

Full Length Research Paper

***trans*-[PtCl₂(NH₂C₆H₄CO₂H)₂]: a platinum complex forming a two-dimensional hydrogen-bonded network**

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The compound *trans*-[PtCl₂(NH₂C₆H₄CO₂H)₂] has been prepared from the hydrolysis of a platinum diimine complex, and has been characterised by X-ray crystallography. The crystal structure revealed that the compound forms a two-dimensional hydrogen-bonded network in the solid state, with pairs of O–H...O hydrogen bonds between carboxylic acid groups linking the molecules into zigzag tapes, which are cross-linked into sheets by pairs of N–H...Cl hydrogen bonds.

Key words: Metal-organic frameworks, metalloligands, two-dimensional hydrogen-bonded network.

INTRODUCTION

Coordination networks, otherwise known as metal-organic frameworks (MOFs) (Rowsell and Yaghi, 2004; Kitagawa et al., 2004; Férey, 2008; Robson, 2008) are currently attracting considerable interest for a wide range of potential applications (Czaja et al., 2009; Gagnon et al., 2012). Many robust, highly porous MOFs have been prepared that may be particularly useful in gas storage and separations (Rosi et al., 2003; Chae et al., 2004; Bennett et al., 2001). A major challenge in the field is the introduction of complex functionality (e.g., catalysis, luminescence, etc.) into MOF assemblies (Hupp and Poeppelmeier, 2005; Wu et al., 2005, 2004; Kitagawa et al., 2004). Efforts to introduce more complex functionality include modification of the ligand structure and forcing sites of unsaturation or labile solvent coordination at the metal nodes. Among the most attractive strategies for introducing new functionality is the use of “metalloligands”—metal complexes that contain ligands that have uncoordinated donor sites that can themselves act as ligands in MOF synthesis. This strategy has enabled the preparation of bimetallic MOFs, in which different metal centres may have different structural and/or functional roles (Noro et al., 2002; Kitaura et al.,

2004; Vreshch et al., 2004; Chen et al., 2004; Halper et al., 2006; Burrows et al., 2007, 2008; Zhang et al., 2008; Garibay et al., 2009). We were interested in preparing bimetallic MOFs by adopting a “two-step self-assembly” approach, where a metalloligand is synthesized in the first step as a framework linker, and then in the second step, the metalloligand is added to another metal ion, which acts as a node in the framework. By using the platinum diimine complex 1 (Buffin and Kundu, 2003), as a metalloligand in MOF construction, we were able to isolate crystals of *trans*-[PtCl₂(NH₂C₆H₄CO₂H)₂]₂, which had formed as a decomposition product of 1. Here we report the characterization of this new platinum(II) complex, which has a two-dimensional hydrogen bonded network in the solid state.

EXPERIMENTAL

Platinum(II) chloride (0.027 g, 0.1 mmol) and 4-aminobenzoic acid (0.027 g, 0.2 mmol) were added to water (2.7 cm³) and THF (4 cm³) in a pressure tube, and the mixture was heated at 95°C for 5 days. On cooling to room temperature, crystals of 2 suitable for single

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Table 1. Crystal data and structure refinement for *trans*-[PtCl₂(NH₂C₆H₄CO₂H)₂] **2**.

Empirical formula	Cl ₄ H ₄ Cl ₂ N ₂ O ₄ Pt
Formula weight	540.26
Temperature	173(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	<i>P</i> -1
Unit cell dimensions	
<i>a</i> =	4.9020(1) Å
<i>b</i> =	5.7840(2) Å
<i>c</i> =	13.5710(4) Å
α =	87.0040(1)°
β =	88.1620(1)°
γ =	89.553(2)°
Volume	384.050(19) Å ³
<i>Z</i>	1
Density (calculated)	2.336 mg/m ³
μ	9.503 mm ⁻¹
<i>F</i> (000)	256
Crystal size	0.37 × 0.37 × 0.05 mm ³
Theta range for data collection	3.01 to 27.42°.
Index ranges	-6 ≤ <i>h</i> ≤ 6, -7 ≤ <i>k</i> ≤ 7, -17 ≤ <i>l</i> ≤ 17
Reflections collected	5396
Independent reflections	1747 [<i>R</i> (int) = 0.0765]
Completeness to theta = 27.42°	99.0 %
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data / restraints / parameters	1747 / 0 / 109
Goodness-of-fit on <i>F</i> ²	1.033
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0584, <i>wR</i> ₂ = 0.1514
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0583, <i>wR</i> ₂ = 0.1514
Largest diff. peak and hole	5.885 and -3.954 e.Å ⁻³

