Thermal solid state synthesis of coordination complexes from hydrogen bonded precursors†

Christopher J. Adams, Paul C. Crawford, A. Guy Orpen,* Thomas J. Podesta and Benjamin Salt

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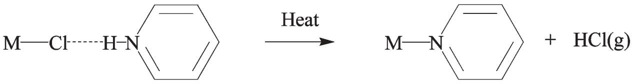
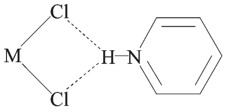
Thermal dehydrochlorination of crystalline 4-picolinium salts of $[PtCl_4]^{2-}$ and $[PdCl_4]^{2-}$ leads to formation of *trans*-$[MCl_2(4\text{-picoline})_2]$ (M = Pt, Pd).

We have developed and applied a strategy for synthesis of novel crystal structures based on two components.[1] In this approach, the molecular components of the product crystalline salts are complex ions – typically anionic metal complexes and organic cations. The peripheral functional groups of these components are chosen to control their supramolecular interactions; in particular the metal complexes are typically functionalised with hydrogen bond acceptor groups such as halides and the cations with protonated nitrogen bases such as pyridines. The resultant pyridinium perchlorometallate crystal structures therefore contain NH…Cl–M interactions in well defined (and in favourable cases pre-planned) arrangements. Here we report the solid state reactivity of such phases. Reactivity studies in crystals are at the heart of the history of crystal engineering[2] and have received sustained and focused attention from a relatively small number of groups, primarily in solid state organic and organometallic chemistry.[3] Whilst there is a wide variety of methods for the preparation of metal complexes of, for example, pyridine ligands, the vast majority require solution phase chemistry and as a result are at the mercy of the essentially isotropic environment that this provides for molecular reaction chemistry. We have sought to explore the possibility of eliminating HCl from crystalline solids such as pyridinium salts of chlorometallates, thereby obtaining access to coordination complexes, by heating precursor hydrogen bonded systems as shown in Scheme 1. Herein we report such a study in which this concept is demonstrated by its application to the 4-picolinium salts of the platinum(II) and palladium(II) tetrachloride dianions.



Scheme 1 Dehydrochlorination of a chlorometallate pyridinium salt to afford a metal pyridine complex.

The 4-picolinium salts of $[PtCl_4]^{2-}$ and $[PdCl_4]^{2-}$ (**1** and **2** respectively) were prepared by treatment of benzyltriphenylphosphonium salts of the anions with 4-picolinium tetrafluoroborate in dichloromethane solution.‡ The crystal structures of the salts (Figs. 1 and 2) show that they have different geometries.§ That of **2** resembles the structure of $[4,4'\text{-}H_2bipy][MCl_4]$ (M = Pt, Pd)[1] in that it consists of (close-packed) neutral, linear ribbons composed of anions which act as chelating hydrogen bond acceptors (through participation in supramolecular synthon[4] **A**) to two pyridinium groups on *trans* edges of the square planar anion (see Fig. 2). In the ribbons in **2** the pyridinium groups interact through Me…Me contacts between 4-picolinium ions rather than through the covalent central C–C bond of the bipyridinium ion seen in the structure of $[4,4'\text{-}H_2bipy][PtCl_4]$.[1] In contrast, in **1**, synthon **A** is formed on two *cis* edges of the dianion (see Fig. 1).



A

Thermogravimetric analysis of the $[4\text{-picolinium}]_2[MCl_4]$ (**1**, M = Pt; **2**, M = Pd) salts showed loss of two equivalents of HCl in both cases.¶ The product of this thermal process was identified by heating **1** and **2** under N_2 for *ca.* 90 minutes at 160 °C.‡ In the case of **1**, the main product of heating for a shorter period has a stoichiometry resulting from loss of just one equivalent of HCl, $[4\text{-picolinium}][PtCl_3(4\text{-picoline})]$ (**3**).

