempts to isolate the species proved unsuccessful [210,212]. This is not surprising in view of our recent X-ray crystal structure study [35] on the iridium(III) species. The second structure for $Ru(bpy)_3(ClO_4)_3 \cdot H_2O$ was proposed to be a covalent hydrate; in this case, it is difficult to understand why the covalent hydrate should be stable in neat CF_3CO_2D solution [208]. However, inasmuch as the compound yields green $Ru(bpy)_3^{3+}$ quantitatively in concentrated H_2SO_4, it would seem impossible for the purple complex to contain unidentate bpy since it would be unable to re-coordinate to ruthenium [208]. These observations must be re-interpreted in the light of our recent work [35] where it was shown that the metal is coordinated to a carbon atom of the bpy ligand. Similar reactions were reported [208] for the ruthenium–phenanthroline complex but the change in color from the green $Ru(phen)_3^{3+}$ to the purple species occurs faster than for the bpy analogue. Because phen cannot form unidentate complexes (and this is not certain), Gillard and co-workers [208] interpret their findings as strong evidence for the covalent hydrate formulation.

Several years ago (ca. 1974–75) we began systematic studies of the photochemical behaviour of $Cr(bpy)_3^{3+}$, inasmuch as this and related phenanthroline complexes luminesce and are photochemically active [1]. Since then, these complexes have afforded novel insights into excited state reactivity under a wide variety of conditions. As part of such studies, we also undertook detailed studies of the ground state species [32]. The kinetics of ligand substitution reaction of $Cr(bpy)_3^{3+}$ were investigated [32] in aqueous solutions at constant ionic strength (1.0 M NaCl) in the pH range 0–10.7; the solvolysis reaction is base- but not acid-catalyzed. At $\mathrm{pH} > 9$, the reaction is

$$\mathrm{Cr(bpy)_3^{3+}} + 2\,\mathrm{OH^-} \xrightarrow{k_{\mathrm{obs}}} \mathrm{Cr(bpy)_2(OH)_2^+} + \mathrm{bpy} \tag{89}$$

$k_{\mathrm{obs}} = [\mathrm{OH^-}]/(B + A[\mathrm{OH^-}])$ where B and A denote a composite of micro-rate constants depending on the proposed mechanism. Several pathways were considered [32] among which are a dissociative mechanism, an associative mechanism, Gillard's covalent hydrate mechanism [6] and an ion-pair (interchange) mechanism; all of these are consistent with the observed expression for k_{obs} above. To the extent that the dissociative mechanism predicts acid catalysis which was not observed, it was discarded, along with the ion-pair pathway since this pathway gives a K_{ip} of ca. $3 \times 10^6\ \mathrm{M^{-1}}$, too high [213] for ion pairs between $+3$ and -1 ions. The kinetic data alone do not distinguish between the Gillard [6] and the associative [214] pathway. The former was thought unlikely [32] for three reasons: (a) the data require that the concentration of the conjugate base, $\mathrm{Cr(bpy)_2(bpy \cdot OH)^{2+}}$, of reaction sequence (90) be $< 1\%$ at $\mathrm{pH} \leqslant 4$ and $> 99\%$ at $\mathrm{pH} \geqslant 9$; (b) no absorption or emission spectral changes are observed with changes in pH; and (c) from equation (91) the calculated $\mathrm{p}K_{\mathrm{a}} \leqslant -6.4$ in contrast to the estimated value [6] of 0. The more plausible associative pathway is described by the sequence (92) where the only criticism that could be made regards the seven-coordinate geometry of the chromium(III) intermediate. We have already commented earlier about the existence of many seven-coordinate

SCHEME 23

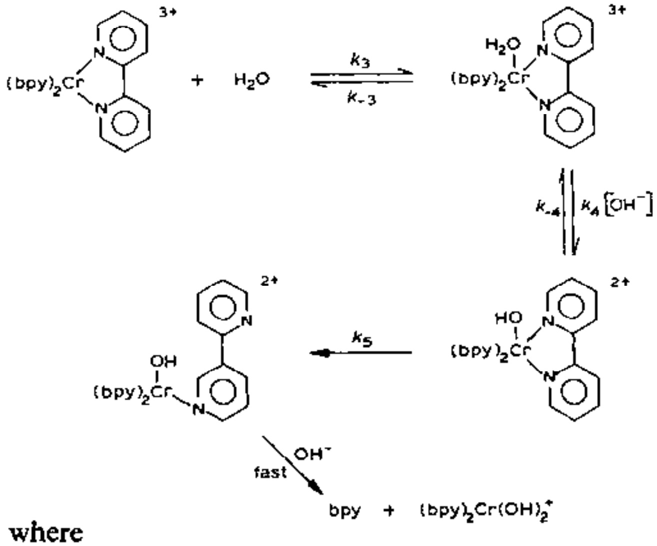


(90)