crystal X-ray analysis were obtained. ¹H NMR (DMSO-*d*₆) δ 7.82 (d 4H), 7.28 (d 4H), 3.48 (br 2H), ¹³C NMR (DMSO-*d*₆) δ 167.82, 153.43, 131.55, 117.28, 112.94. Found: C, 30.2; H, 2.19; N, 5.36%. C₁₄H₁₅N₂O_{4.5}PtCl₂ (2·0.5H₂O) requires C, 30.6; H, 2.75; N, 5.10%.

diffractometer. Details of the X-ray crystallographic analysis are given in Table 1. Fractional coordinates for the refined atoms and equivalent isotropic thermal parameters are presented in Table 2. The crystal structure was solved using SHELXS-97 and refined using SHELXL-97.

NMR

The ¹H NMR and ¹³C NMR spectra of the complex were recorded with a Bruker Advance 300 instrument using *d*₆-DMSO solutions and TMS as internal standard.

Elemental analysis

The C, N and H content of the compounds were determined using a CE-440 Elemental Analyser by Alan Carver at the University of Bath.

Structural analysis

The structural data were collected on a Nonius KappaCCD

RESULTS AND DISCUSSION

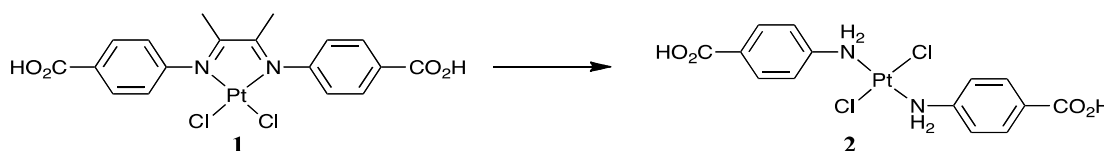
While investigating the use of the platinum diimine complex **1** (Buffin and Kundu, 2003) as a metalloligand in MOF construction, we were able to isolate crystals of *trans*-[PtCl₂(NH₂C₆H₄CO₂H)₂] **2**, which had formed as a decomposition product of **1** (Scheme 1). Following identification of **2**, it was found possible to produce this compound *via* a more rational approach by reacting platinum(II) chloride with 4-aminobenzoic acid in a mixture of water and THF. Crystals of **2** were analysed by single crystal X-ray crystallography.

The asymmetric unit of **2** consists of half a platinum

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters for ($\text{\AA}^2 \times 10^3$) for *trans*-[PtCl₂(NH₂C₆H₄CO₂H)₂] 2.

Parameter	x	y	z	U(eq)
Pt(1)	10000	10000	0	11(1)
N(3)	11248(19)	7842(16)	1162(9)	19(2)
O(4)	2465(19)	7160(17)	4770(7)	24(2)
O(5)	1603(19)	3909(17)	4003(7)	24(2)
C(6)	6610(20)	8390(20)	3355(9)	20(2)
C(7)	8620(20)	8900(20)	2638(9)	18(2)
C(8)	7770(20)	5271(19)	1896(8)	16(2)
C(9)	9220(20)	7332(18)	1920(8)	14(2)
C(10)	2910(20)	5750(20)	4088(8)	15(2)
C(11)	5710(20)	4780(20)	2597(9)	18(2)
C(12)	5130(20)	6337(19)	3343(8)	15(2)
Cl(1)	13162(5)	12603(4)	460(2)	15(1)

U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor



Scheme 1. Formation of 2 from the decomposition of 1.

