Coordination Chemistry Reviews, 16 (1975) 67—94

EQUILIBRIA IN COMPLEXES OF *N*-HETEROCYCLIC MOLECULES. PART III [1, 2]. AN EXPLANATION FOR CLASSICAL ANOMALIES AMONG COMPLEXES OF 1,10-PHENANTHROLINES AND 2,2′-BIPYRIDYLS

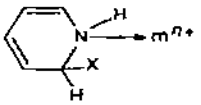
R.D. GILLARD

Inorganic Chemistry Research Laboratories, University College, Cardiff (Gt. Britain)

A lecture delivered at the Bressanone Conference on "Stability and Reactivity of Coordination Compounds", in August, 1974, and based on earlier lectures at Canterbury (1967), Coleraine (1974), Cambridge (1974) and Gregynog (1974).

INTRODUCTION

Some classical anomalies in the aqueous chemistry (kinetics, stabilities, and reactivities) of substituted pyridine complexes, such as 2,2′-bipyridyl and 1,10-phenanthroline, are summarized. The analogy is drawn between quaternization of pyridines (by protons, alkyl, aryl, or other groups) and complexing by metals. In particular, the idea of accessibility to attack by nucleophiles of the 2-position of quaternized pyridines is extended to metal derivatives. This suggestion, that species derived from the partial structure (1) participate in equilibria of such complexes in protic media, is used to interpret available results on systems containing $M(L)_m^{n+}$ and water, hydroxide, cyanide, or alkoxide.



(1)

($HX = H_2O$, HCN, $HOCH_3$ etc.)

Many anomalous properties of complexes such as $[M(bipy)_3]^{n+}$ and $[M(phen)_3]^{n+}$ are rationalized on this basis.

Ligands based on pyridine are widely used and the rather stable complexes of the chelating ligands (L), 2,2′-bipyridyl (B) and 1,10-phenanthroline (P) and of their many derivatives have occupied a central position in coordination chemistry, particularly in aqueous solutions. Because they have been so extensively studied, there is a mass of experimental fact on these systems. Among these many observed properties a surprisingly high proportion have been anomalous in that no ready explanation was available in molecular terms. A few examples of these anomalous properties will suffice to introduce a novel explanation.

(1) The rate of base hydrolysis of $[\mathrm{FeL_3}]^{2+}$ contains [3, 4] dominant terms in $[\mathrm{FeL_3}^{2+}]$ $[\mathrm{OH^-}]$. Similarly, the rate of substitution of L by cyanide ion contains [5] terms in $[\mathrm{FeL_3^{2+}}]$ $[\mathrm{CN^-}]$. Since no pre-equilibrium of conjugate base is possible, there certainly being no protons ionizable at pH's below 12, these rate expressions suggest either a bimolecular reaction or some specific and remarkable association of reacting species.

(2) The reduction potentials of $[\mathrm{ML_3}]^{3+}$ (M = Fe, Ru, Os) and of the bis-complexes with 2,2′,2″-terpyridyl vary* strongly [6, 7] with acidity (although acid is not involved in the equation for the half-cell!).

(3) A number of (at least initially) reversible changes in spectra occur for complexes $[\mathrm{ML}_x]^{n+}$ on the addition of base. These compounds include: $[\mathrm{ML_2}]^{2+}$, with [1] M = Pd, Pt, and L = B or 5,5′-dimethyl-2,2′-bipyridyl; and $[\mathrm{M(5\text{-}NO_2\text{-}P)_3}]^{2+}$, M = Fe [3] and Ru [9].

(4) In the course of this discussion several other anomalies are mentioned for complexes of these *N*-heterocyclic ligands, in protic media, or the presence of water, cyanide, or alkoxide.

THEORY

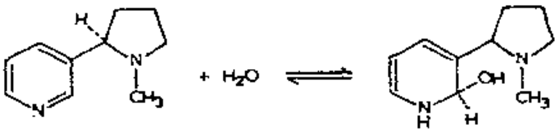
As a means of bringing together the general reactivity of *N*-heterocyclic molecules with our knowledge of their metal complexes, the postulate is that quaternization, whether by proton, alkyl, aryl, oxide, or metal ion, leads to similar electronic changes in the pyridine and consequently to similar reactivities in the ligand. An early calculation actually predicted [10] that the 2(9)-position of 1,10-phenanthroline was most liable to nucleophilic attack and that "if the Coulomb integral of the nitrogen atom in an aza-compound is increased by quaternary alkylation, the reactivity of (such) positions will be enhanced still further". In this paper, the general term "2-position" is used to describe the ring carbon atom adjacent to the nitrogen atom.

To unite effects of metal ions with those of more classical quaternizing agents, observations on metal complexes are discussed in terms of the equilibria shown in (2). The equilibrium described by K_S is exactly that** called "covalent hydration" by Albert [11] and the equilibrium K_A corresponds to

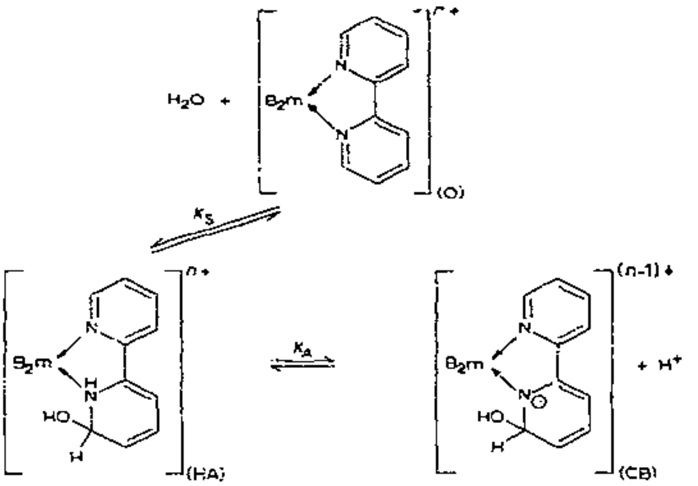
---

* For example, for $[\mathrm{RuB_3}]^{3+} + \mathrm{e} \rightarrow [\mathrm{RuB_3}]^{2+}$, $E_0 = 1.27$ V in 0.1 F $\mathrm{H_2SO_4}$ but [8] 0.98 V in 16.0 F $\mathrm{H_2SO_4}$.

** Lowry suggested [12] such a hydrate to explain the different electronic spectra of (−) nicotine in cyclohexane and water:



the loss of proton [13] from a covalent hydrate. The conjugate base (CB) produced is exactly similar to the pseudo-bases of classical quaternary heterocyclic chemistry.



(2)

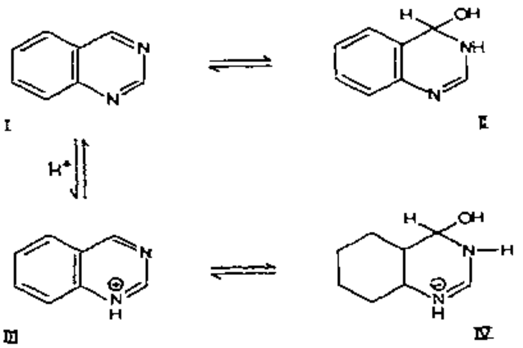
K_S describes the equilibrium between unsolvated complex (O) and its covalent adduct (HA).

$$K_S = \frac{\{HA\}}{\{O\}\{H_2O\}}$$

So that, assuming that activity coefficients of HA and O run parallel, giving a modified constant

$$K_M = \frac{[HA]}{[O]\{H_2O\}}$$

In the quinazoline system, although II is not formed to any great extent in neutral water, acidification gives [11] substantially IV and not III.



$[O] = [HA][K_M]^{-1}\{H_2O\}^{-1}$, i.e., the concentration of O is inversely proportional to the activity of water, at least in acid solutions where CB is unimportant.

K_A describes the acid dissociation of HA to give its conjugate base CB,

$$K_A = \frac{\{CB\}\{H^+\}}{\{HA\}}.$$

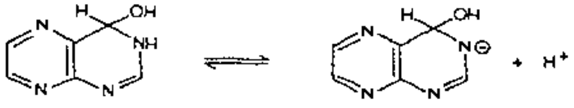
This treatment requires extension for those cases where the remaining ligands B are *N*-heterocycles. Here, the solvation equilibria may give species

$$[ML_3] \rightleftharpoons [ML_2(LH_2O)] \rightleftharpoons [ML(LH_2O)_2] \rightleftharpoons [M(LH_2O)_3] \text{ etc.}$$

and each covalently hydrated species has its own set of pK_a values, e.g.

(a) $[ML_2(LH_2O)]^{n+} \rightarrow [ML_2(LOH)]^{(n-1)+} \rightarrow [ML_2(LO)]^{(n-2)+}$
(b) $[ML(LH_2O)_2]^{n+} \rightarrow [ML(LH_2O)(LOH)]^{(n-1)+} \rightarrow [ML(LOH)_2]^{(n-2)+}$

Albert pointed out [13] that loss of a proton from a covalent hydrate may give a stable anion, e.g. for pteridine, with pK_a 11.21. This suggests that



(3)

typically free covalent hydrates may have acid strengths like those of phenols. Large drops in pK_a (ΔpK_a) ensue on coordinating a protonated atom to metal ions; ΔpK_a for M^{2+} ca. 5 log units; ΔpK_a for M^{3+} ca. 8—10 log units. So we might expect the pK_a for covalently hydrated bipy or phen attached to iron(II), for example, to be ca. 4, but attached to iron(III) to be ca. 0.

Although salts $[ML_3](X)_3$, where HX is a strong acid, give [14] neutral solutions, this is also, in general, true even of those quaternized *N*-heterocyclic salts of HX which on addition of base give pseudo bases. However, the product K_AK_S is unlikely to be large. The bases $[ML_3](OH)_2$ are "strong" in the sense that they absorb CO_2 from the air and liberate ammonia from its salts.

Roughly speaking, some anomalies in the chemistry of $[ML_3]^{n+}$ are now attributed to effects arising from K_S (e.g., the decline of $\{H_2O\}$ in stronger acid media will increase [O], the concentration of unsolvated species). Others (effects of $[OH^-]$) are attributed to K_A, the concentration of the conjugate base being proportional to $[OH^-]$. Other anomalies reflect the similar equilibria for other H—X (e.g. HCN, to account for the high nucleophilicity of $[CN^-]$ toward these complexes).

The relative size of the product K_SK_A for $[ML_3]^{2+}$ and $[ML_3]^{3+}$ is important. The more highly charged the central metal ion, the greater its polarizing power on the C—N bond, so that K_S for $[ML_3]^{3+} > K_S$ for $[ML_3]^{2+}$. In the same way, $K_A(ML_3.H_2O)^{3+} > K_A(ML_3.H_2O)^{2+}$.

Within the complexes $[ML_3]^{n+}$ of a single metal ion in one oxidation state, the size of K_S will presumably follow the intuitive order, i.e., the stronger L is as a base, the less will K_S be. Effects on K_A might be less obvious. This treatment takes no account of steric effects (particularly of substituents in the 2,9-positions of P or the 6,6′-positions of B.)