where

$$k_{\mathrm{obs}} = \frac{k_6 K_{\mathrm{S}} K_{\mathrm{A}} [\mathrm{OH^-}]}{(1 + K_{\mathrm{S}}) + K_{\mathrm{S}} K_{\mathrm{A}} [\mathrm{OH^-}]} \tag{91}$$

SCHEME 24



(92)

where

$$k_{\text{obs}} = \frac{k'_3 k_5 k_4[\text{OH}^-]}{k_{-3}(k_5 + k'_{-4}) + k_5 k_4[\text{OH}^-]} \tag{93}$$

and

$$k'_i = k_i[\text{H}_2\text{O}]$$

complexes of transition metal ions [95,196].

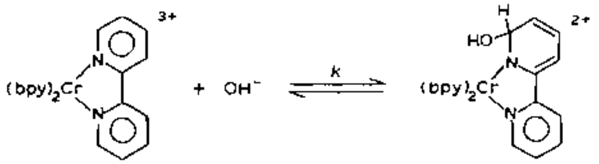
In a comprehensive photochemical and photophysical study of Cr(bpy)$_3^{3+}$ in aqueous solutions, Maestri et al. [38] have noted that the functional dependence of the photoaquation quantum yield on pH is identical to that observed [32] for the rate constant of the thermal aquation reaction (89). Both the thermal and the photochemical reactions involve a common ground-state intermediate with acid-base properties, also described as a seven-coordinate Cr(bpy)$_3$(H$_2$O)$^{3+}$ species generated via an associative mechanism with ground or excited (^2E)Cr(bpy)$_3^{3+}$ [38].

Studies on the base-catalyzed thermal aquation reaction of Cr(bpy)$_3^{3+}$ were extended to include the pH range 10.7–14 [215]. In the pH region 6–14, the pseudo first order rate constant k_{obs} is dependent on hydroxide concentration according to the expression (94), where A, B, C, and D represent

$$k_{\text{obs}} = \frac{[\text{OH}^-]}{(B + A[\text{OH}^-])} + C[\text{OH}^-] + D[\text{OH}^-]^2 \tag{94}$$

composites of micro rate constants. The first order term in [OH$^-$] in equation (94) involves [215] direct attack by the OH$^-$ ion onto Cr(III), while the D[OH$^-$]^2 term is attributed to OH$^-$ attack upon the ion pair {Cr(bpy)$_3^{3+}$,

OH^-). The available data [215] did not afford an unequivocal delineation between direct nucleophilic attack at the metal and Gillard's [6] pseudobase mechanism. However, arguments were presented to show that the latter pathway is unlikely [215]. It was noted for example that the rate constant equivalent to k of reaction (95) has been identified by Nord and Wernberg [190] as the rate-determining step in the OH^- reduction of $Fe(bpy)_3^{3+}$ and $Os(bpy)_3^{3+}$ with $k = 8$ and $2\ M^{-1}\ s^{-1}$, respectively. The rate constant for the first-order dependence of k_{obs} on $[OH^-]$ in the aquation of $Cr(bpy)_3^{3+}$ is ca. $10^{-3}\ M^{-1}\ s^{-1}$. To the extent that this complex is nearly identical to $Fe(bpy)_3^{3+}$ (charge, size) it is difficult to explain why the rate constants differ by as much as 4 orders of magnitude if the same pseudobase is formed in the initial step of the reduction of $Fe(bpy)_3^{3+}$ (see earlier discussion on this complex) and of the aquation of $Cr(bpy)_3^{3+}$. In addition, no spectral variations in $Cr(bpy)_3^{3+}$ solutions are initially observed, even in very alkaline solution ($[OH^-] = 0.50$ M) as would have been expected if the pseudobase $Cr(bpy)_2(bpy \cdot OH)^{2+}$ were the intermediate in the aquation reaction. Also, hydroxide ion quenches the phosphorescence from $(^2E)Cr(bpy)_3^{3+}$ via a mechanism which probably involves the seven-coordinate species $Cr(bpy)_3(OH)^{2+}$ [38]; the hydroxide ion is a non-innocent quencher [216]. Finally, it is worth noting that OH^- ions quench the phosphorescence from $(^2E)Cr(en)_2(NCS)_2^+$ apparently also via the formation of a seven-coordinate intermediate since no Gillard-type covalent hydrate or pseudobase is possible for this species [216]. The photoaquation of $Cr(bpy)_3^{3+}$ ion in acidic aqueous solution has been studied and it appears that the same seven-coordinate species $Cr(bpy)_3(H_2O)^{3+}$ is involved [217]. A pertinent IR study of the structure of $Cr(bpy)_3^{3+}$ and $Ru(bpy)_3^{2+}$ species adsorbed in the interlamellar space of hectorite reveals that an extensive covalent (hydrate) modification of the bpy ligands even in these adsorbed complexes is unlikely [218].