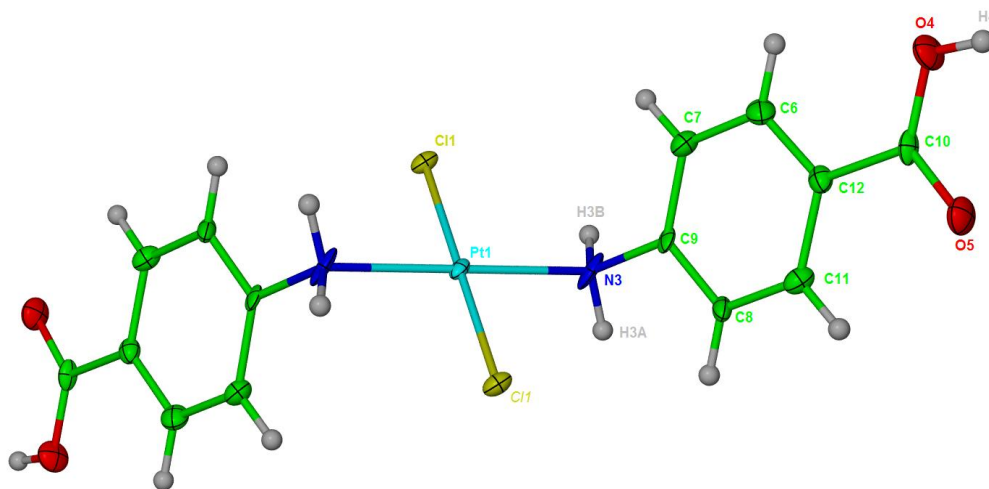


Figure 1. Molecular structure of *trans*-[PtCl₂(NH₂C₆H₄CO₂H)₂] 2.

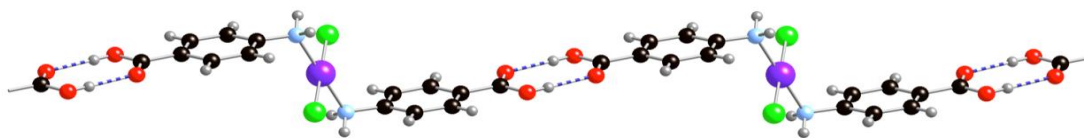
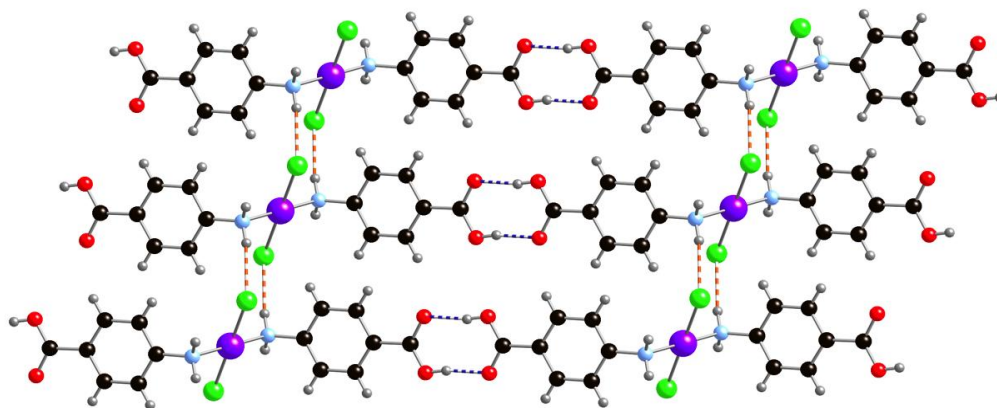
atom, a coordinated chloride ion and a 4-aminobenzoic acid molecule that is coordinated to the platinum centre through the nitrogen atom. The partial-occupancy platinum atom resides on an inversion centre, which serves to generate the remainder of the molecule. The molecular structure of 2 is shown in Figure 1. The

structural analysis revealed that the platinum centre has the expected distorted square planar geometry (Table 3), with *cis* angles of 87.4(3) and 92.6(3) $^\circ$. The Pt–N and Pt–Cl bond distances (2.057(10) and 2.293(2) \AA respectively) lie within the expected ranges (Orpen et al., 1989). The only previous structurally characterised

Table 3. Selected bond lengths (Å) and angles (°) for 2.

Pt(1)–N(3)	2.057(10)
Pt(1)–Cl(1)	2.293(2)
O(4)–C(10)	1.275(15)
O(5)–C(10)	1.263(15)
N(3)–C(9)	1.435(14)
N(3)–Pt(1)–Cl(1)	87.4(3)
N(3)–Pt(1)–Cl(1)'	92.6(3)
C(9)–N(3)–Pt(1)	115.4(6)

Primed atoms generated by the symmetry operation $-x + 2, -y + 2, -z$.