Blocking by alkyl substituents is often used in heterocyclic ions as a test [11] for covalent hydration and as a means of identifying the position of attack. However, despite the steric hindrance of the methyl group at the 7-position, 2-methylimino-6,7,8-trimethylpteridinium ion is [15] readily hydrated. Further, it is conceivable in sterically hindered metal complexes of such ligands, that the relief of steric compression may encourage reaction at the C-substituted positions (cf. ref. 1).

EFFECTS OF HYDROXIDE

A. With M(II): substitution

The general scheme proposed for the attack of hydroxide ion upon $[ML_3]^{2+}$ is shown as (4).

The scheme contains three possible fates for the common intermediate, HA (a covalent hydrate). It can react by an intramolecular shift of hydroxyl within the covalent hydrate (rate constant k_{H_2O}), by protonation* to give the conjugate acid (CA) followed by an intramolecular shift of water from C-2 to Fe (k_{H^+}), or by deprotonation with hydroxide, giving CB, the conjugate base, which then reacts by an intramolecular shift (C-2 to Fe) of hydroxyl (k_3). The kinetic pattern observed for solvolysis of $[FeL_3]^{2+}$ in aqueous media is similar to that [16] for other covalent hydrates, where the rate of covalent hydration is accelerated by acid or base. The effects of substituents on the aromatic rings upon the rates of the reactions have been explained [17] in terms of changes in electron density at the iron atom. However, changes of the substitutent will also lead to changes in the ease of attack by nucleophile at the carbon—nitrogen double bond.

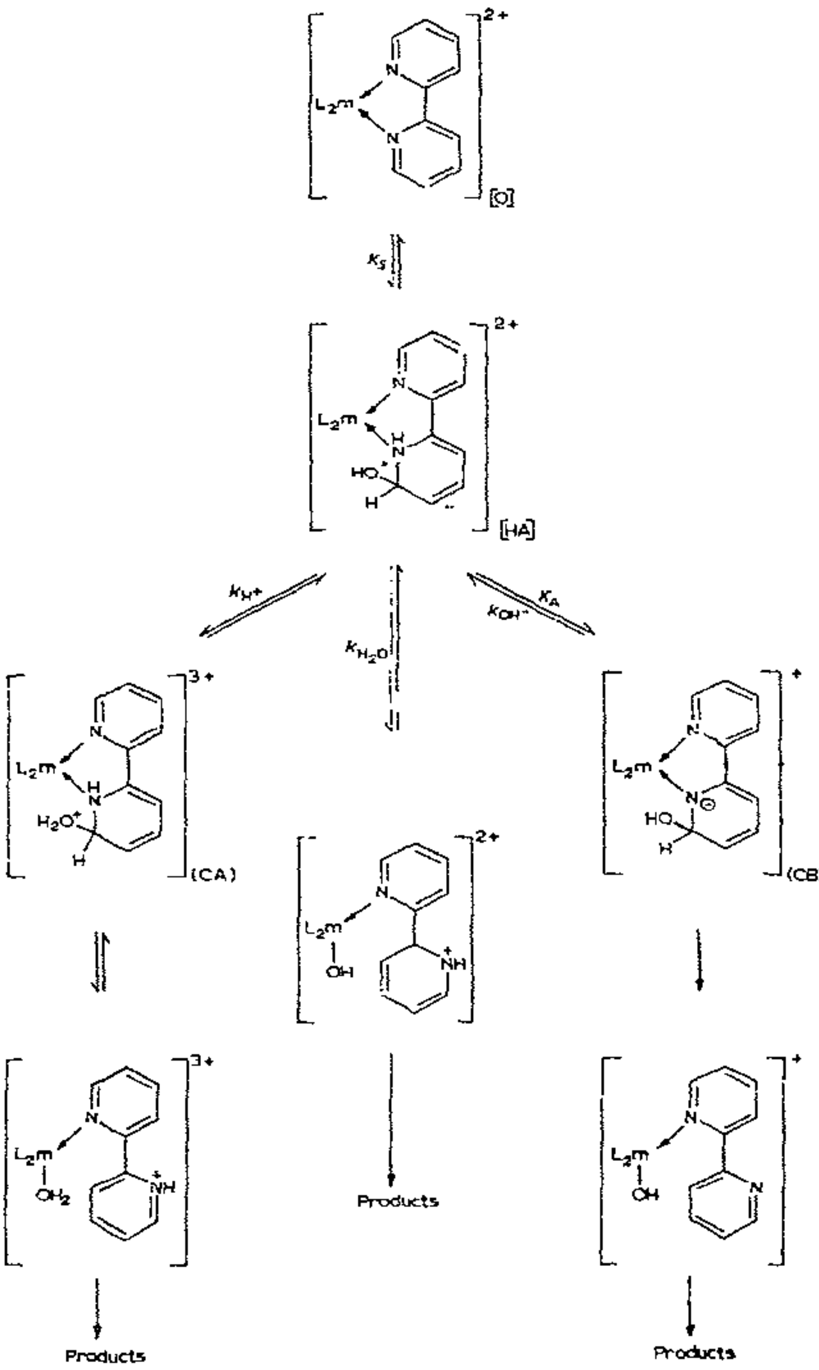
Some recent observations of spectroscopic changes with pH are most easily explicable in terms of shifts in the equilibrium K_A (or the equivalent direct formation of the conjugate base by attack of hydroxide).

(i) The reversible spectroscopic changes [1] with increased pH of $[PtL_2]^{2+}$, (L = B, 5,5′-DMB, P etc.) were attributed to hydroxylation at the 6 position of B or the 2 position of P.

(ii) The complex $[Fe(5\text{-}NO_2P)_3]^{2+}$ shows [3] an initially reversible shift of its electronic spectrum with pH, the neutral solution having $\lambda = 510$ and the alkaline solution, initially, $\lambda > 528$ nm. The absorbance at 510 nm of $[Fe(5\text{-}NO_2P)_3]^{2+}$ falls [3] from 0.54 in neutral solution to 0.44 in 0.2 *M* alkali, an effect probably related to the shift of maximal absorbance.

---

* In the acid hydrolysis of metal complexes of these ligands, protonated intermediates are often proposed to account for the remarkable variation of rate with pH, e.g., for $[Ni(phen)(H_2O)_n]^{2+}$ [18] at $H^+ > 0.5\ M$, for $[Fe(phen)_3]^{3+}$ [19] and $[FeP_3]^{2+}$ [20].

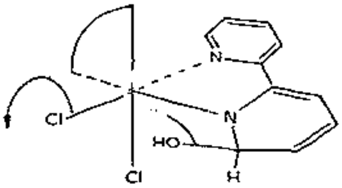

[O]
K_S
[HA]
k_H+
k_H2O
K_A
k_OH-
(CA)
(CB)
L₂m
HO
H₂O⁺
OH
OH₂
Products
Products
Products

(4)

(iii) Likewise, $[Ru(5\text{-}NO_2P)_3]^{2+}$ in neutral solution has [9] $\lambda = 440$, $\log \epsilon = 4.3$; $\lambda = 330$, $\log \epsilon = 4.0$ (not a peak); $\lambda = 265$, $\log \epsilon = 5.0$, but in alkaline solution, $\lambda = 450$, $\log \epsilon \sim 4.4$; $\lambda = 340$, $\log \epsilon = 4.5$; $\lambda = 270$, $\log \epsilon = 4.7$; $\lambda = 265$, $\log \epsilon = 4.5$. The new peak at 340 nm in alkaline conditions is most noteworthy. Most striking of all is the fact that the circular dichroism spectrum changes sharply in alkaline solution.

The Cotton effects in the so-called 'exciton' region (ca. 270 nm) diminish strongly* in intensity, suggesting that the long-axis polarised transitions of coordinated P have been markedly modified. Simultaneously, in the visible region, the intensity of circular dichroism increases sharply*, supporting the notion that new chiralities (e.g. the newly tetrahedral 2-carbon atom) have been induced. A number of kinetic observations may be interpreted in terms of pathways through the conjugate base. The anomalous kinetic behaviour [3] of $[Fe(5\text{-}NO_2P)_3]^{2+}$ with base, which was ascribed to deprotonation at the 6-position of the ligand, may result from addition of hydroxide ion to the ligand. Certainly no hydrogen exchange of the free ligand occurs with alkaline D_2O.

The observed promotion [21] by base of hydrolysis of the first chloride ion from $[M(AA)_2Cl_2]^+$ (where AA = bipy or phen; M = Co or Cr) is envisaged as occurring through (5).



(5)

The *cis*-halo groups in a-halo- b-pyridine- metal complexes, e.g. $[Co(en)_2(C_5H_5N)Cl]^{2+}$ hydrolyse [22] very rapidly in base. It has been suggested [23] that the special properties of the pyridine contribute in some way to the removal of the chloride ion. The intermediate may best be thought of as the pseudo base with hydroxyl covalently attached at the 2-position of the pyridine.

B. With M(III): reduction

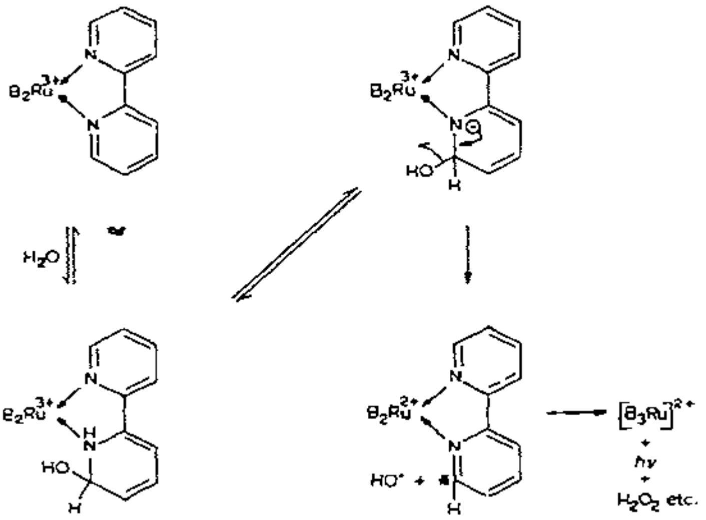
$[ML_3]^{3+}$ is very unstable in the presence of hydroxide ion, being reduced by it. Blau was unable [24] to isolate $[Fe(B)_3](OH)_3$, and $[OsB_3]^{3+}$ instantly gave [14] $[OsB_3]^{2+}$ with base. Davies and Dwyer pointed out [25] that since $[FeL_3]^{3+}$ with hydroxide gives ozone, and that since E^0 is ca. 1 volt, there is "a special interaction of hydroxyl ions with this type of complex ion". $[ML_3]^{3+}$

---

* Neutral: $\lambda = 475$, $\Delta\epsilon = 5.5$; $\lambda = 400$, $\Delta\epsilon = +8.5$; $\lambda = 275$, $\Delta\epsilon = -150$; $\lambda = 250$, $\Delta\epsilon = +100$. Alkaline: $\lambda = 485$, $\Delta\epsilon = -13.5$; $\lambda = 415$, $\Delta\epsilon = +15$; $\lambda = 296$, $\Delta\epsilon = -65$; $\lambda = 255$, $\Delta\epsilon = +25$. (approximate values from Fig. 6 of ref. 9).

