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Concomitant polymorphism and conformational polymorphism in diiodobis[1,2-bis(diphenylphosphino)ethane]platinum(II)

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Abstract

The title organometallic compound crystallizes in two different polymorphic modifications. The conformational differences between the two crystalline modifications lead to differences in crystal packing and thus result in the formation of the two polymorphic forms. Both structures are stabilized by weak non-covalent interactions. The change in the phenyl ring rotation from one structure to the other results in the formation of two distinct network structures in the dimorphs.

Keywords: Polymorphism; Conformational differences; Hydrogen bonding; Networks; X-ray crystal structures

1. Introduction

Polymorphism is a well-known serendipitous solid state phenomenon wherein the same chemical substance forms at least two different solid-state packing arrangements [1,2]. Theoretically, the packing of a molecule can be arranged in many ways in the crystal in a given symmetry and polymorphism is a reflection of alternative ways in which molecules in a crystal strive towards a free energy minimum. Analyses of the polymorphic crystal structures pose a challenge in understanding why molecules would adopt more than one crystalline arrangement. The existence of polymorphism implies that the free energy difference between two solid state arrangements of the same compound is negligible [3,4]. Polymorphism has been an integral part of crystal engineering and has emerged as a solid state property of fundamental importance especially in pharmaceutical industries where product specifications often rely on structurally dependent properties [5–10]. It is vital that researchers involved in the formulation of crystalline products be able to select the polymorph with correct properties and anticipate problems such as unwanted crystallization of other polymorphs so as to avoid changing bioavailability, solubility and stability of the pharmaceutical. Since the physical properties of a given substance are directly affected by the solid state, polymorphism has a direct effect on properties such as electric and thermal conductivity, color, magnetism, thermal stability, hygroscopicity, density, solubility, bioavailability, and dissociation rate. The development of novel polymorphs, salts and solvates of potential and existing pharmaceutical compounds has for some time been a method for modifying and improving these properties [11]. Also, the control of polymorphism will lead to knowledge about the process of nucleation or crystal growth at the beginning of crystallization from solvents. Therefore, crystal engineering, including the control of morphology and polymorphism is essential to achieve optimized molecular configurations and physical properties and to understand the structure–property relationships of new materials [12]. Polymorphism is manifested through different packing motifs in rigid molecules and through different low-energy conformational arrangements in conformationally flexible molecules [13–17]. In many cases, the same crystallization condition produces crystals of more than one polymorph in the same

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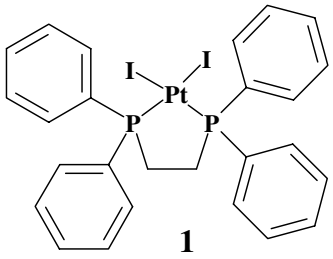
crystallization batch, a phenomenon known as concomitant polymorphism [18], which makes the control of polymorphism even more challenging. In reported studies, the formation of concomitant polymorphs has been attributed to several mechanisms [19–22]. To date, most polymorphic forms have been identified serendipitously and polymorph prediction is still in its infancy [23]. As a result, there is a need to discover and systematically analyze the crystal structures of different polymorphic modifications in organic and organometallic compounds. Polymorphism can also occur in materials that form solid-state polymer networks in which individual molecules are connected via distinct intermolecular interactions. In these instances, different network superstructures are observed as a result of polymorphism and these systems are described by the terms supramolecular isomerism [24] and architectural isomerism [25].

We have undertaken a study of a platinum compound diiodo [1,2-bis(diphenylphosphino)ethane]platinum(II), [PtI_2(dppe)] (**1**) that forms two concomitant polymorphs. The dimorphs also form an example of supramolecular isomerism through self-assembly of pillared-layer structure and hexagonal network. Both structures are stabilized by weak non-covalent interactions.



