Novel Species in Ruthenium–Bipyridyl Systems

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Summary Bipyridyl and related ligands on ruthenium(II) are shown to behave as if quaternized, giving pseudobases with hydroxide ion.

Chelated compounds of ruthenium(II) with 1,10-phenanthroline and 2,2′-bipyridyl (L) have been known for many years,[1,2] and were among the first co-ordination compounds to reveal the potential of 'bio-inorganic' agents. Further, much interest has recently been generated by reports that such compounds are capable of catalysing the photo-dissociation of water.[3] The apparent simplicity of these co-ordination compounds in aqueous media is illusory, and we draw attention here to a feature which must be considered in a full understanding of their properties, including their photochemistry.

When compounds of ions of the type $[RuL_2L'_2]^{2+}$ (L = 1,10-phenanthroline, 2,2′-bipyridyl, 5-nitro-1,10-phenanthroline, or 5,5′-dimethyl-2,2′-bipyridyl; L′ = pyridine or 4-methylpyridine) in aqueous solutions are treated with such nucleophiles as hydroxide, cyanide, or alkoxide ions, new species are formed, with new electronic spectra (Figure 1). These changes are reversible on acidification; equilibria of the type shown[4] in equation (1) are clearly operative.

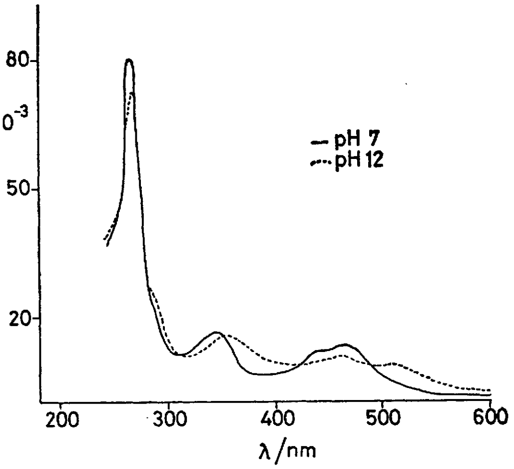
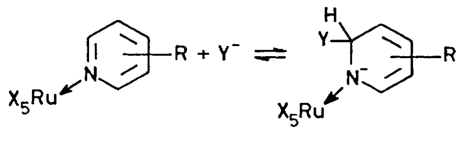


Figure 1

The ^1H n.m.r. spectrum of $[Ru(bpy)_2(py)_2]Cl_2$ (bpy = 2,2′-bipyridyl, py = pyridine) in neutral solution is shown in Figure 2 (a). On adding alkali, a new spectrum is obtained [Figure 2 (b)]. The changes which occur are rapidly and fully reversed on acidification, so the compound is not losing pyridine.



(1)

(Y = OH, OR, CN, *etc.*)