(M = Fe, Ru, Os, L = B or P) with base is instantly reduced; this is reversed on immediate [26] acidification but not after standing. Products on standing include [26] H_2O_2 and O_3, neither of which oxidises* $[ML_3]^{2+}$ to $[ML_3]^{3+}$. "An unstable intermediate product of OH^- must be formed which decomposes irreversibly to ozone and hydrogen peroxide" [26]. Similarly, hydroxide is said [27] to attack $[FeP_3]^{3+}$ with degradative oxidation of the ligand and reduction of iron(III) to (II).

The reduction for $[FeL_3]^{3+}$ is known [29] to have a rate = $k[FeL_3][OH^-]$. Taking $[RuB_3]^{3+}$ as an example, the rapid reaction may be seen as arising from the intramolecular contact of the C(6)-hydroxo group with the metal ion, as in (6).



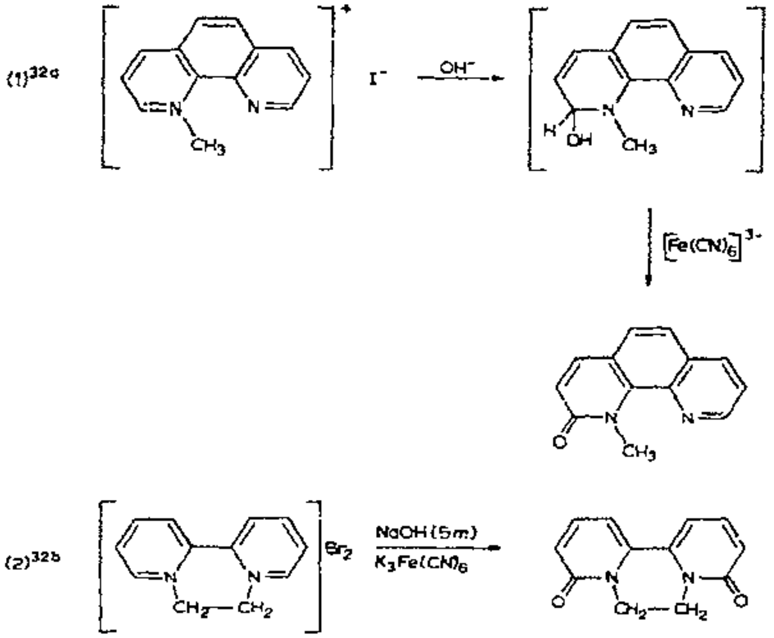
(6)

Chemiluminescence is observed [30] on mixing acid solutions of $[RuL_3]^{3+}$ (L = B, 5 MeP, 6,7-DMP, 3,5,6,8-tetraMP) with base. In the case of $[RuB_3]^{2+}$ in 9 *N* H_2SO_4 mixed with 9 *M* NaOH, the emitted light coincides with the fluorescence spectrum of $[RuB_3]^{2+}$; the intensity of emitted light depends on the strength of acids and bases used. The intermediates in this scheme (the covalent hydrate and the derived pseudo base) are identical with those in (4) relating to substitution, except for the oxidation state of the metal ion. The step involving intramolecular reduction of M(III) to M(II) by C(6)-OH is strongly reminiscent of the well-known [31] intermolecular reduction of

---

* In this context, the observation [28] that neutral $[FeB_3]^{2+}$ and hydrogen peroxide at once give a blue tint, not due to $[FeB_3]^{3+}$, is particularly striking. Slow degradation of the organic ligand then ensues.

alkaline ferricyanide by pseudo bases, which themselves yield pyridones*, e.g., (7).



(7)

C. *Redox potentials*

The redox potentials (and consequently the reactivities in a redox context) of tris(phenanthroline), bis(2,2′,2″-terpyridyl), and similar complexes of Fe, Ru and Os vary strongly with acidity**. This has been explained [34] in terms of extensive formation of very stable ion pairs. Schilt said [35] that such a pH-dependent behaviour indicates very marked changes in the species

---

* Such oxidations to pyridone have been used [31] to show the position of covalent hydration, but have not yet been deliberately applied to metal complexes, though the formation [33] of phenanthrid-2-one from phenanthridine in aqueous $CaCl_2$ in presence of cobalt ions probably represents such a case.

** For example [8], for the complex $[RuB_3]^{3+/2+}$, $E_0 = 1.27$ V in 0.1 F H_2SO_4, but 0.98 V in 16.0 F H_2SO_4. Similarly, over the range $0.05 < H^+ < 2\,M$, E^0 for the half-cell $[FeP_3]^{3+} + e \rightarrow [FeP_3]^{2+}$ drops [19] by ca. 0.1 V.

present. The availability of pH-dependent equilibria involving the solvent supplies an explanation particularly attractive in view of the analogy with the effect of strong acids in depressing covalent hydration of uncomplexed *N*-heterocycles.

The species present are as follows:

M^{3+}		M^{2+}
$[ML_3]^{3+}$	O	$[ML_3]^{2+}$
$[ML_2(HLOH)]^{3+}$	HA	$[ML_2(HLOH)]^{2+}$
$[ML_2(LOH)]^{2+} + H^+$	CB	$[ML_2(LOH)]^{+}$

For M^{3+}, O is much more stable than CB. So, in strong acid, where $\{H_2O\}$ is small and [O] is large, $[ML_3]^{3+}$ is stabilized relative to less acid media. In neutral media, of course, the conjugate base is formed and instantly reduced, i.e. an increase of pH destabilizes $[ML_3]^{3+}$.

The most convincing support for the existence of more than one species $[Fe(L)_3]^{n+}$ is the visual evidence noted originally [36] by Brandt and Wright in oxidation cells made by treating $[Fe(T)_2]^{2+}$ in sulphuric acid with ceric sulphate in sulphuric acid, i.e.

$$[FeT_2]^{2+} + Ce^{4+} \rightleftharpoons [FeT_2]^{3+} + Ce^{3+}.$$

For 0.1 *F* H_2SO_4, the initially deep wine red solution instantly became light green; the light green solution then slowly (ca. 1—2 min) became bright yellow. In 1.0 *F* H_2SO_4, the light green intermediate stage was not seen. The three species are, crudely,

$[FeT_2]^{2+} \rightarrow$	$[FeT_2]^{3+} \rightarrow$	$[FeT(TH_2O)]^{3+}$
wine red	light green	bright yellow

Similarly, the redox potentials of the ruthenium and iron complexes are greatly affected by inert electrolytes; 5 *N* $(NH_4)_2SO_4$ (which presumably acts by changing $\{H_2O\}$) has almost the same stabilizing effect [14] upon the M(III) state as does 5 *N* H_2SO_4.

A classical anomaly is that [37] the partial molar entropies in water for $[Fe(AA)_3]^{3+} + e \rightarrow [Fe(AA)_3]^{2+}$ are negative; —21 e.u. for AA = phen and —23 e.u. for AA = bipy (for Ru and Os complexes with bipy the values are —16 and —15 e.u.). In aprotic acetonitrile, however, the values are positive as expected (and usually found) for such systems, where the ordering of solvent is greater around the ion of greater charge. The explanation is that K_S for $[FeL_3]^{3+} > K_S$ for $[FeL_3]^{2+}$ (and probably K_A for $[FeL_2(L.H_2O)]^{3+} > K_A$ for $[Fe(L)_2(LH_2O)]^{2+}$). So $[CBFe(III)] > [CBFe(II)]$, i.e. the true half cell includes

$$[FeL_2(LOH)]^{2+} + e \rightarrow [FeL_2(LOH)]^{+} \rightleftharpoons [FeL_3]^{2+} + OH^-$$

The release of hydroxyl ion on reduction implicit in $[CBFe(III)] > [CBFe(II)]$ would account for the negative ΔS. Clearly, the less K_S, the smaller should be the anomaly in $\Delta S(H_2O) - \Delta S(CH_3CN)$. Indeed, among the methylated phenanthrolines, where covalent hydration would be smallest, the values for $\Delta S(H_2O)$ are (cf. P — 20.5): 5-MP, −2.8; 4,7-DMP, 1.4; 5,6-DMP, 1.8.

OTHER NUCLEOPHILES

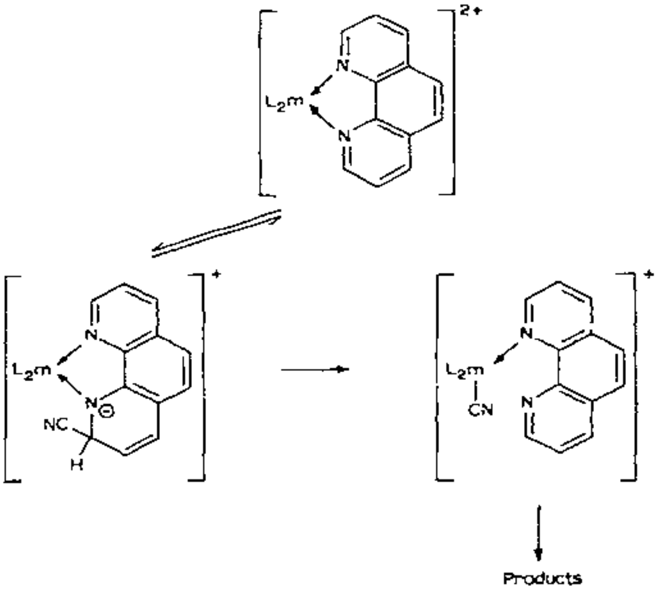
Among the classical nucleophiles which attack the 2-position of quaternized pyridines are cyanide (cf. the Reissert reaction) and alkoxides*. In exactly the same way, cyanide and alkoxides are superior nucleophiles towards $[FeL_3]^{2+}$. The rate expression for

$$[FeP_3]^{2+} + 2\,CN^- \rightarrow [FeP_2(CN)_2] + P$$

includes [5] a term dependent on incoming nucleophile, i.e.

$$\frac{-d[FeP_3]}{dt} = \{k_1 + k_2[CN^-]\}[FeP_3]^{2+}.$$

The mechanism proposed is that a Reissert compound is formed**, which then undergoes an intramolecular shift of cyanide (8). Details of the pathway remain to be elucidated. For example, does cyanide attack the unsolvated species [O] or the covalent hydrate and does the cyanide shift lead to an isocyanide which then isomerizes? The stereochemical information on this sub-



(8)

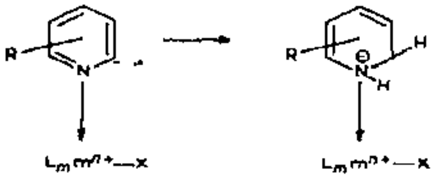
---

[*] Bisulphite also readily adds [38] to quaternary ions, but there seems to be no work upon metal complexes with this reagent.