**Figure 2.** Zigzag hydrogen-bonded tapes in the supramolecular structure of *trans*-[PtCl₂(NH₂C₆H₄CO₂H)₂] 2.**Figure 3.** Hydrogen-bonded sheets present in the supramolecular structure of *trans*-[PtCl₂(NH₂C₆H₄CO₂H)₂] 2.

example of a dichlorobis(phenylamine)platinum complex contains 2-(3-aminophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Vogels et al., 1999), and this has a very similar coordination geometry, with identical bond lengths and angles [Pt–Cl 2.290 Å, Pt–N 2.053 Å, N–Pt–Cl 88.1, 91.9°].

Each carboxylic acid group in 2 forms a hydrogen bonded dimer with the equivalent group on a neighbouring molecule with the parameters O(4)⋯O(5) 2.612 Å, H(4)⋯O(5) 1.78 Å, O(4)–H(4)⋯O(5) 170° [O(5) generated by the symmetry operation $-x, -y + 1, -z + 1$]. The carboxylic acid dimer, described by the graph set R²₂(8) (Bernstein et al., 1995), is a common motif in crystal engineering, where there is an absence of

competing donors and acceptors (Allen et al., 1999; Ayi et al., 2001; Burrows, 2004), and in the case of 2, these hydrogen bonds link the molecules into zigzag tapes, as shown in Figure 2. The zigzag nature of the tapes arises from the platinum coordination plane and the aminobenzoic acid ligand being non-coplanar, as evidenced by 107° angle between the mean plane containing Pt(1), Cl(1) and N(3), and that containing N(3), C(6)–C(12), O(4) and O(5).

Additional hydrogen bonds between the coordinated amine groups and one of the chloride ligands link the chains into a two-dimensional network, shown in Figure 3. The N–H⋯Cl hydrogen bonds occur pairwise, generating R²₂(8) rings with the hydrogen bonding

parameters N(3)···Cl(1) 3.339 Å, H(3A)···Cl(1) 2.43 Å, N(3)–H(3A)···Cl(1) 172° [Cl(1) generated by the symmetry operation $x, y - 1, z$]. These parameters are within the expected range for N–H···Cl interactions when the chloride is coordinated to a metal (Brammer, 2003; Brammer et al., 2001). There are no significant interactions between the sheets, and neither the amino hydrogen atom H(3B) nor the chlorine atom Cl(2) is involved in hydrogen bond formation.

In conclusion, a new platinum(II) complex of aminobenzoic acid, *trans*-[PtCl₂(NH₂C₆H₄CO₂H-4)₂] 2, has been prepared under mild hydrothermal conditions and structurally characterized. A study of 2 as a metalloligand in the formation of mixed-metal MOFs is currently underway.

