# A Pseudo-base of Pyridine

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*Summary* Hydroxide ion readily adds to the co-ordinated N-heterocycles in the ions *trans*-$[PtL_4Cl_2]^{2+}$ (L = pyridine or 4-methylpyridine).

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Organic pseudo-bases formed from quaternized N-heterocycles are well known.[1] There are a number of cases where a chelated N-heterocycle (*e.g.* a 1,10-phenanthroline) co-ordinated to a metal ion adds a hydroxide ion (or some other nucleophile) at an aromatic carbon to give a species like a pseudo-base. We report here the first case of such an addition to a co-ordinated pyridine. This is particularly significant in that there seems[1] to be no physical evidence for pseudo-base formation by *N*-methylpyridinium itself.

Kinetically inert *trans*-dichlorotetrakis(pyridine)platinum(IV) nitrate, freshly dissolved in water, gives an acid solution, but no chloride ion is initially released. This fact had been mentioned[2] some years ago, without explanation. As an example, we find that a $10^{-2}$ M solution has a pH of 2·87. We attribute this formation of free protons to the formal equilibrium (1); (py = pyridine, pyOH = 2-hydroxy-1,2-dihydro-1-pyridyl). The actual mechanism

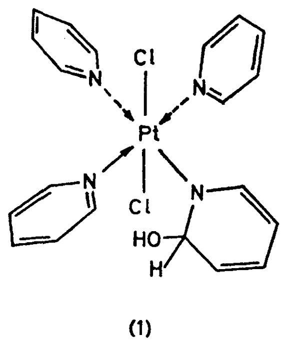
$$[Pt(py)_4Cl_2]^{2+} + H_2O \rightleftharpoons [Pt(py)_3(pyOH)Cl_2]^{+} + [H^{+}] \qquad (1)$$

seems (on charge grounds) likely to involve nucleophilic attack by hydroxide ion, followed by a much slower release of chloride ion, with the formation of the chlorohydroxoplatinum(IV) cation, equation (2).

$$trans\text{-}[Pt(py)_3(pyOH)Cl_2]^{+} \rightarrow [Pt(py)_4Cl(OH)]^{2+} + Cl^{-} \qquad (2)$$

We take this displacement of chloride by hydroxide to be intramolecular, corresponding to a shift of hydroxide from carbon to platinum.

Assuming[†] that platinum(IV) remains six-co-ordinated, the structure of the singly charged pseudo-base intermediate is as shown in the Figure.



(1)

Figure

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[†] Clearly, the addition of one hydroxide (or other) ion to a kinetically inert six-co-ordinated complex compound without expulsion of an initial ligand could represent either an expansion of co-ordination number to 7, or attack at the co-ordinated ligand. In other cases {*e.g.* additions to $[Cr(bipy)_3]^{3+}$ (bipy = 2,2′-bipyridyl)}, other workers have favoured the seven-co-ordinate structure. We take our present view because octahedral six-co-ordination in co-ordination cations containing N-heterocyclic and halide ligands is much more common than any other. In particular, for platinum (IV), seven-co-ordination has not been discovered.

Two reasons favour the 2-hydroxy-compound rather than the 4-isomer. First, the $\gamma$-picoline analogue behaves in an entirely similar fashion, and the received view for organic systems is that methyl substitution inhibits nucleophilic addition at the site concerned. Secondly, the rapid hydrolysis (in this and other metal complexes containing the *cis*-1-halogeno-2-heterocyclic nitrogen moiety) is best explained by the structure shown. The true situation may well involve attack at either site, with the 4-isomer as a 'dead-end' for subsequent chloride replacement.

From measurements of pH, we have evaluated from equation (3) the apparent acid dissociation constant (at

$$K = [\mathrm{Pt(py)_3(pyOH)Cl_2}^+][\mathrm{H}^+]/[\mathrm{Pt(py)_4Cl_2}^{2+}] \qquad (3)$$

25 °C) of complex (**1**) as $10^{-3}$.[4] The value for the $\gamma$-picoline analogue is the same. The equilibrium constant for the addition of hydroxide (equation 4) is therefore $10^{10\cdot 6}$.

$$[\mathrm{Pt(py)_4Cl_2}]^{2+} + \mathrm{OH}^- \rightleftharpoons [\mathrm{Pt(py)_3(pyOH)Cl_2}]^+ \qquad (4)$$

This compares very favourably with values[1,3] for organic quaternary pyridinium ions; roughly speaking, in the present case, platinum (IV) activates pyridine much more than an *N*-methyl group does. Polarization of N-heterocycles by metal ions in the presence of nucleophiles may result in the presence of such pseudo-basic species as (**1**), often at surprising levels. The phenomenon is likely to be of widespread occurrence; certainly any complex of an N-heterocycle with a metal ion in a high oxidation state will contain some very electrophilic carbon atoms. For example, the remarkable properties of the family of *trans*-dihalogenotetrakispyridinerhodium(III) cations (autocatalytic solvolyses, antibacterial action) probably arise from the presence of pseudo-bases like (**1**).

It has recently been said[4] that 'the chemistry of this important and large group of complexes has been relegated (*sic*) to . . . . the organic chemistry of the ligands' by observations of the present kind. Be that as it may, the link between one major branch of inorganic chemistry and a major branch of organic chemistry seems likely to offer useful explanations for many and varied phenomena in the highly important systems involving an N-heterocycle, a metal ion, and a nucleophile.

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[1] J. W. Bunting, *Adv. Heterocycl. Chem.*, 1979, **25**, 1 and references therein.

[2] A. A. Grinberg, Kh. I. Gil'dengershel', and V. F. Budanova, *Russ. J. Inorg. Chem.*, 1966, **11**, 1351.

[3] C. T. Hughes, R. D. Gillard, W. S. Walters, and P. A. Williams, *J. Chem. Soc., Dalton Trans.*, 1979, 1769.

[4] O. Farver, O. Mønsted, and G. Nord, *J. Am. Chem. Soc.*, 1979, **101**, 6118.