[**] 1,10-Phenanthroline itself (like other 8-substituted quinolines) is not known [39] to form a Reissert compound. However, the mono-*N*-oxide does react with potassium cyanide and benzoyl chloride to give [40] 2-cyano-1,10-phenanthroline.

stitution is contradictory. One report claims [41] that optical activity is retained in the *cis*-product, but with inversion of optical configuration: the second (with at least some runs under identical conditions) found [42] only racemic products. The rate of displacement of ligand from the chelated iron(II) complexes is greatly enhanced [43] by methoxide or cyanide ion in methanolic solution, and pathways involving nucleophilic attack upon the 2-position of the ligand seem likely to occur here also.

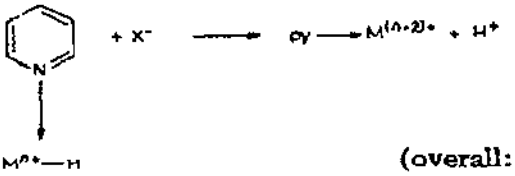
The other nucleophile which may attack the metal via a primary attack at the 2-position of the ligand is the hydride ion. Certainly, the involvement of zinc ions in NAD reactions has been said to arise from a similar enhancement of electrophilicity at the 2-position when nicotinamide becomes coordinated to zinc. Pyridinium ions are [38] certainly favoured hydride acceptors, and species such as that shown in (9) (or its isomers) may well occur as intermediate or product in two electron 'reductions' of metal complexes of *N*-heterocyclic ligands in the presence of protons.



(9)

There are many cases where complexes of *N*-heterocyclic ligands may be reduced (often by borohydride) where reformulations may be necessary. For example, on treating *cis*-dichlorobisbipyridyl—rhodium(III) salts with borohydride, the final product is [44] a red—blue substance of stoichiometry $[Rh(bipy)_2](ClO_4)$. This may well involve attack by hydride at the 1,6 (or possibly 1,4 position).

While there are no experiments directly supporting the existence of (9), very similar species are intermediates in the nucleophilic attack (A) by metal salts on pyridines (10).



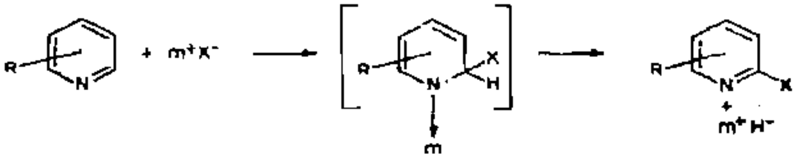
(overall: $[L_MMX]^{n+} + H^- \rightarrow [L_MM]^{(n-2)+} + HX$

{M^+X^- = $NaNH_2$ (Chichibabin reaction*); Grignard reagent or lithium phenyl; cf. KOH [45] or NaOEt [46].}

Tautomerism between the quaternized form and the covalent adduct is not restricted to those nucleophiles so far considered. It occurs [48] in other cases where the 'inium' ion (containing the pyridine in a quaternized form similar to that in a metal complex) is brought into a solution containing the anion of a

---

* Here, with 2,2′-bipyridyl, the product [47] is 6,6′-diamino-2,2′-bipyridyl.



(10)

very weak acid (cf. cyanide, hydroxide, hydride). Michael reagents or carbanions would fit this category.

EFFECTS OF WATER

There has, until now, been no suggestion of the involvement of covalent hydration in solutions or solid derivatives of any 2,2′-bipyridyl or 1,10-phenanthroline, although it is widespread [13] among the 1,3-diazanaphthalenes, quinazolines. Some anomalous changes which may well reflect the operation of covalent hydration (K_S) are now collected.

A. Solutions

(a) Some spectroscopic changes in solutions of $[ML_3]^{2+}$ may be interpreted[*] as arising from changes in the activity of water and hence of [O] resulting from addition of "inert" salts.

(i) For optically active $[RuP_3](ClO_4)_2$, $[FeT_2](ClO_4)_2$, and $[NiP_3](ClO_4)_2$, shifts in absorbance bands (both visible and UV) are recorded [50] on adding an excess of such large ions as β-naphthalenesulphonate or bromocamphorsulphonate.

(ii) Similarly, Jensen et al. [51] found that the UV maxima of $[FeP_3]^{2+}$ ($\lambda = 266$) and of 1,10-P itself ($\lambda = 265$) in water shift in 0.1 *M* racemic camphorsulphonate to 268 and 267 nm respectively. In the presence of sodium lauryl sulphonate (10^{-3} *M*), the UV maximum of $[FeP_3]^{2+}$ was again shifted from 266 to 268, and the visible maximum was also shifted 10 nm to longer wavelength and broadened.

(b) A number of rates are altered by "inert" solutes, which presumably alter $\{H_2O\}$ and hence [O].

(i) The rate of racemization of $[NiP_3]^{2+}$ is [52] very much reduced by 5 *N* $(NH_4)_2SO_4$.

(ii) [51] The rate of dissociation of $[FeP_3]^{2+}$ is cut by ca. 10% in 1 *M* chloride, nitrate or bisulphate, and sodium lauryl sulphonate reduces the rate greatly.

(iii) [53] The rate of racemization of (−)$[NiP_3]I_2$ in mixed solvents also

---

[*] Little is known of the effect of saturating double bonds in B, P, or similar ligands, upon the electronic spectra of their metal complexes. Irving and Hampton showed [49] that the spectrum of the stable red iron(II) complex of 3:4-dihydro-1,2′-pyridyl-isoquinoline was like that of 1:1 1-2′-pyridyl-isoquinoline, but more intense. Perhaps only relatively minor changes would be expected to follow covalent hydration. The solvent dependences of the electronic spectra of the Schilt—Barbieri compounds and others e.g. $[Pt(bipy)Cl_2]$, have been analyzed in terms of the E_T and Z parameters. However, these parameters are themselves derived from spectroscopic changes of quaternized pyridines, and it may be that covalent hydration of related effects underlie the observed shifts in any case. For example, *N*-methylpyridinium iodide does not obey the Beer—Lambert law in water.

shows the effect of changes in $\{H_2O\}$. For methanol, ethanol, or acetone, the addition of a small amount of water to the "dry" organic solvents produces large increases in rate. Similarly, the high rate in pure water is depressed on adding up to ca. 20% of any of these solvents.

Mixed protic/aprotic solvent systems [53, 54] seem likely to be particularly sensitive to the effects of covalent solvation, which will be a delicate function of the activity of the protic component.

(c) Some of the known consequences of the decrease of water activity in strong acids are

(i) The rate of dissociation of $[Fe(phen)_3]^{3+}$ decreases and its stability increases with increasing sulphuric acid concentration (this was attributed [55] to the formation of $[FeHP_3]^{4+}$). The first order decomposition of $[FeP_3]^{3+}$ in sulphuric media at 100.7°C is [56] "very markedly dependent on the concentration of unprotonated water in the solvent", with an almost millionfold decrease from $2M$ to 95% H_2SO_4.

(ii) The quantum yield for the photochemical reduction of $[FeP_3]^{3+}$ in aqueous sulphuric acid decreases [57] with increasing acid concentration from ca. 2.4×10^{-2} at $[H_2SO_4] \leqslant 10M$ to ca. 0 at $[H_2SO_4] \geqslant 16M$.

(iii) The electronic spectrum of *trans*-$[Rh(py)_4(H_2O)Br]^{2+}$ shows [58] a marked shift in $11M$ perchloric acid.

(iv) Similarly, reflecting an effect on K_S due to the lowering of $\{H_2O\}$, the hydrolysis

$$[Co(B)_2Cl_2]^+ + H_2O \rightarrow [CoB_2(H_2O)Cl]^{2+} + Cl^-$$

is markedly retarded [59] in 50% methanol or $3M$ hydrochloric acid.

All these findings are consistent with the view that the unsolvated species [O] has a different spectrum and is much less reactive than [HA]. Decrease of $\{H_2O\}$ (by the addition of miscible solvents, surfactants, or ammonium sulphate, or by adding strong acids) leads to a decrease in the concentration of the reactive covalent hydrate [HA]. This feature is commonplace in quinazoline chemistry: the quaternized forms are least covalently hydrated in the strongest acids*.

B. Solids

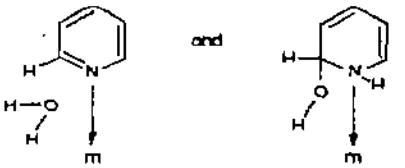
Although, of course, the mere existence of a solid solvate does not comment on the function of the solvent in the lattice (i.e. whether it be solvent of crystallization or of constitution), when quaternary salts crystallise from protic solvents, the solvent (e.g. water or ethanol) is often held [61] very tenaciously. γ-Hydroxypyridine readily yields [45] a monohydrate. Quinazoline methiodide is very deliquescent (as is indeed pyridinium hydrochloride) and crystallises [62] as a methanol solvate. Quinazoline-3-oxide readily forms [63] a covalent hydrate.

---

* Complexes of B and P are often remarkably stable in very strong acid. The increase in redox stability of $[ML_3]^{3+}$ in strong sulphuric acid is one example of this, and the fact [60] that $[Pd(phen)Cl_2]$ may be crystallized from the concentrated acid is another.

The regular occurrence and importance of solvation by water in solid complexes of phenanthroline and bipyridyl has been frequently emphasised. Thus two molecules of water may be fitted "neatly" [64] in each of the three pockets formed by the planar ligands of a tris-phenanthroline complex. Such water molecules would immediately occupy any coordination site made vacant by loss of phenanthroline. In connection with their synthesis of $[Ni(P)(B)_2]$-$Cl_2 5H_2O$ and $[Ni(P)_2(B)]Cl_2.6H_2O$, Broomhead and Dwyer remarked [65] on the possible "pockets" for water between chelate ligands. Similarly, for $[Rh(bipy)_3]X_3.nH_2O$ and $[Rh(terpy)_2]X_3.yH_2O$ which become more deeply coloured upon dehydration, the water of crystallization was thought [66] to be located in the angles between the ligands. Very high hydration numbers are known for some complexes, e.g. [67] 9 and 17 for $[Fe(B)_3]^{2+}$ and $[Fe(P)_3]^{2+}$, respectively, in aqueous media. Each tris(4,7-diphenyl-1,10-phenanthroline) iron(II) ion extracted from water into chloroform, nitrobenzene or 1-decanol carries with it [68] up to 60 molecules of water. Many complexes containing *N*-heterocyclic ligands crystallise with protic solvent (usually water) in the lattice, e.g. NaP_2ClO_4, 3 H_2O, $CaP_4(ClO_4)_2$, 3 H_2O and MB_3Br_2, 6 H_2O (M = Fe or Ru).

Whether this is water of constitution or of crystallisation is never clear. Even in cases where crystal and molecular structures have been established by diffraction methods, the question has not usually been resolved (in the sense that the distinction between the structural elements (11) is not great and might be difficult to resolve in the presence of heavy metal ions)*.