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REFERENCES

- Allen FH, Motherwell WDS, Raithby PR, Shields GP, Taylor R (1999). Systematic analysis of probabilities of formation of bimolecular hydrogen-bonded ring motifs in organic crystal structures. *New J. Chem.* 23:25-34.
- Ayi AA, Choudhury A, Natarajan S, Rao CNR (2001). Cyclic acetate dimmers formed by C–H···O hydrogen bonds in an open-framework zinc phosphate-acetate. *New J. Chem.* 25:213-215.
- Bennett MV, Beauvais LG, Shores MP, Long JR (2001). Expanded Prussian Blue Analogues Incorporating [Re₆Se₈(CN)₆]^{3-/4-} Clusters: Adjusting Porosity via Charge Balance. *J. Am. Chem. Soc.* 123:8022-8032.
- Bernstein J, Davis RE, Shimoni L, Chang NL (1995). Patterns in hydrogen bonding: Functionality and graph set analysis in crystals. *Angew. Chem. Int. Ed. Engl.* 34:1555-1573.
- Brammer L (2003). Metals and hydrogen bonds. *Dalton Trans.* 3145–3157.
- Brammer L, Bruton EA, Sherwood P (2001). Understanding the Behavior of Halogens as Hydrogen Bond Acceptors. *Cryst. Growth Des.* 1:277-290.
- Buffin B, Kundu A (2003). Synthesis, characterization, and crystal structure of platinum(II) and palladium(II) chlorides with an acidic α -diimine ligand. *Inorg. Chem. Commun.* 6:680-684.
- Burrows AD (2004). Crystal Engineering Using Hydrogen Bonds. *Struct. Bonding* 108:55-96.
- Burrows AD, Cassar K, Mahon MF, Warren JE (2007). The stepwise formation of mixed-metal coordination networks using complexes of 3-cyanoacetylacetonate. *Dalton Trans.* 2499-2509.
- Burrows AD, Mahon MF, Wong CTF (2008). Complexes as metalloligands in network formation: synthesis and characterization of a mixed metal coordination network containing palladium and zinc. *Cryst. Eng. Comm.* 10:487-489.
- Chae HK, Siberio-Pérez DY, Kim J, Go Y, Eddaoudi M, Matzger AJ, O'Keeffe M, Yaghi OM (2004). A route to high surface area, porosity and inclusion of large molecules in crystals. *Nature.* 427:523-527.
- Chen B, Fronczek FR, Maverick A (2004). Porous Cu–Cd mixed metal-organic Frameworks constructed from Cu(Pyac)₂{Bis[3-(4-pyridyl)pentane-2,4-dionato]copper(II)]}. *Inorg. Chem.* 43:8209-8211.
- Czaja AU, Trukhan N, Müller U (2009). Industrial applications of metal-organic frameworks. *Chem. Soc. Rev.* 38:1284-1293.
- Férey G (2008). Hybrid porous solids: past, present, future. *Chem. Soc. Rev.* 37:191-214.
- Gagnon KJ, Perry HP, Clearfield A (2012). Conventional and Unconventional Metal-Organic Frameworks Based on Phosphonate Ligands: MOFs and UMOFs. *Chem. Rev.* 112:1034-1054.
- Garibay SJ, Stork JR, Cohen SM (2009). The Use of Metalloligands in Metal-Organic Frameworks. *Prog. Inorg. Chem.* 56: 335-378.
- Halper SR, Do L, Stork JR, Cohen SM (2006). Topological Control in Heterometallic Metal-Organic Frameworks by Anion Templating and Metalloligand Design. *J. Am. Chem. Soc.* 128:15255-15268.
- Hupp JT, Poepelmeier KR (2005). Better Living through Nanopore Chemistry. *Science* 309:2008-2009.
- Kitagawa S, Kitaura R, Noro SI (2004). Functional Porous Coordination Polymers. *Angew. Chem. Int. Ed.* 43:2334-2375.
- Kitaura R, Onoyama G, Sakamoto H, Matsuda R, Noro SI, Kitagawa S (2004). Immobilization of a Metallo Schiff Base into a Microporous Coordination Polymer. *Angew. Chem. Int. Ed.* 43:2684-2687.
- Noro S, Kitagawa S, Yamashita M, Wada T (2002). New microporous coordination polymer affording guest-coordination sites at channel walls. *Chem. Commun.* pp. 222-223.
- Orpen A, Brammer L, Allen F, Kennard O, Watson DG, Taylor R (1989). Supplement. Tables of bond lengths determined by X-ray and neutron diffraction. Part 2. Organometallic compounds and coordination complexes of the d- and f-block metals. *J. Chem. Soc. Dalton Trans.* S1-S83.
- Robson R (2008). Design and its limitations in the construction of bi- and poly-nuclear coordination complexes and coordination polymers (aka MOFs): a personal view. *Dalton Trans.* 5113-5131.
- Rosi NL, Eckert J, Eddaoudi M, Vodak DT, Kim J, O'Keeffe M, Yaghi OM (2003). Hydrogen storage in microporous Metal-Organic Frameworks. *Science* 300:1127-1129.
- Rowell J, Yaghi O (2004). Metal-organic frameworks: a new class of porous materials. *Micropor. Mesopor. Mat.* 73:3-14.
- Vogels CM, Wellwood HL, Biradha K, Zaworotko MJ, Westcott SA (1999). Reactions of aminoboron compounds with palladium and platinum complexes. *Can. J. Chem.* 77:1196-1207.
- Vreshch V, Lysenko A, Chernega A, Howard J, Krautscheid H, Sieler J, Domasevitch K (2004). Extended coordination frameworks incorporating heterometallic squares. *Dalton Trans.* 2899-2903.
- Wu CD, Hu A, Zhang L, Lin WB (2005). A Homochiral Porous Metal-Organic Framework for Highly Enantioselective Heterogeneous Asymmetric Catalysis. *J. Am. Chem. Soc.* 127:8940-8941.
- Wu CD, Ngo HL, Lin WB (2004). Luminescent homochiral silver(I) lamellar coordination networks built from helical chains. *Chem. Commun.* pp. 1588-1589.
- Zhang Y, Chen B, Fronczek FR, Maverick AW (2008). A nanoporous Ag-Fe mixed metal-organic framework exhibiting single-crystal-to single-crystal transformation upon guest exchange. *Inorg. Chem.* 47:4433-4435.