The crystal structure of **3** was determined§ from a sample recrystallised from dichloromethane/hexane solution. As shown in

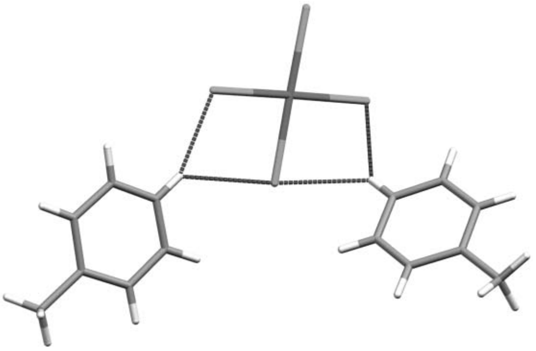


Fig. 1 Structure of $[4\text{-picolinium}]_2[PtCl_4]$ (**1**).

Fig. 2 Structure of $[4\text{-picolinium}]_2[PdCl_4]$ (**2**).

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† Electronic supplementary information (ESI) available: details of syntheses of **1**–**5**. See http://www.rsc.org/suppdata/cc/b5/b501555c/

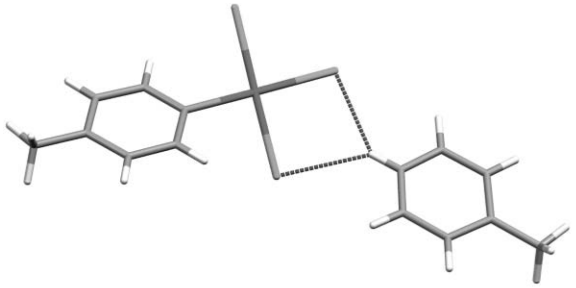

Fig. 3 Structure of [4-picolinium][PtCl$_3$(4-picoline)] (**3**).

Fig. 3, **3** has one picoline which is coordinated directly to the Pt(II) centre and a second which is protonated and forms an interaction of form **A** with the resultant [PtCl$_3$(4-picoline)]$^-$ anion. The powder diffraction pattern of the reaction product *prior* to recrystallisation indicates that phase **3** is formed during the thermal treatment of **1** and is the main component of the crude product (which contains some starting material **1** as well as **4**). The formation of highly crystalline **3** in this reaction is interesting and implies phase reconstruction after the first dehydrochlorination. The mechanism of this reaction deserves investigation.

Complete dehydrochlorination of **1** and **2** is readily achieved in bulk by more prolonged treatment under N_2 at 160 °C. The products, *trans*-[MCl$_2$(4-picoline)$_2$] (M = Pt, **4**, M = Pd, **5**), were characterised by elemental analysis and powder and single crystal X-ray diffraction§ (the latter on a sample of **5** recrystallised from dichloromethane/hexane solution). While the molecular structures of **4** and **5** are very similar (see Fig. 4), the *crystal* structures of **4** (which is known[5]) and **5** are substantially different. They crystallise in the same space group and have the long molecular axis approximately parallel to the unit cell *c* axis, which is itself the longest of the cell dimensions and approximately equal to the length of the molecules (from methyl to methyl). However the packing is significantly different as reflected in the cell dimensions.§

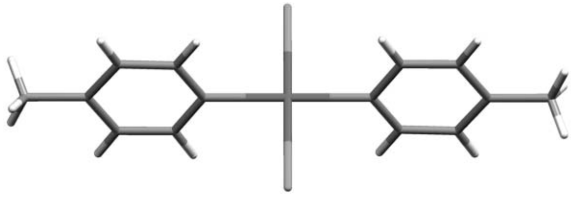

Fig. 4 Structure of *trans*-[PtCl$_2$(4-picoline)$_2$] (**4**).

Complexes **4** and **5** are coordination complexes of platinum(II) and palladium(II) that are accessible by conventional solution phase routes[4] but which are here prepared by apparently direct routes in the solid phase. The different course of the reactions for **1** and **2** implies that their crystal structures affect their reactivity, as is required if solid state structure is to confer selectivity on such reactions.

In conclusion we note that:

(i) The hydrogen-bonded complex salts **1** and **2** can be readily transformed into coordination complexes by thermal dehydrochlorination.

(ii) The (apparent) simplicity of this observation implies that this may be a general phenomenon.