(95)

The nature of the compound(s) containing three 2,2′-bipyridine per iridium atom has been the subject of a controversial debate [40,41,219–221] since the first report by Flynn and Demas [222] of the successful preparation of the $Ir(bpy)_3^{3+}$ cation. This species was formulated to have all three bipyridine ligands ligated to iridium(III) via the nitrogen atoms as demonstrated by ^{13}C NMR spectroscopy (D_3 symmetry; five well resolved ^{13}C resonances (see Fig. 27)) [222]. Later, Watts et al. [40] identified another complex also

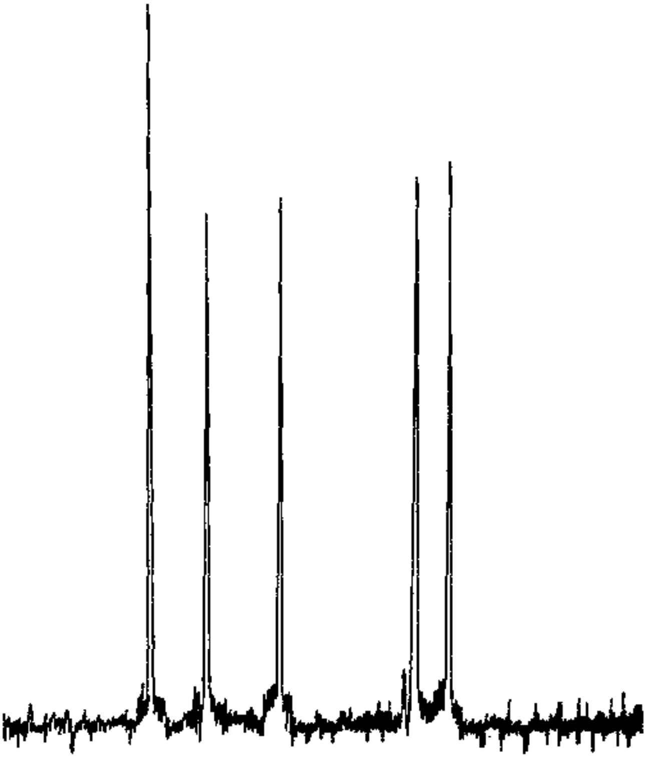
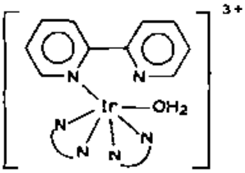


Fig. 27. ^{13}C NMR spectrum of $[Ir(bpy)_3](NO_3)_3$ in H_2O-D_2O. Chemical shifts starting at left are: −89.46, −83.77, −76.69, −63.34, −60.04 ppm relative to internal dioxane standard. No additional peaks occur above the noise level from − −110 to +90 ppm. Reprinted with permission from ref. 222.

containing three bipyridine ligands per iridium but having distinct absorption and emission spectral properties as well as different photophysical characteristics from $Ir(bpy)_3^{3+}$. This other complex was described [40], on the basis of the data below, as comprised of iridium, two bidentate bpy ligands, one water molecule, and one monodentate bpy′, $Ir(bpy)_2(H_2O)(bpy')^{3+}$, **(72)**



