Letters

'A pseudo-base of pyridine': A refutation

A WELL known feature of the preparative chemistry of co-ordination complexes is their tendency to crystallize as acid salts. For tetrakis(pyridine) complexes of Pt^{IV} this has been known for nearly a century. Thus Gmelin[1] lists not only *trans*-$[Pt(py)_4Cl_2][NO_3]_2{\cdot}H_2O$ but also *trans*-$[Pt(py)_4Cl_2][NO_3]_2{\cdot}2HNO_3{\cdot}2H_2O$, both of which were prepared in 1886.[2] In agreement with this, Grinberg *et al.*,[3] during the preparation of the pure anhydrous *trans*-$[Pt(py)_4Cl_2][NO_3]_2$, found it necessary to wash the crude product '. . . until there was no acid reaction to methyl orange (a long time!), . . .'

Recently, aqueous solutions of a *trans*-$[Pt(py)_4Cl_2]^{2+}$ nitrate (formula and analysis not given) have been reported[4] to be acidic. The pH of a freshly prepared 0.01 mol dm^{-3} solution is said to be 2.87 and this is taken as evidence for the formation of a pseudo-base of a co-ordinated pyridine. In an attempt to support this thesis the authors of ref. 4 have apparently misinterpreted the earlier work[3] which clearly states that a millimolar aqueous solution prepared from pure *trans*-$[Pt(py)_4Cl_2][NO_3]_2$, on standing at room temperature for 20 h, both released about 0.94% of Cl^- and became acid. This earlier work[3] also includes the explanation that this acidity (pH *ca.* 5.1) arises from a substitution reaction of co-ordinated Cl^- by OH^-. The much lower pH values observed by the authors of ref. 4 in aqueous solutions of their salt must therefore arise from an acid impurity. Thus, for example, 5% of the known HNO_3 adduct in an incompletely washed product will account for the data in ref. 4.

The present refutation of the continuing attempts to apply the pseudo-base hypothesis to describe the chemical properties of aromatic amine complexes is particularly significant at this time because recently *all* the reported structural evidence for pseudo-base formation in solutions of both free and co-ordinated 2,2′-bipyridine and 1,10-phenanthroline has also been shown to be spurious.[5,6]

OLE MØNSTED
GWYNETH NORD

Chemistry Department I
Inorganic Chemistry
H.C. Ørsted Institute
Universitetsparken 5
DK-2100 *Copenhagen Ø*
Denmark

[1/240 *Received*, 15*th June*, 1981]

---

[1] 'Gmelins Handbuch der Anorganischen Chemie,' Verlag Chemie, Weinheim, 1957, vol. 68, p. 510.

[2] S. G. Hedin, *Acta Univ. Lund., Sect.* 2, 1886, **22**, 1.

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

[4] R. D. Gillard and R. J. Wademan, *J. Chem. Soc., Chem. Commun.*, 1981, 448.

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

[6] G. Nord and B. V. Agarwala, *Acta Chem. Scand., Ser. A*, 1981, **35**, 231, and refs. therein.

GILLARD and WADEMAN reply. We recently reported[1] that '. . . *trans*-dichlorotetrakis(pyridine)platinum(IV) nitrate, freshly dissolved in water, gives an acid solution, but no chloride ion is initially released.' Earlier workers had noted the same peculiarity.

Leonora and Evstaf'eva,[2] distinguishing between this nitrate and the nitric acid adduct (hydrogendinitrate) of the same cation, said, '. . . the pH of a 0.001 mol dm^{-3} solution of $[Pt(py)_4Cl_2][H(NO_3)_2]_2$ is 3.10, whereas the pH of a 0.001 mol dm^{-3} solution of $[Pt(py)_4Cl_2][NO_3]_2$ is 5.10 (ref. 2).' Their reference 2 is to a paper by Grinberg *et al.*[3] Grinberg *et al.*[3] had said 'The potentiometric titration of the tetramine $[Pt(py)_4Cl_2][NO_3]_2$ is specially interesting; an amido-reaction by the equation $M \cdots R \rightleftharpoons M{-}R^- + H^+$ is ruled out for this substance.' Furthermore, 'The great acidity of the salt $[Pt(py)_4Cl_2][NO_3]_2$ (the pH of a 0.001 mol dm^{-3} solution is 5.10) may be due either to the presence of outer-sphere association of the type $[Pt(py)_4Cl_2]^{2+} + OH^- \rightleftharpoons \{[Pt(py)_4Cl_2]OH\}^+$ with *subsequent* introduction of OH^- into the inner sphere . . . '

We reiterate that *fresh* aqueous solutions of $[PtL_4Cl_2][NO_3]_2$ (L = py or 4-methylpyridine) are acidic, and do not *initially* contain free chloride ion. Our equilibrium constants for addition of hydroxide to the cations agree fairly well with that calculated from the results of ref. 2.

The existence of hydrogendinitrate salts of these pyridine complexes of the platinum metals is well known to us; indeed, we *discovered*[4] the hydrogendinitrate ion as its rhodium(III) salt, *trans*-$[Rh(py)_4Cl_2][H(ONO_2)_2]$. In a further recent paper[5] on hydrogendinitrates we re-examined the variously reported reactions of nitric acid with platinum–pyridine complexes and the existence of nitric acid adducts.

The Letter from Mønsted and Nord assembles the following facts and comments. (i) The existence of acid nitrates of co-ordination compounds. Yes, about half of these were discovered in our laboratory. (ii) The specific existence of these for tetrakis(pyridine)platinum complexes. Yes, this is discussed in ref. 5. (iii) The necessity[3] to wash crude *trans*-$[Pt(py)_4Cl_2][NO_3]_2$ '. . . until there was no acid reaction to methyl orange (a long time!) . . .' This is indeed necessary. (iv) '. . . Formula and analysis not given . . . .' The formula is that in the reference given[1] for the preparation, which we had no difficulty in following to the letter. The analyses of our product were (16th October, 1979; calculated values in parentheses): C, 33.5 (33.9); H, 2.85 (3.25); N, 12.0 (11.9)%. Other properties (i.r. and electronic spectra, thermogravimetric behaviour) were characteristic. (v) '. . . Misinterpreted the earlier work . . .' (present ref. 3). See quotations above. (vi) '. . . all the reported structural evidence . . . spurious.[5,6]' These references 5 and 6 are concerned only with two complexes of platinum(II); there is a good deal of structural evidence (including chiroptical spectra) on complexes of other metal ions (including octahedral ones), on which those papers offer no comment.

We reiterate that [1] '. . . 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 . . .', despite such remarks [6] as '. . . the chemistry of this important and large group of complexes has been relegated (*sic*) to . . . the organic chemistry of the ligands.'

R. D. GILLARD
R. J. WADEMAN

Inorganic Chemistry Laboratories
University College
P.O. Box 78
*Cardiff CF*1 1*XL*
Wales

[1] R. D. Gillard and R. J. Wademan, *J. Chem. Soc., Chem. Commun.*, 1981, 448.

[2] T. N. Leonora and O. I. Evstaf'eva, *Russ. J. Inorg. Chem.*, 1975, **20**, 746.

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

[4] R. D. Gillard and R. Ugo, *J. Chem. Soc. A*, 1966, 549.

[5] Nabila S. Al-Zamil, E. H. M. Evans, R. D. Gillard, D. W. James, T. E. Jenkins, R. J. Lancashire, and P. A. Williams, *Polyhedron*, in the press.

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