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2. Experimental

2.1. Synthesis of [PtI_2(dppe)] (**1**)

To a solution of [$PtCl_2$(dppe)] (0.10 g, 0.15 mmol) in 20 mL CH_2Cl_2, KI (0.13 g, 0.78 mmol) was added. The reaction mixture was stirred overnight and filtered through neutral alumina. The solvent was removed and product was crystallized from CH_2Cl_2/diethyl ether and dried *in vacuo*, yielding a yellow solid (0.12 g, 87%). X-ray quality crystals were grown by slow diffusion of diethyl ether into a CH_2Cl_2 solution.

^{1}H NMR ($CDCl_3$) at 25 °C: δH 7.27–7.95 (m, 20H, PPh_2), 2.36 (d, ^2JPH = 18 Hz, 4H, PCH_2). ^{31}P{^{1}H} NMR ($CDCl_3$) at 25 °C: δP 46.6 (s, $^1J_{PtP}$ = 3368 Hz).

2.2. X-ray crystallography

Preliminary examination and data collection were performed using a Bruker SMART CCD area detector system single-crystal X-ray diffractometer. The SMART and SAINT packages were used for data collection and data reduction, respectively. SHELXTL-PLUS software package was used for structure solution and refinement [26,27]. Hydrogen atoms were calculated at their idealized geometries and treated isotropically using appropriate riding models. The crystallographic data for form **A** and **B** are given in Table 1.

Table 1
Crystallographic data for forms **A** and **B**

	Form **A**	Form **B**
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$
a (Å)	9.4718(12)	9.04(2)
b (Å)	19.877(2)	14.3186(3)
c (Å)	14.1889(17)	20.3657(4)
α (°)	90	90
β (°)	105.068(2)	92.963(1)
γ (°)	90	90
V (Å^3)	2579.5(5)	2631.3(1)
Temperature (K)	223(2)	213(2)
Calculated density (Mg/m^3)	2.182	2.139
Absorption coefficient (nm^{-1})	7.970	7.813
F(000)	1576	1576
θ Range for data collection (°)	2.33–28.07	2.4–27.5
Reflections collected	13 231	49 590
Independent reflections	3190	5443
Number of parameters	280	317
R_1	0.0415	0.0261
wR_2	0.0848	0.061

3. Results and discussion

The platinum compound [PtI_2(dppe)] (**1**) was prepared by stirring a CH_2Cl_2 solution of [$PtCl_2$(dppe)] with KI overnight at room temperature. The ^{31}P{^{1}H} spectrum of [PtI_2(dppe)] in $CDCl_3$ solution shows a single peak at 46.6 ppm with $^1J_{PtP}$ = 3368 Hz. Its one bond coupling to platinum is smaller than that of [$PtCl_2$(dppe)] (3622 Hz), which is consistent with the greater *trans*-influence of iodide compared to chloride. X-ray quality crystals were grown by slow diffusion of diethyl ether into a CH_2Cl_2 solution. Single crystal X-ray diffraction studies of two

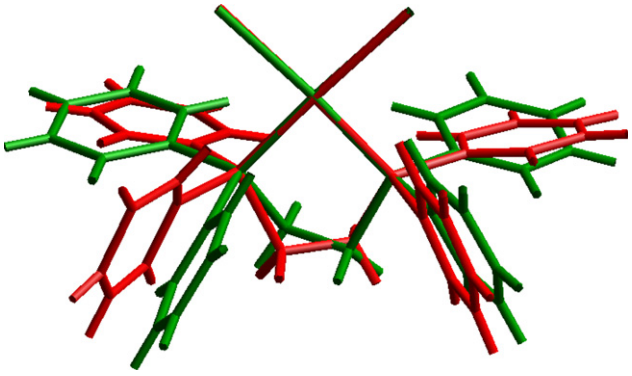
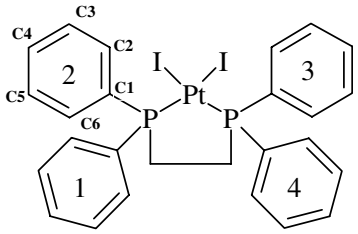


Fig. 1. Overlay diagram of the two polymorphs observed in **1**. Notice that the two forms of **1** differ in the rotation of the phenyl rings (form **A** – green, form **B** – red). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 2
Torsional angles observed in the dimorphs of **1**