(11)

The free energy change of hydration in solution includes contributions from the formation of C—OH and N—H bonds and from loss of aromatic character with changes of a more subtle type in the solvation energies of the two species. When covalently hydrated [HA] and unhydrated [O] complexes co-exist in solution, the nature of the crystallized solid obtained by adding particular counter ions will depend (assuming thermodynamic control of crystallization) upon the value of K_S and K_A and the individual lattice energies and solvation energies for the alternative possibilities. Albert pointed out [13] that some substances (e.g. pteridine and formaldehyde) which are covalently hydrated in aqueous media, instantly lose all water when removed from solution even at 20°C.

---

* Little attempt has been made among metal complexes to find the extra IR absorption at ca. 1474 and 1240 cm^{-1}, arising [31] from the C—H and O—H of the C(H)(OH) grouping. Some lines of evidence used in the *N*-heterocyclic field, such as [31] the conversion of hydrates to alcoholates by boiling with alcohol are inappropriate in studying metal complexes.

It seems likely that the following properties arise from changes in $\{H_2O\}$ (altering the concentration ratio of [O] to [HA]).

(a) The solubility of (+) and of (−)$[RuP_3](ClO_4)_2$ increases in [69] strong solutions of large ions (e.g. bromocamphorsulphonate) as does that of $[FeT_2](ClO_4)_2$.

(b) A similar finding concerns the remarkable (and unusual) synergic solubility in water:acetone or water:1,4-dioxane of $[FeL_2(CN)_2]$. Insoluble in either component alone, a small amount of water added to either organic solvent confers [70] solubility.

(c) The reportedly anomalous spectroscopic behaviour [71] for $[FeB_3]^{2+}$ in strong perchloric acid has recently been said [72] to arise from oxidation. However, the equilibrium solubility of $[FeB_3](ClO_4)_2.2H_2O$ as a function of pH (at $\mu = 0.10$ and $T = 24.2°C$) shows [73] a marked sudden fall at pH ca. 3.2, whereas in perchloric acid solutions stronger than 4 M, the solubility increases rapidly. Similarly, $[CoB_3](ClO_4)_3$ is not very soluble in neutral or weakly acid solution, but is extremely soluble in strong perchloric acid.

(d) Polymorphism (often involving hydrates) is common [74, 75] in phenanthroline and bipyridyl metal compounds (e.g. [59] for $[ML_2Cl_2]X.yH_2O$; M = Co or Cr, X = Cl or ClO_4) and may indicate the existence in solution of equilibria between complexes containing unhydrated and covalently hydrated ligands. Hydrated complexes may involve covalent hydration rather than water of crystallization. Several observations could be rationalised on this basis, including the following results on desolvation:

(i) [76] On adding potassium hexafluorophosphate(V) to a solution containing $[RuB_3]^{3+}$ in 6 M sulphuric acid, bright green $[RuB_3](PF_6)_3.nH_2O$(A) crystallizes which is "very unstable toward reduction". On standing in the mother liquor for a few hours, a more stable crystalline form (with 2 or 3 H_2O) results; this is still liable to form ruthenium(II). The deeper green anhydrous crystals obtained in the preparation of form A on adding more sulphuric acid are stable. It seems likely that form A contains a 2-hydroxylated phenanthroline ligand.

(ii) [75] $cis[Ir(P)_2Cl_2]Cl.3H_2O$ (crystal form A) $\xrightarrow{\text{rapidly}}$ $cis[Ir(P)_2Cl_2]Cl.2H_2O$ (crystal form B).

(iii) [77] $\underset{\text{red}}{[PtB_2]I_2.2H_2O} \rightarrow \underset{\text{black}}{[PtB_2]I_2}$

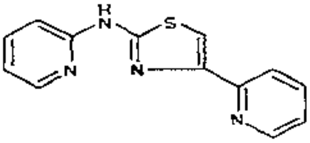
Interestingly, Livingstone and Wheelahan demonstrated [78] the instability of the anhydrous black form, which slowly loses bipyridyl. In a similar way, when the water is removed (vacuum) from $PtB_2\ I.ClO_4.2H_2O$, bipyridyl is simultaneously lost.

(iv) [66]

$$\left.\begin{array}{l}[RhB_3]X_3.nH_2O\\ \\ [RhT_2]X_3.yH_2O\end{array}\right\}\ \text{dehydration} \rightarrow \left\{\begin{array}{l}\text{more}\\ \text{deeply}\\ \text{coloured complexes}\end{array}\right.$$

$$[FeB_3]SO_4.2H_2O \xrightarrow[\text{over magnesium perchlorate}]{196^\circ\text{, in vacuo}} \text{simultaneous loss of water and bipyridyl}$$

(e) The basis for the formulation [79] of the grey-green cobalt(III) complex containing 2,2′,2″,2‴-tetrapyridyl (T^1) as *trans*-$[CoT^1Cl_2]Cl.3H_2O$ is not clear (there is [74a] a lack of evidence for any six-coordinate complex containing two *trans* bipyridyls or phenanthrolines). However, the water may be constitutive: indeed it is hard to envisage a possible *cis*-structure other than involving saturation of ring carbons, so giving some stereochemical flexibility.
(f) A relationship between solvation, magnetic properties and colour is shown in complexes of the terdentate ligand papth [80] (12) where different



(12)

hydrates of $[Fe(papth)_2]X.nH_2O$ have different properties. Thus the brown hydrated nitrate has different magnetic behaviour from the anhydrous salt, and similar differences are found between the pentahydrated brown sulphate and the orange-yellow 3.5 hydrate.

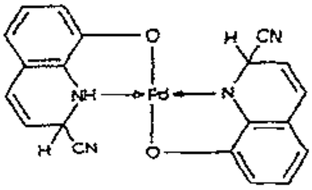
Similar magnetic anomalies are those recorded by Schilt, for [81] yellow $Ni(phen)(CN)_2.H_2O$ (μ_{eff} = 1.67 BM) and lavender $Ni(phen)(CN)_2(H_2O)_{0.5}$ (μ = 2.26 BM) and by Barbieri [82] and Schilt [70] for hydrates of $[FeL_2(CN)_2]$ and hydrated salts of $[FeL(CN)_4]^-$ (ca. 0.6 BM).
(g) It has been suggested that the intramolecular racemisation of the iron(II) complexes of phenanthroline and bipyridyl may result from a process of expansion, in which metal—nitrogen distances are increased and the compound becomes high spin and labile. The present alternative view of the labile intermediate would involve the carbinolamine formulation which might well have high spin (cf. the magnetic anomalies in $[Fe(papth)_2]X.yH_2O$). Similarly, the rate acceleration by pressure of the racemisation in the solid state of $[Fe(phen)_3](ClO_4)_2.xH_2O$ and of $[Ni(phen)_3](ClO_4)_2.nH_2O$, attributed [83] to the twist mechanism or possible increase of coordination number of the metal, may in fact be due to increased covalent addition of water to the organic ligand.

SOME EXTENSIONS

A. Alternative structures for some known compounds

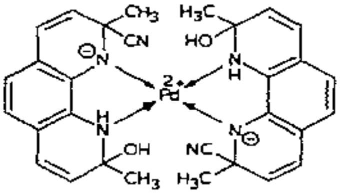
Some anomalies of cyanide and/or hydroxide with complexes of heterocyclic ligands are known which may well reflect Reissert or pseudo-base behaviour, for example,

(a) On treatment of palladium(II) cyanide with 8-hydroxy-quinoline, one product is $Pd(oxine)_2(CN)_2$ [84]. It seems likely* that this is in fact the isomeric complex of the Reissert adduct (13).



(13)

(b) On treating $[Pd(CN)_4]^{2-}$ with an excess of 2,9-DMP. Plowman and Power obtained [85] white $Pd(DMP)_2(CN)_2(H_2O)_2$, a non-electrolyte, which did not lose water over P_2O_5. At 110°C for a period of 48 h, water and ligand were lost together, leaving buff $[Pd(DMP)(CN)_2]$. This compound is probably (14) or some similar isomer. The relief of steric compression here is akin to (but greater than) that [1] in the $[M(L)_2]^{2+}$ systems (M = Pd, Pt).



(14)

Similarly [87], the water cannot be removed from $[Pt(DMP)(NO_2)_2]H_2O$ without causing decomposition of the organic molecule. The compounds [87] $Pd(2,9\text{-}DMP)_2X_2.yH_2O$ (X = Cl, $y = 4$; X = Br, $y = 3$; X = I, $y = 2$) which lose water over P_2O_5, but then pick it up again on exposure to the atmosphere, may well be covalent hydrates.

(c) Miller and Prince, in attempting to make *cis*-$[CoP_2(CN)_2](CN)$, found [88] that analyses for C, H, and N were neither satisfactory nor reproducible.

(d) In view of the fact that either water or hydrogen cyanide might saturate the C=N link in phenanthroline, and that all the Schilt—Barbieri compounds are hydrated as solids, (e.g. $Fe(phen)_2(CN)_2(H_2O)_2CHCl_3$ [43] $Ru(bipy)_2(CN)_2(H_2O)_3$ [89]) it is clear that there is a range of possible structures for these compounds, including (1) coordinated cyanide, covalently hydrating waters; (2) coordinating hydroxyls, covalently saturating Reissert-type hydrogen cyanide; (3) various mixed forms of (1) and (2), and those with other proton distributions, rather akin to the platinum(II) species.

The behaviour of the charged species $[ML_3]^{n+}$ in their differing interactions with protic solvents is strongly reminiscent of that of the Schilt—Barbieri compounds, $[Fe(L)_2(CN)_2]$, L being 2,2'-bipyridyl or 1,10-phenanthroline. Here, [70] the electronic absorption spectrum of the iron(II) species is remark-

---

* 8-Hydroxyquinoline is not known to form a Reissert adduct, and 8-methoxyquinoline gave an as yet uncharacterised product [86] under Reissert conditions.

ably dependant upon solvent, although the analogous iron(III) species shows little such dependence. The protonations of the Schilt—Barbieri compounds have been attributed [90] to protonations at the coordinated cyanide group, but then it seems odd that Schilt reports [91] no change in the cyanide stretching frequency, and little change in the overall character of the spectrum in passing from unprotonated to protonated forms. Murmann and Healey, noting this and other effects of acid, concluded [73] that "interaction of protons with the aromatic portion of the ligand seems to be indicated", a conclusion also reached [92] by Baxendale and George in formulating a species $[FeB_3H]^{3+}$ whose presence they deduced from the limiting rate of dissociation of $[FeB_3]^{2+}$ in 2 *N* hydrochloric or 2 *N* sulphuric acids.

(e) The remarkably stable hydroxides and cyanides of such compositions as $[ML_3](OH)_2.xH_2O$ (e.g. [93] $[RuB_3](OH)_2.8H_2O$) or $[ML_3](CN)_2.yH_2O$ (e.g. [89] $[RuB_3](CN)_2.6H_2O$) are not necessarily as formulated.