(72)

which can be converted to the hydroxo form and isolated by treatment with base. UV–visible absorption spectra in 0.1 M acid solutions show intense bands at 250, 305 and 315 nm characteristic of 2,2′-bipyridine when complexed to a metal centre; at the longer wavelength region, (**72**) shows shoulders at 360, 448 and 470 nm [40]. For the hydroxo species, the spectra reveal no 470 nm feature. The luminescent states of the compound with the monodentate bpy arise [223] primarily from interligand $\pi-\pi^*$ transitions of the bpy ligands, and some mixing with charge transfer from iridium(III) to bpy was noted. Such MLCT contribution to the emitting state of (**72**) should decrease the electron density at the coordinated water oxygen of $Ir(bpy)_2(H_2O)(bpy')^{3+}$, leading to an enhancement of proton ionization from this oxygen site [41]. The pk_a of the ground state of (**72**) is 3.0 ± 0.1 [40] while the pK_a^* (see Fig. 28) for the emitting state is 3.5 ± 0.1 [41]. This observed suppression of acid dissociation in the luminescent excited state indicates that the proton is bonded to the nitrogen of the "monodentate bpy" (but see below) which would have enhanced electron density due to the MLCT contribution to its character [41]. No evidence was found for formation of the protonated $Ir(bpy)_2(H_2O)(Hbipy)^{4+}$ complex at pH as low as 0 [40]. The emission of the complex blue shifts when it is converted from the aquo to the hydroxo form in contrast to the large red shifts observed in the emission of $Ir(bpy)_2Cl(H_2O)^{2+}$ and $Ir(bpy)_2(H_2O)_2^{3+}$ when converted to the corresponding hydroxo species [40]. The luminescence lifetime and the

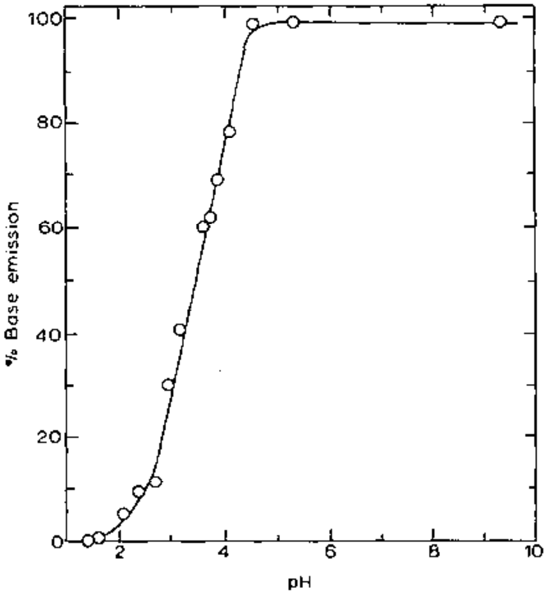
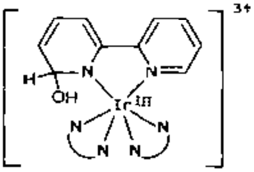


Fig. 28. Luminescence titration of $Ir(bpy)_2(H_2O)(bpy')^{3+}$. Reprinted with permission from ref. 41.

related emission quantum yield of the emitting excited state of $Ir(bpy)_2(H_2O)(bpy')^{3+}$ and $Ir(bpy)_2(OH)(bpy')^{2+}$ at room temperature in H_2O solutions (0.1 M H^+ or 0.1 M OH^-) are, respectively, 12.2 ± 0.2 and 0.30 ± 0.01 μs, and 10.0 ± 0.2 and 0.35 ± 0.01 μs; in D_2O solutions, the corresponding values are, respectively, 14.7 ± 0.2 and 0.35 ± 0.01 μs, and 11.6 ± 0.3 and 0.04 ± 0.02 μs [40]. The complex described as (**72**) reveals an IR spectral band at 2650 cm^{-1} characteristic of an N–H immonium stretch [223], which is absent in the hydroxo form [40]. It is also observed in $Ir(bpy)_2(H_2O)_2^{3+}$ species, and in addition, an IR band appears at 1292 cm^{-1} that is not present in other iridium–bpy species [40]. The ca. 1300 cm^{-1} region is normally associated with C–C stetching frequencies [223]. These above data and observations are also consistent with a formulation of the complex as the covalently hydrated species (**73**); however, because there is no facile equilibrium between $Ir(bpy)_3^{3+}$ and the covalent hydrate $Ir(bpy)_2(bpy \cdot H_2O)^{3+}$ as revealed by the identical emission spectra in both 0.1 M base and 0.1 M acid for $Ir(bpy)_3^{3+}$, the nature of the complex isolated by Watts et al. cannot be (**73**) [40]. Gillard et al. [220] have argued that, "because there is no facile equilibrium, it is not to say that no equilibrium exists", and explained the "puzzling" properties of the compound in terms of the species (**73**).