τ_1- Pt-P-C1-C2

τ_2- Pt-P-C1-C6

		Phenyl ring 1	Phenyl ring 2	Phenyl ring 3	Phenyl ring 4
Form **A**	τ_1	−166.21	57.04	27.83	−16.13
	τ_2	6.44	125.00	140.79	163.48
Form **B**	τ_1	−23.32	113.10	−117.63	0.36
	τ_2	157.58	−66.72	61.47	162.71

sets of crystals taken from the same crystallization flask proved them to be concomitant polymorphs of $[PtI_2(dppe)]$ (form **A** and **B**). Both forms crystallize in the same space group $P2_1/n$. The crystallographic data for the two forms are given in Table 1. The independent molecules observed in the dimorphs of **1** differ in their rotation about the C–P bond between the phenyl ring and the central heterocyclic ring. The conformational differences between the two polymorphic modifications are shown in Fig. 1. The conformation of each phenyl ring with respect to the central heterocyclic ring may be defined according to the two torsion angles τ_1 and τ_2 (Table 2). Conformational changes from one structure to the other lead to formation of the two different polymorphs; hence, these concomitant polymorphs also may be termed conformational polymorphs [28]. Each polymorph forms a distinct network stabilized by weak C–H···metal and C–H···I interactions [29].

In form **A**, the structure is extensively stabilized by weak C–H···I interactions. The molecule has phenyl donors and iodine, platinum and phosphorus acceptors for hydrogen bonding. *n*-Glide related molecules along the *x*-axis are connected through C–H···I (3.18 Å, 160.1°) interactions to form a one dimensional chain. Such translation related chains are connected through C–H···I interactions (3.18 Å, 142.9°) to furnish a 2D grid pattern as shown in Fig. 2. The inversion related grids are inter-connected by a linear C–H···I interactions (3.22 Å, 177.2°) producing a pillared-layer structure [30] (shown in Fig. 3) to achieve close packing. Additional C–H···I interactions between the layers further stabilize the overall architecture. The central metal atom and the phosphorus atoms do not form any non-covalent interactions.

In form **B**, one of the phenyl groups and one of the backbone carbons of the dppe ligand are disordered. One of the phenyl group hydrogens and a hydrogen from the ethylene group act as donors, whereas one of the iodine atoms and the platinum atom act as acceptors. The iodine

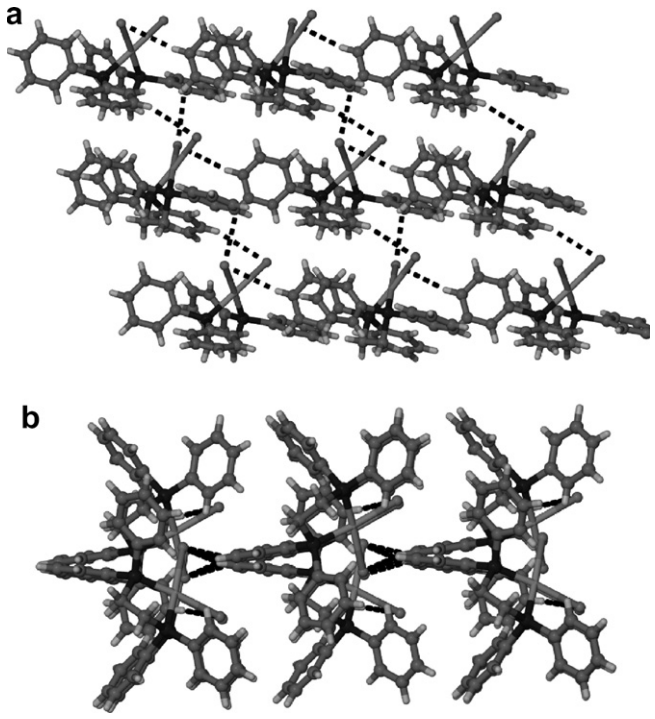


Fig. 2. (a) The 2D grid pattern observed in the polymorphic form **A**. (b) Layer view of the 2D grid.