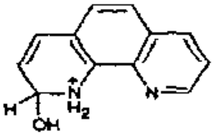
(f) Similarly, sodium hydroxide is said [43] to "suppress the solubility" of $[NiP_3]I_2$ or $(ClO_4)_2$. It may be that the complex species in the solid in the presence of hydroxide is either $[Ni(P)_2(POH)]^+$ or $[Ni(P)(POH)_2]$. The similar recent statement [41] that $[FeP_3]X_2$ proved to be insoluble in saturated aqueous potassium cyanide may reflect the presence of a Reissert-type cyano group, covalently attached to carbon.

B. The nature of the ligands and some derivatives

A number of properties of the ligands, currently unexplained, may arise from covalent hydration.

(a) Linnell and Kaczmarczyk found [94] several spectroscopic anomalies for 1,10-phenanthroline (e.g. in aqueous solutions at pH 11—14, a small shoulder occurred at 290 nm which disappeared on protonation; further, they were unable to account for spectra of mixtures of $[PH]^+$ and [P] in terms of two contributing species alone). They suggested, implicitly, a hydrated species with hydrogen bonding of water to nitrogen as a possible explanation, but it is equally likely that the mono cation is covalently hydrated.

(b) The pK_2 values of both 2,2'-bipyridyl and of 1,10-phenanthroline have long been thought [95] anomalous: pK_1 is small, whereas pK_2 is relatively large. The possible intermediate species (15) may be important.



(15)

(c) Anomalies occur in titration with acids of 1,10-phenanthroline (P). For instance, [96] in adding hydrochloric acid to aqueous P, "K_a increases by ca. 30% from beginning to end of neutralization". Fahsel and Banks confirmed [95] this anomaly, and explained it in terms not only of PH^+, but of higher complexes $[HP_2]^+$ and $[HP_3]^+$. Indeed, solid salts of an ion $[HP_2]^+$ are known [97, 98]. However, there is also the possible explanation in terms of a covalently hydrated monocation, a typical source of anomalies in p*K* in other *N*-heterocyclic systems. The less anomalous behaviour found [95] by Fahsel and Banks for 2,9-dimethyl-1,10-phenanthroline would then correspond exactly to the recommended method [11] of reducing covalent hydration by methyl substitution at the position of hydroxide attack.

(d) A similar unexplained finding [99] is that stability constants for a particular metal complex with B or P measured by pH titration and by other methods often disagree. Martin and Lissfelt found it necessary [100], in studying the equilibrium between Fe^{2+} and 2,2′,2″-terpyridyl, to formulate the product as $[FeT_2H_2]^{4+}$ to obtain an equilibrium constant, for $0.98 < pH < 4.61$. The equilibrium constants measured [101] at 45° for pH's 2.58, 2.45, and 2.24, for $Fe^{2+} + B \rightleftharpoons [FeB_3]^{2+}$ were 12.7, 4.36, and 1.22 ($\times\ 10^{-10}$). To obtain constancy Baxendale and George had to multiply by (H^+) [3]. This need would arise because as the activity of water decreases, so the proportion of non-solvated species (kinetically distinct from the covalent hydrate) increases. Many examples of such behaviour are given later.

(e) Other unexplained variations in properties of the aqueous phenanthrolines may also arise from covalent hydration of the monocation. For example, the distribution coefficients for 5-methyl-1,10-phenanthroline between water and either chloroform or chloroform:carbon tetrachloride showed [102] a slight variation with pH, being largest in the more alkaline conditions*. This may indicate that covalent hydration is more important for the cation than for neutral P. Irving and Mellor also mention [103] the irreproducibility of measurements of distribution coefficient for 2,9 DMP between water and carbon tetrachloride, which perhaps indicates the slow establishment of an equilibrium with solvent. Albert had already commented [63] that the distribution coefficient for a heterocyclic compound between lipids and water was greatly reduced by covalent hydration.

(f) The changes described [95] in the IR spectrum of P in hydrochloric acid (at $P_T:HCl_T > 1$, new bands arise at 1570, 1515, and 1145 cm^{-1}, and the band at 1425 cm^{-1} increases in intensity) are consistent with changes in aromatic character.

(g) The solid salts and derivatives of P with $H^+:P = 0$ or 1 are often hydrated. There is [104] a solid $P.HCl.H_2O$, of unknown structure**; $P_2.H_2Cr_2O_7.2H_2O$ and $P_2.H_2PtCl_6.1\frac{1}{2}(2)H_2O$ are also recorded [105] P and several of its derivatives are remarkably ready to form solid monohydrates. These have high stability. For example, 4-chloro-1,10-phenanthroline and 2-carboxy-phenanthroline are [40] hygroscopic and Grigg and Hall found [106] water of crystallization in 3,8-DMP, 4,7-DMP, 2,4,7,9-tetra MeP, and $5NO_2P$: 3,8-dibutyl-6-bromo-P has methanol of solvation. Fritz et al. gave [107] for the equilibria

* McBryde pointed out [99] that H_2L^{2+} is much too acidic to account for this effect.

** cf. $PH\ ClO_4.\frac{1}{4}H_2O$ obtained [98] after drying in vacuo over P_2O_5.

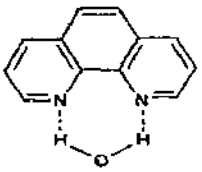
$$\underset{(s)}{\{L.H_2O\}} \rightleftharpoons \underset{(s)}{\{L\}} + H_2O_{(g)}$$

values of ΔH for L = P, 5BrP, and 5-methyl-P, of 14.5*, 13.0, and 13.2 kcal mole^{-1} respectively, with ΔS = 37.1, 33.8, and 33.6 eu. In the light of these results it is no surprise that the mass spectrum of $P.H_2O$ is a superposition of that of P with that of water.

(h) The hemihydrate of 2,9-dimethyl-1,10-phenanthroline forms extremely readily from anhydrous 2,9 DMP. However, the report [103] that it sublimes unchanged is not confirmed [108]. The hemihydrate, on crystallization from water, yields the dihydrate $\{2{,}9\ DMP\}_2H_2O$ and 2,9 DMP $2H_2O$ have IR spectra [108] which differ considerably from 1300—800 cm^{-1}, suggesting that a modification of the phenanthroline nucleus may have occurred.

(j) The salts recently described [87] as $[H_3O]^+[2{,}9\text{-}DMP\ H]^+[PtCl_4]$ and as $[2{,}9\ DMP\ H^+]_2[PtCl_4]2H_2O$ could well be $[2{,}9\text{-}DMP(H_2O)(H^+)_2][PtCl_4]$ and $[2{,}9\text{-}DMP(H_2O)H^+]_2[PtCl_4]$. The *trans*-bis complexes of this ligand may be even more prone (on stereochemical grounds) to covalent hydration or related nucleophilic attack, than the complexes of P itself.

The structure of any such hydrate of phenanthroline is as yet unknown. There is no evidence at all for the frequently quoted (16). Studies by crystallographic morphology and X-ray diffraction have not yet solved the structure of $P.H_2O$, which presents [109] a difficult crystallographic problem, with $Z = 9$ in an ambiguous space group. There is evidence [104] from IR spectroscopy that the monohydrate persists (at least partially) as such in benzene but not in diethyl ether. In marked contrast to the salts of (PH^+), which are commonly crystallized from dilute acid (in which the activity of water is high), the numerous salts of $(PH_2)^{2+}$, which are commonly crystallized from strong HCl (~ 8—10 M), are usually anhydrous, e.g. [110] $[PH_2][MnCl_5]$ and [111] $[PH_2][CoCl_4]$, $[PH_2][CdCl_4]$, $[PH_2][PtCl_6]$.


(16)

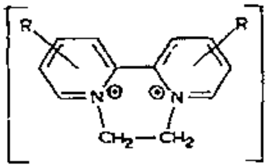
2,2′-Bipyridyl, B, (which, like pyridine, distils in steam) is anhydrous, *trans* and planar [112] when crystalline**. No evidence for covalent solvation has been given, though the pK anomaly might be so explicable. There is the finding [96] of Krumholz which suggests that this anomalous pK_1:pK_2 ratio is found for α:x-bipyridyl, where $x = \alpha', \beta'$, or γ'. As might be expected from

---

* cf. the value [8] 14.60 kcal mole^{-1} for $\{P.D_2O\}_{(s)}$.

** Indeed, from its measured dipole moment of 0.91 D, it is not far [113] from *trans*-planar in benzene.

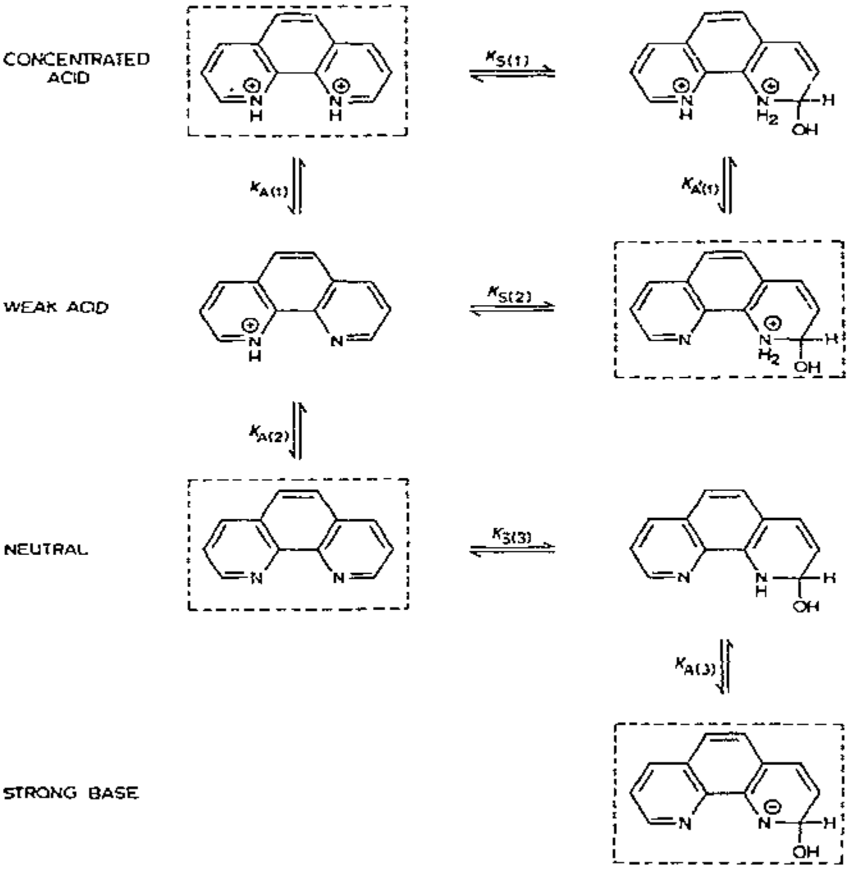
the low activity of water in 8—10 *M* hydrochloric acid, salts of the cation $(BH_2)^{2+}$ are anhydrous, e.g. [110] $[BH_2][MnCl_5]$ and $[BH_2][ReCl_6]$. Whereas the solid dihydrochloride of B is anhydrous the monohydrochloride is [104] dihydrated, $(B)(HCl)2H_2O$. Many salts of the "diquat" series (perhaps best of all models for electronic shifts in 2,2′-bipyridyls coordinated to metal ions) form stable solvates with protic solvents. For example, the compounds shown [114] (17) are all monohydrates, for R = H, 3,3′-dimethyl, or 4,4′-



$(Br)_2 \cdot H_2O$ (17)

dimethyl. 2,2′-Terpyridyl gives [115] 2,2′,2″-terpy $(HCl)_2.H_2O$.

