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An Explanation for Anomalies among Complexes of N-Heterocyclic Ligands

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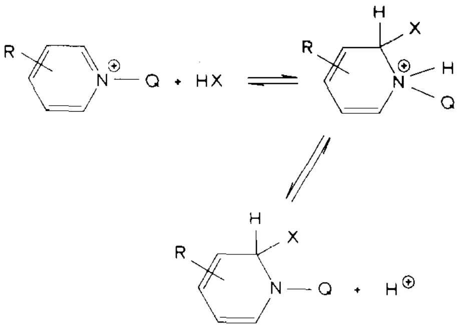
In aqueous solutions of the well-studied complex compounds of the N-heterocyclic ligands (L) 2,2′-bipyridyl and 1,10-phenanthroline (phen), there are many long-standing unexplained properties, kinetic, thermodynamic and spectroscopic. For example: i) the rates for substitution in $[\mathrm{FeL}_3]^{2+}$ by the nucleophiles (N) hydroxide[1] and cyanide[2] include terms in $[\mathrm{FeL}_3]$ [N]; ii) the rates of reduction of $[\mathrm{FeL}_3]^{3+}$ by hydroxide are[3] $k[\mathrm{FeL}_3^{3+}]\,[\mathrm{OH}^-]$; iii) the redox potentials (and consequently reactivities) of $[\mathrm{ML}_3]^{2+}$ and of $[\mathrm{M(terpy)}_2]^{2+}$ (M = Fe, Ru, Os) vary remarkably[4] with acidity: $[\mathrm{ML}_3]^{3+}$ is very unstable in the presence of hydroxide, suggesting[5] "a special interaction of hydroxide ions with this type of complex ion"; iv) the partial molar entropies in water for $[\mathrm{ML}_3]^{3+} + e \rightarrow [\mathrm{ML}_3]^{2+}$ are[6] *negative* (whereas in aprotic acetonitrile, they are positive, as expected); v) polymorphs (very common among solvates of $[\mathrm{ML}_3](\mathrm{X})_n$) may differ remarkably in properties; thus,[7] bright green $[\mathrm{Ru(bipy)}_3](\mathrm{PF}_6)_3\cdot n\mathrm{H}_2\mathrm{O}$ is very unstable toward reduction; a more stable crystalline form with 2 or 3 $\mathrm{H}_2\mathrm{O}$ exists, and the anhydrous salt is stable; vi) the electronic spectra of 5-nitrophenanthroline[8] and of $[\mathrm{M(5\text{-}NO_2\text{-}phen)}_3]^{2+}$ (M = Fe,[8] Ru[9]) show a reversible change with pH. The circular dichroism for the exciton region of the resolved ruthenium complex shows[9] a concomitant reversible decrease, suggesting that the ligand is being altered. However, no conjugate base is involved, since there is[10] no exchange of C–H in alkaline $\mathrm{D}_2\mathrm{O}$; vii) $[\mathrm{Pt(L)}_2]^{2+}$ gives a reversible spectroscopic change with pH (with apparent pK's around 9) because[10a] hydroxyl ion attacks the ligand at the position adjacent to nitrogen.

It is the purpose of this letter to make more explicit the original suggestion[10a,11] that any quaternized N-heterocycle, whether the quaternizing agent (Q) is proton, alkyl, aryl, aroyl, oxide, *or metal ion,* may participate in the equilibria (1) and (2) shown.



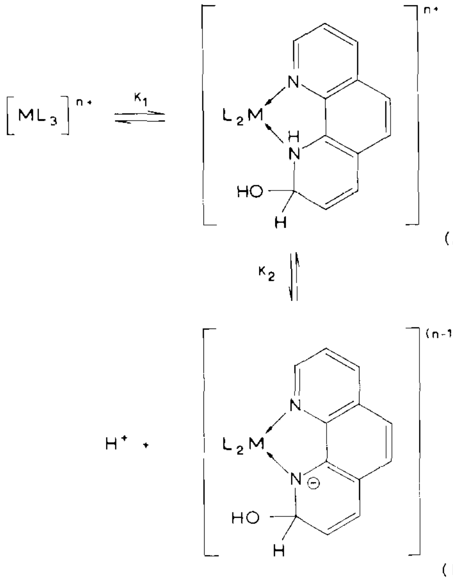
(1)

(2)

Nearly all the anomalies among coordination compounds involve cyanide, hydroxide, or alkoxide. These are, of course, the classical nucleophiles for the 2-position of quaternized heterocycles (*i.e.*, HX = HCN, $\mathrm{H}_2\mathrm{O}$, or HOR).

Equilibrium (1) is typified by covalent hydration[12] (HX = $\mathrm{H}_2\mathrm{O}$, Q = H^+), or the Reissert reaction (HX = HCN, Q = $\mathrm{C}_6\mathrm{H}_5\mathrm{CO}$). The product of equilibrium (2) is exemplified by the pseudo-base phenomenon[13] (X = OH^-, Q = CH_3 *etc.*), or by the attack[10a] of hydroxyl ion on metal complexes (X = OH^-, Q = Pd^{2+} or Pt^{2+}).

An example of the proposed equilibria is given in full



(A)

(B)

The sizes of the equilibrium constants for solvation (K_1) and for acid dissociation of the solvent (K_2) will depend upon the individual case. Clearly, however,

K_1 for compounds of highly charged metal ions will be greater than for those less highly charged, *i.e.* an aqueous solution of $[ML_3]X_3$ will contain more of species (A) and (B) than will an equimolar solution of $[ML_3]X_2$.

Species B is proposed as the intermediate in the substitution by hydroxide (and *cf.* cyanide) at $[Fe(L)_3]^{2+}$ or the rapid reduction of $[M(L)_3]^{3+}$ by hydroxide. Hydrated salts will often contain species A.

The explanation of many anomalies in the chemistry of $[M(L)_3]^{n+}$ using the present suggestion has been the subject of a lecture,[14] which will be published elsewhere. The present intention is to suggest that in any study involving an N-heterocyclic ligand in protic media, the presence (and possibly high intramolecular reactivity) of species like A and B should be considered.

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