(73)

One source for the controversy about the composition of the iridium(III) complex (**72**) or (**73**) in solution appears to rest on the ^1H NMR spectrum which consists (in DMSO-d_6) of broad multiplets at ca. 9.2, 8.4 and 7.8 ppm (vs. TMS) in addition to a doublet at δ6.65 ppm and a doublet of doublets at 7.14 ppm [219–221]; the NMR spectra are illustrated in Fig. 29 for both DMSO-d_6 and 0.1 M DCl/D_2O. Gillard et al. [220] interpreted the spectrum in Fig. 29(A) as evidence for the existence of the covalent hydrate (**73**) and assigned the ca. 6.65 ppm doublet to the proton on the tetrahedral sp^3 carbon C(6) of (**73**). In contrast, the two upfield multiplets are absent in DCl/D_2O solutions; also, the completely proton-decoupled ^{13}C NMR spectrum, illustrated in Fig. 30, consists of about 25 peaks in the region 120–160 ppm downfield from TMS and no other resonance signal appears upfield of 120 ppm [221] where signals from covalently hydrated carbon atoms are expected to be found as in 1,3-diazanaphthalene [224] (72.4 ppm vs. TMS) and pteridine (73.9 ppm vs. TMS) [224,225]. Clearly, these data preclude the

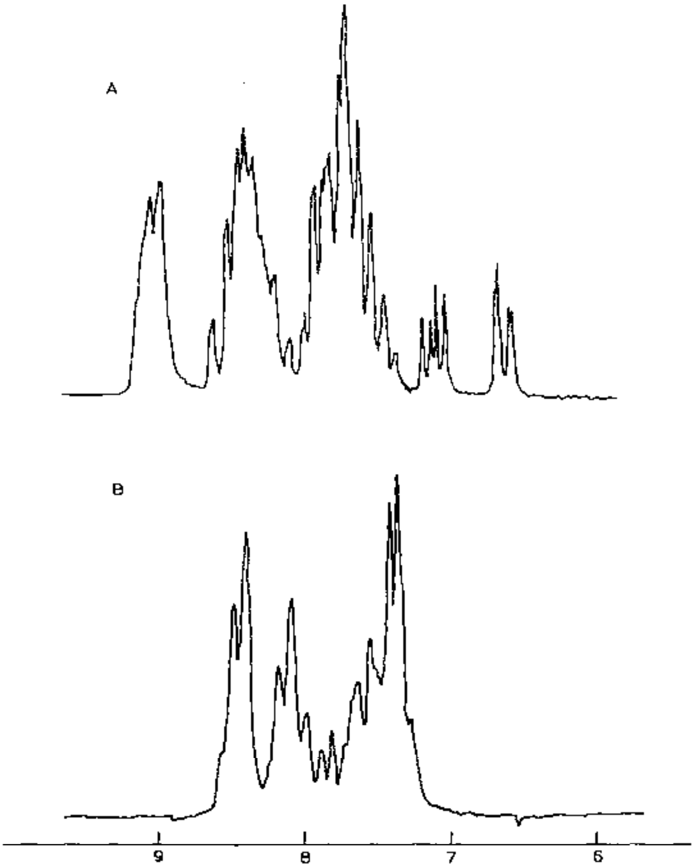


Fig. 29. (A) ^{1}H NMR spectrum of Ir(bpy)$_2$(H$_2$O)(bpy')$^{3+}$ in DMSO-d_6; (B) ^{1}H NMR spectrum of Ir(bpy)$_2$(H$_2$O)(bpy')$^{3+}$ in 0.1 M DCl/D$_2$O. Reprinted with permission from ref. 221.

existence of (**73**) and were taken as consistent with (**72**) [222].