All the properties of phenanthroline (and probably of 2,2′-bipyridyl) are consistent with the equilibria shown in (18).



(18)

$K_{S(1)}$ is probably greater than $K_{S(2)}$, but K_{A1} is also very much larger than K_{A2}. At the concentrations of acid where the di-cation is a significant species, the activity of water is so low that the covalent hydrate is unimportant. By similar arguments, the species in boxes dominate at equilibrium over the acidity range indicated.

The nature of solid species is consistent with this — $[PH_2]^{++}$ salts are anhydrous, but salts of $[PH]^+$ are usually hydrated. The equilibrium, K_{A3}, representing the formation of a conjugate base explains the initially reversible shift with pH of the electronic spectrum [3] of 5-nitro phenanthroline. The spectra of the neutral and alkaline* solutions are related by a clear isosbestic point.

C. *Optical activity*

There are stereochemical consequences [117] of covalent hydration (or of nucleophilic attack at the 2-position). Thus attack at *trans*-bis-complexes (e.g. $[PtB_2]^{2+}$) may lead to net relief from steric strain, and there do not seem to be any obvious disadvantages in terms of non-bonded interactions for addition to tris- and *cis*-bis-octahedral complexes. Further, the saturated carbon centre formed by nucleophilic attack is asymmetric (denoted R or S). In the case of a single ligand, such as phenanthroline, in a non-chiral environment there is no distinction between α- and β-hydroxylation. However, if the metal complex is chiral (denoted D or L) (e.g. *cis*-$[Co(en)_2(py)Cl]^{2+}$, $[FeP_3]^{2+}$, $[Co(en)_2B]^{3+}$) then the relevant equilibria are complicated by the possibilities of diastereoisomerism in the products

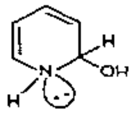
$$\text{D-}[ML_5A]^{n+} + OH^- \overset{K_{DR}}{\rightleftharpoons} \text{D-}[ML_5\text{R-}(AOH)]^{(n-1)+}$$

$$\text{L-}[ML_5A]^{n+} + OH^- \overset{K_{LS}}{\rightleftharpoons} \text{L-}[ML_5\text{S-}(AOH)]^{(n-1)+}$$

$$\text{D-}[ML_5A]^{n+} + OH^- \overset{K_{DS}}{\rightleftharpoons} \text{D-}[ML_5\text{S-}(AOH)]^{(n-1)+}$$

$$\text{L-}[ML_5A]^{n+} + OH^- \overset{K_{LR}}{\rightleftharpoons} \text{L-}[ML_5\text{R-}(AOH)]^{(n-1)+}$$

Since DR and LS are enantiomers, $K_{DR} = K_{LS}$; similarly $K_{DS} = K_{LR}$. However, $K_{DR} \neq K_{DS}$. While, as yet, nothing is known of the ratio $K_{DR} : K_{DS}$, any deviation from 1 would have striking consequences, because of the complicated isomerism shown (19), with three new sources of chirality, (a)—(c).


(19)

---

* The pseudo basic product is of course an internal aldehyde—ammonia. 5-Nitrophenanthroline, with base, slowly gives [116] ca. 40% NH_3!

(a) "Asymmetric carbon atom"
(b) "Asymmetric nitrogen atom"
(c) Skewed diene chromophore

From the enhancement [9] of the circular dichroism of $[Ru(5NO_2P)_3]^{2+}$ in basic solution, it does seem likely that $K_{DR} \neq K_{DS}$.

The present suggestion of the intervention of a covalent hydrate (with the polar substituents C(2)—OH and N—H) gives a plausible account of yet another well-known phenomenon, the Pfeiffer effect. Here, the present suggestion is that the asymmetry of added charged species (anions or cations) is readily transmitted to the covalent hydrate through selective solvation by hydrogen bonding of one of the possible diastereoisomers. In detail, the proposal is as follows

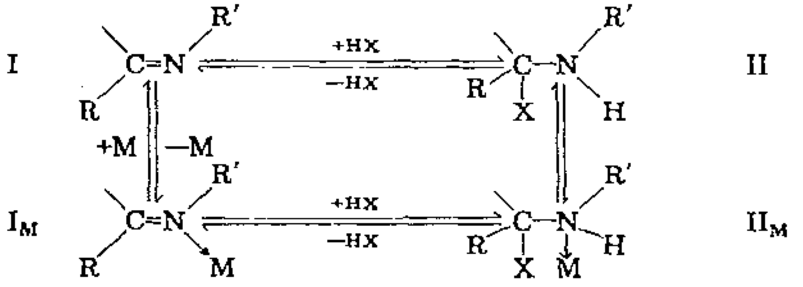
$$D[ML_2(L\alpha OH)] \rightleftharpoons L[ML_2(L\beta OH)]$$

$$D[ML_2(L\beta OH)] \rightleftharpoons L[ML_2(L\alpha OH)]$$

If, say, $D[ML_2(L\beta OH)]$ is more stabilised by the addition of an optically active anion, then the equilibrium will shift toward the D side, giving a net excess of D over L, which is the Pfeiffer effect.

CONCLUSION

The importance of specific solvation in the reactions of coordination compounds is widely acknowledged, though ill understood. For example, equilibria involving interactions of ligand with protic solvent (HS), which are unimportant for a free molecule, may be enhanced for it when complexed as a ligand:



$\{II\}/\{I\} = K_{solv}$ for the free ligand, but in the presence of metal ions

$$\{II_M\}/\{I_M\} = K_{solv}K_{II_M}/K_{I_M}$$

where K_{I_M}, K_{II_M} are stability constants for the appropriate complexes. Depending upon the ratio of these stability constants, binding the ligand molecule to a metal ion may lead to its form II becoming less or more important than when free.

Such effects are known in preparative chemistry: for example, metal complexes of carbinolamines (Dimroth bases) have been made from complexes of

Schiff bases* both with alcohols [119, 120] and water [121, 122]. Such complexes may well be kinetically important at a higher level than their stoichiometric activity would suggest, particularly as the advantageous location of the added solvent (HX) relative to other groups in the molecule may [122] facilitate further reaction.

Carbinolamine formation ("covalent hydration") in complexed pyridines is of obvious significance in coordination chemistry, since the nucleophilic hydroxo group is then adjacent to the metal ion**. Saturation is known to occur [1] in the case of carbon—nitrogen double bonds in 2,2′-bipyridyl and 1,10′-phenanthroline attached to platinum(II); the wider significance of this equilibrium has been presented with respect to some facts and anomalies in the chemistry of complexes of *N*-heterocyclic ligands with metal ions.

This paper suggests that attack by nucleophiles at the 2-position of complexed pyridines may be as relevant and widespread in the general field of coordination chemistry as it is among other quaternized pyridines in the general field of heterocyclic chemistry. In any system involving metal ions and *N*-heterocyclic ligands in protic solvents, equilibria and/or reaction pathways involving solvent attack at the 2-position of the ligand are likely to occur. Such equilibria may be invoked to explain anomalous experimental results.

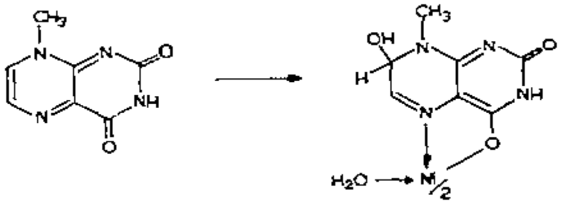
REFERENCES

1 R.D. Gillard and J.R. Lyons, Chem. Commun., (1973) 585.
2 R.D. Gillard, Inorg. Chim. Acta, 11 (1974) L21.
3 J. Burgess and R.H. Prince, J. Chem. Soc., (1965) 4697.
4 D.W. Margerum, J. Amer. Chem. Soc., 79 (1957) 2728.
5 J. Burgess (a) J. Chem. Soc. Dalton, 1061 (1972); (b) Inorg. Chim. Acta, 5 (1971) 133.
6 F.P. Dwyer and E.C. Gyarfas, J. Amer. Chem. Soc., 76 (1954) 6320.
7 A.A. Schilt, Anal. Chem., 35 (1963) 1599.
8 W.W. Brandt and G.F. Smith, Anal. Chem., 21 (1949) 1313.
9 R.D. Gillard and R.E.E. Hill, J. Chem. Soc. Dalton, (1974) 1217.
10 H.C. Longuet-Higgins and C.A. Coulson, J. Chem. Soc., (1949) 971.
11 A. Albert, Angew. Chem., Int. Ed. Engl., 6 (1967) 919.

---

* The chemical properties of pyridines have been compared [118] with those of Schiff bases.

** In the one case of a proposed covalent hydration of an *N*-heterocyclic ligand when attached to a metal ion, the nickel(II) complex of 8-methyl-2,4-pteridinedione, of structure shown,



the hydration was thought [123] to occur remote from the metal ion.

12 T.M. Lowry, Optical Rotatory Power, Longmans, 1935, p. 329ff.

13 A. Albert, in W. Pfleiderer and F.C. Taylor (Eds.), Pteridine Chemistry, Pergamon, Oxford, 1964, p. 143.

14 G.T. Barnes, F.P. Dwyer and E.C. Gyarfas, Trans. Faraday Soc., 48 (1952) 269.

15 N.W. Jacobson, J. Chem. Soc., (C) (1966) 1065.

16 e.g. Y. Inoue and D.D. Perrin, J. Chem. Soc., (1963) 3936.

17 A. Jensen, F. Basolo and H.M. Neumann, J. Amer. Chem. Soc., 80 (1958) 2355.

18 D.W. Margerum, R.I. Bystroff and C.V. Banks, J. Amer. Chem. Soc., 78 (1956) 4211.

19 T.S. Lee, I.M. Kolthoff and D.L. Leussing, J. Amer. Chem. Soc., 70 (1948) 2348.

20 P. Krumholz (a) Nature (London), 163 (1949) 725 and (b) An. Acad. Brasil. Cienc., 22 (1950) 263; Chem. Abs., 45 (1951) 3209.