(iii) The availability of a wide range of "crystal engineered" salts of anionic metal halide complexes of pyridinium and other protonated nitrogen bases offers the prospect of applying this and related reactions under the control of crystalline environments.

Christopher J. Adams, Paul C. Crawford, A. Guy Orpen,*
Thomas J. Podesta and Benjamin Salt
School of Chemistry, University of Bristol, Bristol, UK BS8 1TS

Notes and references

‡ Syntheses of **1–5**. Details are given in Electronic Supplementary Information. Salts **1** and **2** were prepared by treatment of the benzyltriphenylphosphonium salt of the anion with two equivalents of 4-picolinium tetrafluoroborate in dichloromethane solution. Thermolysis reactions were carried out under N_2 at 160 °C for 40 minutes for **3** and 90 minutes for **4** and **5**. All compounds gave satisfactory elemental analyses except crude **3** as recovered from the thermolysis reaction (because of contamination with **1** and **4**).

§ *Crystal structure analyses of* **1**, **2**, **3** and **5**: *Crystal data*: [4-picolinium]$_2$[PtCl$_4$] (**1**), $C_{12}H_{16}Cl_4N_2Pt$, $M = 525.16$, triclinic, space group $P\bar{1}$ (no. 2), $a = 7.430(6)$, $b = 8.401(6)$, $c = 14.686(11)$ Å, $\alpha = 102.459(11)$, $\beta = 91.078(11)$, $\gamma = 114.901(11)°$, $U = 805.7(10)$ Å^3, $Z = 2$, $\mu = 9.358\ \mathrm{mm}^{-1}$, $T = 173$, 3653 unique data, $R_1 = 0.0255$. [4-picolinium]$_2$[PdCl$_4$] (**2**), $C_{12}H_{16}Cl_4N_2Pd$, $M = 436.47$, monoclinic, space group *C2*/*m* (no. 12), $a = 10.592(3)$, $b = 11.311(3)$, $c = 7.4277(17)$ Å, $\beta = 112.81(2)°$, $U = 820.3(4)$ Å^3, $Z = 2$, $\mu = 1.770\ \mathrm{mm}^{-1}$, $T = 173$, 986 unique data, $R_1 = 0.0245$. [4-picolinium][PdCl$_3$(4-picoline)] (**3**), $C_{12}H_{15}Cl_3N_2Pd$, $M = 488.70$, monoclinic, space group $P2_1/n$ (no. 14), $a = 9.5223(19)$, $b = 16.206(3)$, $c = 9.6271(19)$ Å, $\beta = 102.73(3)°$, $U = 1449.1(5)$ Å^3, $Z = 4$, $\mu = 10.219\ \mathrm{mm}^{-1}$, $T = 100$, 3330 unique data, $R_1 = 0.0250$. *trans*-[PdCl$_2$(4-picoline)$_2$] (**5**), $C_{12}H_{14}Cl_2N_2Pd$, $M = 363.55$, monoclinic, space group $P2_1/n$ (no. 14), $a = 10.461(2)$, $b = 3.9775(8)$, $c = 15.911(3)$ Å, $\beta = 98.73(3)°$, $U = 654.4(2)$ Å^3, $Z = 2$, $\mu = 1.804\ \mathrm{mm}^{-1}$, $T = 100$, 1503 unique data, $R_1 = 0.0252$. All hydrogen atoms were located in difference maps and included in idealised positions. Bulk samples of **1–5** gave powder diffraction patterns consistent with the structures determined by single crystal methods. CCDC 263081–263084. See http://www.rsc.org/suppdata/cc/b5/b501555c/ for crystallographic data in CIF or other electronic format.

¶ Thermogravimetric analysis of the [4-picolinium]$_2$[MCl$_4$] salts (**1**, M = Pt; **2**, M = Pd) was carried out on a Netzsch STA 409EP DSC/TGA instrument under N_2 flow for temperature range 20–400 °C at a heating rate of 5.0 K/min. Salt **1** showed a mass loss of 14% (*cf.* 13.9% calculated for loss of 2 HCl) between 140 and 240 °C while **2** showed a mass loss of 16% between 120 and 190 °C (*cf.* 16.7% calculated for loss of 2 HCl).

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