The complex isolated by Watts et al. [40] presented a golden opportunity to verify whether the structure of the compound is as that shown by (**72**) or as that given by (**73**). A recent single crystal X-ray structural study [35] on the ClO_4^- salt of this complex demonstrates unequivocally that the species contains neither a monodentate nor a covalently hydrated bipyridine ligand, at least in the solid state. The molecular geometry is depicted in Fig. 31 and shown as (**74**); all three bipyridine ligands are chelated to iridium(III) but one bipyridine ligand is ligated via the nitrogen of one ring and the C(3) carbon of the other ring, reminiscent of *ortho*-metallated compounds [226]. The data of Watts et al. [40,41], DeArmond and co-workers [219] and Gillard et al. [220] can now be understood and are all consistent with

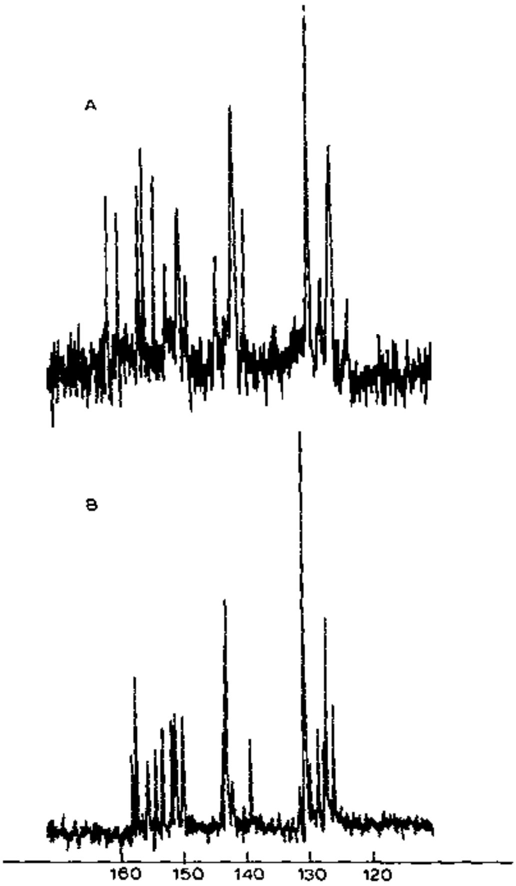
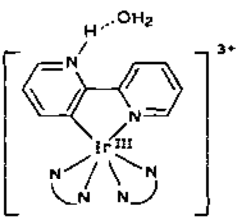


Fig. 30. ^{13}Carbon Fourier Transform NMR spectrum of $Ir(bpy)_2(H_2O)(bpy')^{3+}$ in (A) DMSO-d_6 and (B) in 0.1 M DCl/D_2O. Reprinted with permission from ref. 221.

structure (**74**). Thus, the appearance of the IR band at 2650 cm^{-1} is consistent with an N—H stretching band in (**74**). Also, observation of only one pK value (3.0 ± 0.1) [40] and one pK^* value (3.5 ± 0.1) [41] is in keeping with the expectation for (**74**). It is also clear that the ^{13}C NMR spectrum of



(74)

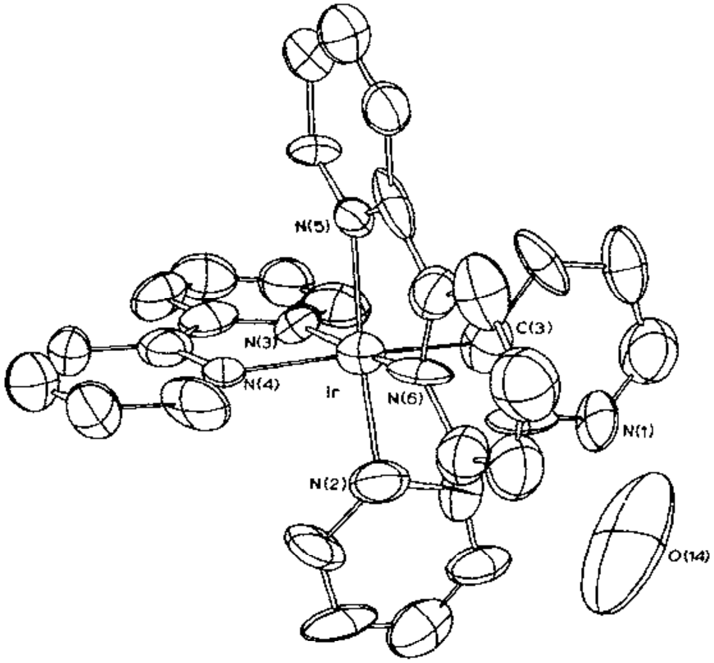
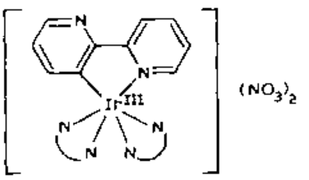


Fig. 31. Structure of the $\mathrm{Ir(bpy)_2(Hbpy)^{3+}}$ cation with the water molecule. Reprinted with permission from ref. 35.