21 J. Josephsen and C.E. Schäffer, Chem. Commun., (1970) 61.

22 F. Basolo, J.G. Bergmann, R.E. Meeker and R.G. Pearson, J. Amer. Chem. Soc., 78 (1956) 2676.

23 M.L. Tobe, Accounts Chem. Res., 3 (1970) 377.

24 F. Blau, Monatsh. Chem., 10 (1898) 647.

25 N.R. Davies and F.P. Dwyer, Trans. Faraday Soc., 50 (1954) 244.

26 F.P. Dwyer and E.C. Gyarfas, J. Amer. Chem. Soc., 74 (1952) 4699.

27 C.S.G. Phillips and R.J.P. Williams, Inorganic Chemistry, Vol. 2, Oxford Univ. Press, 1967, p. 360.

28 W.G. Barb, J.A. Baxendale, P. George and K.R. Hargrave, Trans. Faraday Soc., 51 (1955) 935.

29 G. Nord and O. Wernberg, J. Chem. Soc. Dalton, (1972) 866.

30 D.M. Hercules and F.E. Lytle, J. Amer. Chem. Soc., 88 (1966) 4745.

31 A. Albert and W.L.F. Armarego, Advan. Heterocycl. Chem., 4 (1965) 1.

32 (a) B.E. Halcrow and W.O. Kermack, J. Chem. Soc., (1946) 155;
(b) A. Calderbank, D.F. Charlton, J.A. Farrington and R. James, J. Chem. Soc., (Perkin I) (1972) 138.

33 E.H. Rodd, Chemistry of Carbon Compounds, Vol. IVA, Elsevier, 1st edn., 1957, p. 694.

34 F.P. Dwyer and E.C. Gyarfas, J. Amer. Chem. Soc., 76 (1954) 6320.

35 A.A. Schilt, Anal. Chem., 35 (1963) 1599.

36 W.W. Brandt and J.P. Wright, J. Amer. Chem. Soc., 76 (1954) 3082.

37 B. Kratochvil and J. Knoeck, J. Phys. Chem., 70 (1966) 944.

38 K. Wallenfels, in H. Sund (Ed.), Pyridine Nucleotide Dependent Dehydrogenases, Springer, Berlin, 1970.

39 F.D. Popp, Advan. Heterocycl. Chem., 9 (1968) 1.

40 E.J. Corey, A.L. Borror and T. Foglia, J. Org. Chem., 30 (1965) 288.

41 R.D. Archer, L.J. Suydam and D.D. Dollberg, J. Amer. Chem. Soc., 93 (1971) 6837.

42 G. Nord, Acta Chem. Scand., 27 (1973) 743.

43 D.W. Margerum and L.P. Morgenthaler, J. Amer. Chem. Soc., 84 (1962) 706.

44 B. Martin, W.R. McWhinnie and G.M. Waind, J. Inorg. Nuclear Chem., 23 (1961) 207.

45 N.V. Sidgwick's "Organic Chemistry of Nitrogen", 2nd edn., (by T.W.J. Taylor and W. Baker), Oxford Univ. Press, 1937, p. 531.

46 H.J. den Hartog and J.P. Wibaut, Rec. Trav. Chim., 55 (1936) 122.

47 F.H. Burstall, J. Chem. Soc., (1938) 1662.

48 Ref. 45, p. 525.

49 H.M. Irving and A. Hampton, J. Chem. Soc., (1955) 430.

50 N.R. Davies and F.P. Dwyer, unpublished work quoted in ref. 25.

51 A. Jensen, F. Basolo and H.M. Neumann, J. Amer. Chem. Soc., 80 (1958) 2354.

52 N.R. Davies and F.P. Dwyer, Trans. Faraday Soc., 48 (1952) 244.

53 N.P. Davies and F.P. Dwyer, Trans. Faraday Soc., 50 (1954) 1325

54 H.P. Bennetto and E.F. Caldin, J. Chem. Soc., A, (1971) 2207.

55 T.S. Lee, I.M. Kolthoff and D.L. Leussing, J. Amer. Chem. Soc., 70 (1948) 3596.

56 A.F. Richards, J.H. Ridd and M.L. Tobe, Chem. Ind., (1963) 1726.

57 E.L. Wehry and R.A. Ward, Inorg. Chem., 10 (1971) 2660.
58 A.W. Addison, Ph.D. thesis, University of Kent, 1970.
59 J.G. Gibson and E.D. McKenzie, J. Chem. Soc., (1969) 3627.
60 D.E. Ryan, Analyst (London), 77 (1952) 46.
61 G.F. Duffin, Advan. Heterocycl. Chem., 3 (1964) 1.
62 D.J. Fry, J.D. Kendall and A.J. Morgan, J. Chem. Soc., 1960, 5062.
63 A. Albert, in ref. 13, p. 127.
64 F. Basolo and R.G. Pearson, Mechanism of Inorganic Reactions, New York, 2nd edn., Wiley, 1967, p. 324.
65 J.A. Broomhead and F.P. Dwyer, Aust. J. Chem., 16 (1963) 63.
66 C.M. Harris and E.D. McKenzie, J. Inorg. Nucl. Chem., 25 (1963) 171.
67 T. Kurucsev, A.M. Sargeson and B.O. West, J. Phys. Chem., 61 (1957) 1567.
68 D. Gere and C.E. Meloan, J. Inorg. Nucl. Chem., 25 (1963) 1507.
69 F.P. Dwyer, E.C. Gyarfas and M.F. O'Dwyer, J. Proc. Roy. Soc., N.S.W., 89 (1956) 146.
70 A.A. Schilt, J. Amer. Chem. Soc., 82 (1960) 3000.
71 E.A. Healey and R.K. Murmann, J. Amer. Chem. Soc., 79 (1957) 5827.
72 G.B. Briscoe, M.E. Fernandopulie and W.R. McWhinnie, Inorg. Chim. Acta, 6 (1972) 598.
73 R.K. Murmann and E.A. Healey, J. Amer. Chem. Soc., 83 (1961) 2092.
74 E.D. McKenzie, Coord. Chem. Rev., 6 (1971) 187.
75 L.H. Berka, R.R. Gagne, G.E. Philippon and C.E. Wheeler, Inorg. Chem., 9 (1970) 2705.
76 R.E. DeSimone and R.S. Drago, J. Amer. Chem. Soc., 92 (1970) 2343.
77 G.T. Morgan and F.H. Burstall, J. Chem. Soc., (1934) 965.
78 S.E. Livingstone and B. Wheelahan, Aust. J. Chem., 17 (1964) 219.
79 G.T. Morgan and F.H. Burstall, J. Chem. Soc., (1938) 1672.
80 R.N. Sylva and H.A. Goodwin, Aust. J. Chem., 20 (1967) 479.
81 A.A. Schilt, J. Amer. Chem. Soc., 81 (1959) 2966.
82 C.A. Barbieri, Atti Acad. Naz. Lincei, 20 (1934) 273.
83 J. Brady, F. Dachille and C.D. Schmulbach, Inorg. Chem., 2 (1963) 803.
84 F. Feigl and G.B. Heisig, J. Amer. Chem. Soc., 73 (1951) 5630.
85 R.A. Plowman and L.F. Power, Aust. J. Chem., 24 (1971) 309.
86 A.R. Pinnington, D. Phil. thesis, Oxford, 1956; personal communication from H.M. Irving.
87 R.A. Plowman and L.F. Power, Aust. J. Chem., 24 (1971) 303.
88 J.D. Miller and R.H. Prince, J. Chem. Soc., (1969) 519.
89 A.A. Schilt, J. Amer. Chem. Soc., 85 (1963) 904.
90 N.K. Hamer and L.E. Orgel, Nature (London), 190 (1961) 439.
91 A.A. Schilt, J. Amer. Chem. Soc., 82 (1960) 5279.
92 J.H. Baxendale and P. George, Trans. Faraday Soc., 46 (1950) 736.
93 F.H. Burstall, J. Chem. Soc., (1936) 173.
94 R.H. Linnell and A. Kaczmarczyk, J. Phys. Chem., 65 (1961) 1196.
95 M.J. Fahsel and C.V. Banks, J. Amer. Chem. Soc., 88 (1966) 878.
96 P. Krumholz, J. Amer. Chem. Soc., 73 (1951) 3487.
97 M.P. Marzocchi and P. Paoletti, Chem. Commun., (1968) 1063.
98 J.V. Rund and P.C. Keller, J. Chem. Soc., A, (1970) 2827, where NMR results are given.
99 W.A.E. McBryde, Can. J. Chem., 43 (1965) 3472.
100 R.B. Martin and J.A. Lissfelt, J. Amer. Chem. Soc., 78 (1956) 938.
101 J.H. Baxendale and P. George, Trans. Faraday Soc., 46 (1950) 55.
102 W.A.E. McBryde, D.A. Brisbin and H.M. Irving, J. Chem. Soc., (1962) 5245.
103 H.M. Irving and D.H. Mellor, J. Chem. Soc., (1962) 5237.
104 I.R. Beattie and M. Webster, J. Phys. Chem., 66 (1962) 115.
105 R.C. Elderfield, Heterocyclic Compounds, Vol. 7, Wiley (New York), p. 350.
106 E.C.M. Grigg and J.R. Hall, Aust, J. Chem., 15 (1962) 864.
107 J.S. Fritz, F.W. Cagle and G.F. Smith, J. Amer. Chem. Soc., 71 (1949) 2480.

108 E.C.M. Grigg, J.R. Hall and R.A. Plowman, Aust. J. Chem., 15 (1962) 425.
109 (a) C. Donnay, J.D.H. Donnay and M.J.C. Harding, Acta Crystallogr., 19 (1965) 688;
(b) Professor D. Rogers, Imperial College, personal communication.
110 H.A. Goodwin and R.N. Sylva, Aust. J. Chem., 18 (1965) 1743.
111 H.A. Goodwin and R.N. Sylva, Aust. J. Chem., 19 (1966) 1735.
112 L.L. Merritt and E.D. Wiberley, Acta Crystallogr., 9 (1956) 801.
113 P.E. Fielding and R.J.W. LeFevre, J. Chem. Soc., (1951) 1811.
114 R.F. Homer and T.E. Tomlinson, J. Chem. Soc., (1960) 2498.
115 K. Nakamoto, J. Phys. Chem., 64 (1960) 1420.
116 E. Bielli and R.D. Gillard, unpublished work following ref. 9.
117 R.D. Gillard and B.T. Heaton, J. Chem. Soc., A, (1969) 451.
118 E.H. Rodd, Chemistry of Carbon Compounds, vol. IVA, Elsevier, 1st edn., 1957, p. 506.
119 C.M. Harris and E.D. McKenzie, Nature (London), 196 (1962) 670;
M. Creasey, E.D. McKenzie and S. Yates, J. Chem. Soc., A, (1971) 2677.
120 B.F. Hoskins and F.D. Williams, Chem. Commun., (1966) 798.
121 D.H. Busch and J.C. Bailar, J. Amer. Chem. Soc., 78 (1956) 1137.
122 R.D. Gillard and R. Wootton, J. Chem. Soc., B, (1970) 364.
123 P. Hemmerich in W. Pfleiderer and F.C. Taylor (Eds.), Pteridine Chemistry, Pergamon, 1964, p. 143.