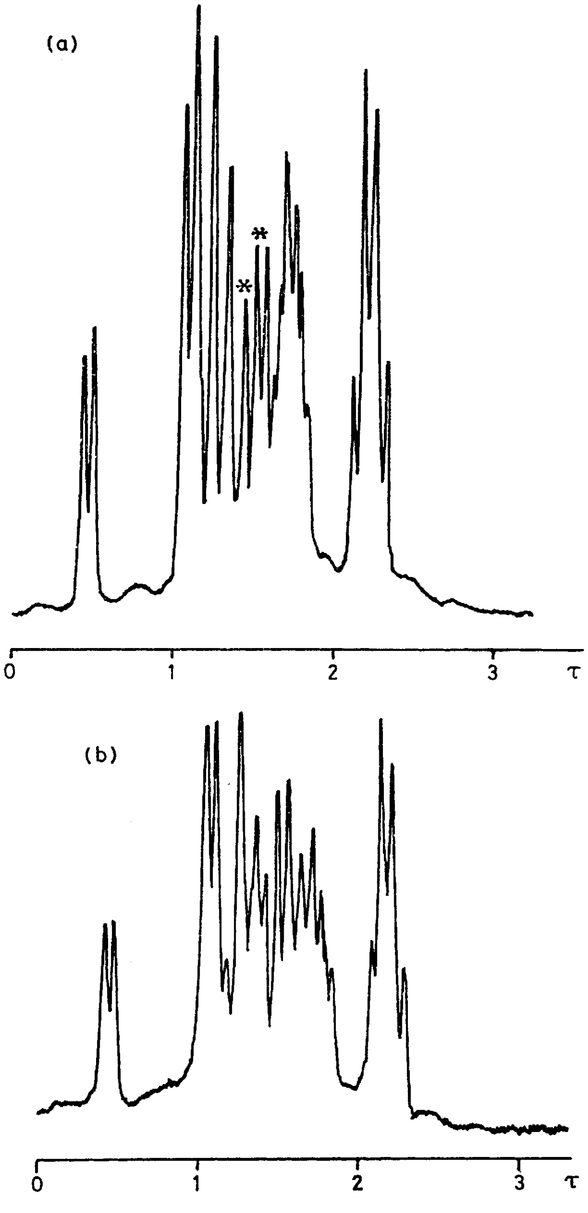


Figure 2

Compound $[Ru(bpy)_2(py)_2]Cl_2$ (Figure 3) has a two-fold axis of symmetry. Its n.m.r. spectrum is made up of a total of five doublets and six triplets due to signals from pyridine and bipyridyl protons. Using the complex ion containing deuteriopyridine and the spectrum of $[Ru(bpy)_3]^{2+}$ we assign the doublet at τ 1·10 to α(pyridine) and the doublets at τ 0·45 and 1·45 and to H-6′ and H-6, respectively. The H-6′ proton, next to pyridine, will be deshielded relative to H-6.

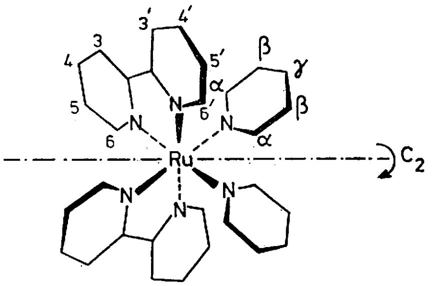
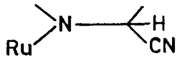


Figure 3

The n.m.r. spectrum in alkali is typical of a chemically exchanging system, where the equilibrium constant is small, such as that shown in equation (1). The signal (indicated by asterisks) assigned to H-6 is most affected, which indicates that the adduct has the hydroxide ion attached at C-6. In this position the hydroxide ion may subsequently displace pyridine in a concerted fashion.

The present observation of the ready formation of a pseudo-base in *N*-heterocyclic ligands offers a unified explanation for numerous phenomena in ruthenium chemistry. For example: (a) while substitution at Ru^{II} is generally slow, the complexes $[Ru(terpy)(bpy)X]^+$, $[Ru(bpy)_2X_2]$, and $[Ru(phen)_2X_2]$ (X = Cl, Br, *etc.*, terpy = 2,2′,2″-terpyridyl, phen = 1,10-phenanthroline) hydrolyse very rapidly to the per-aquo-species.[5] A pseudo-base presumably forms at one or more of the 6-positions in the molecule and migration of the hydroxy group to ruthenium then facilitates halide ion loss. Since pyridine is not so good a leaving group as the chloride ion, we can observe the spectral changes which accompany hydroxide ion attack at the bis-pyridine complex. If however, the temperature is raised, pyridine is lost and irreversible changes occur; (b) in *o*-dichlorobenzene, attack by cyanide ion upon $[Ru(phen)_2(py)_2]^{2+}$ is rapid and shows second-order kinetics,[6] suggesting a Reissert-adduct (**A**) as intermediate.



(A)

Related behaviour may underly many anomalies in the chemistry of compounds formed from *N*-heterocycles and metal ions. Hydroxide ion promotes the hydrolysis of $ML_2Cl_2^+$ (M = Cr or Co; L = bpy or phen)[7] (*cf.* RuL_2X_2 above) presumably through the intermediacy of a pseudo-base. Among recent examples, we note the anomalously rapid ('almost diffusion controlled') rates[8] of the reaction shown in equation (2).

$$MeHgL^+ + OH^- \rightarrow MeHgOH + L \qquad (2)$$

Wherever metal ions and *N*-heterocyclic ligands are together in protic media, the apparent (and invariably assumed) simplicity of the system may in reality be spoilt by equilibria of the kind we describe here.

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