(74) would show more than five ^{13}C lines [221] and would have a more complicated ^{1}H NMR spectrum [219–221] than the simple tris-NN′-chelated $\mathrm{Ir(bpy)_3^{3+}}$ cation. It is clear that cases where monodentate bpy or covalently hydrated species have been suggested to explain data must now be reconsidered in the light of **(74)** or equivalent species. Indeed this is now being done. The ^{13}C and ^{1}H NMR data are being reconsidered by both Watts [227] and by Seddon [228]. For example, Watts has indicated [227] the absence of the C(3) ^{1}H NMR signal in the "monodentate bpy" structure **(72)** in DMSO-d_6 and $\mathrm{CD_3CN}$. Evidence for the ^{13}C signal of the Ir—$\underline{\mathrm{C}}$ carbon is being sought actively [227,228]. It is also interesting to note that in view of the pK of (74) of 3.0, recrystallization in neutral aqueous media should yield the cation



(75)

$Ir^{III}(bpy)_2(bpy')^{2+}$. Recent studies in one of our laboratories [229] reveal that the nitrate salt of such a cation contains two NO_3^- units per iridium(III), thus consistent with structure (**75**).

E. CONCLUDING REMARKS

Covalent hydration and pseudobase formation in several, free N-quaternized organic heterocycles have been demonstrated. The presence of several doubly-linked nitrogen atoms in an aromatic ring is not a sufficient condition for covalent hydration; resonance stabilization must also occur. Even though these two conditions may be met, covalent hydration may not necessarily occur (examples have been given in Section B).

Complexation of N-heterocycles to transition metals quaternizes the nitrogen atoms. The resulting complex now presents two positions for nucleophilic attack: the metal centre and the "activated" carbons near the nitrogen atoms. All the data presented here definitely indicate that covalent hydration and pseudobase formation in transition metal complexes have not been demonstrated (except perhaps the 5-nitrophenanthroline species) despite the continuing claims to the contrary. Many of the claims have been based upon kinetic studies; these claims must be taken lightly since suggested covalent hydrates as potential intermediates in chemical reactions are merely suggestions, and have no physical reality unless proven (by definite experiments) otherwise. As is well known, there are always alternative mechanisms and intermediates, equally valid, to explain kinetic data.

For divalent metal polypyridyl complexes, Gillard and co-workers continue to claim the presence of covalent hydration; however, in all cases, there exist alternative models to rationalize the experimental data without having to invoke covalent hydrates. The results that have accumulated recently in other laboratories negate Gillard's claims. Indeed, the recent results demonstrate unequivocally that in the reactions of $Pt(phen)_2^{2+}$ and $Pt(bpy)_2^{2+}$ with either OH^- or CN^-, the nucleophile attacks the Pt(II) centre consistent with an associative mechanism generally accepted for substitution reactions in platinum(II) complexes.

The data reported by Gillard's school on $Pt(py)_4Cl_2^{2+}$ are in marked contrast to those found by Nord and by Seddon.

For $Cr(bpy)_3^{3+}$ and $Cr(en)_2(NCS)_2^+$ complexes which have been extensively studied in several laboratories, the thermal, photochemical and photophysical data support an associative mechanism for the substitution reactions. Moreover, for the highly controversial nature of the $[Ir(bpy)_2(H_2O)(bpy)]^{3+}$ cation, one of our laboratories has shown that this complex has a cyclometallated bpy ligand and all the data presently available for this complex can now be explained without invoking a covalent hydrate species.

The reduction of M(polypyridine)$_3^{3+}$ complexes (M = Fe(III), Os(III), Ru(III)) by OH$^-$ anions had been earlier suggested to occur via formation of a precursor complex containing a covalently hydrated polypyridyl ligand. Recent work by Nord and co-workers seems to indicate otherwise. This notwithstanding, the unexpected and recently demonstrated acidity of the 3,3′-protons in Ru(bpy)$_3^{2+}$ and Os(bpy)$_3^{2+}$ complexes suggest yet an alternative and attractive mechanism to rationalize the OH$^-$-reduction of the above M(III) complexes.

This article was not intended to show that covalent hydrates and pseudobases are non-existent, only that their existence in coordination compounds has not been demonstrated by hard, convincing evidence.

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