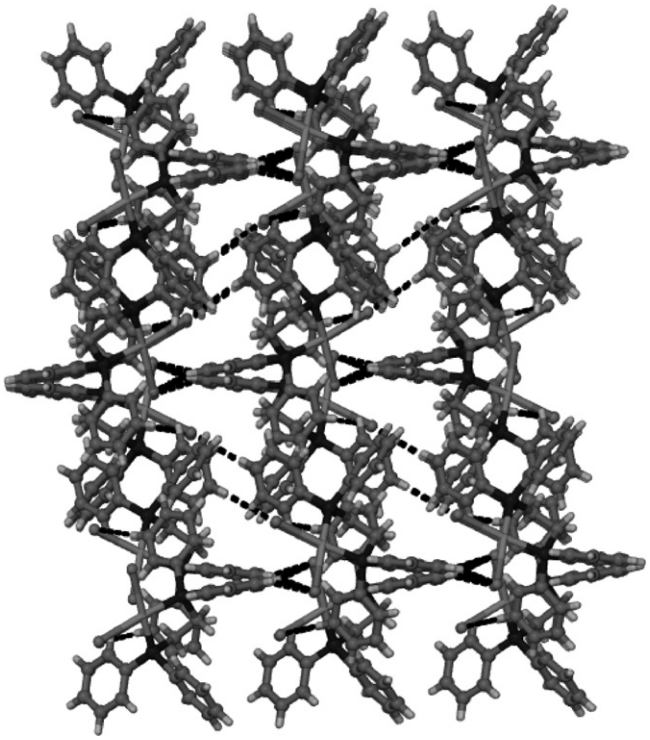


Fig. 3. Pillared-layer structure observed in form **A**.

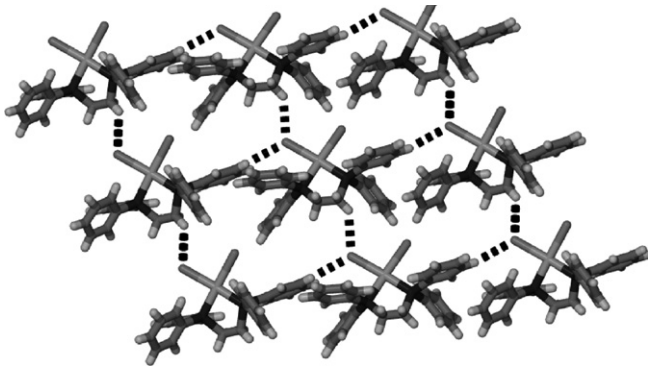


Fig. 4. Hexagonal pattern observed in form **B**.

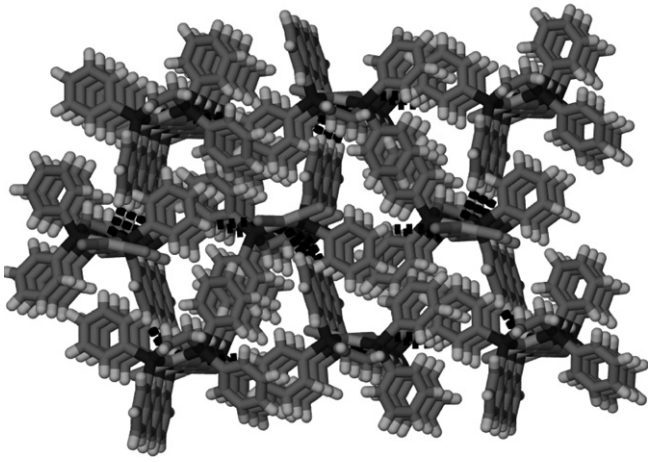


Fig. 5. The 3D structure in form **B**.

atom forms bifurcated hydrogen bonds. Each molecule in form **B** is connected through two distinct C–H···I interactions. One C–H···I interaction (3.0 Å, 148.9°) connects the *n*-glide related molecules while the other C–H···I interaction (3.04 Å, 137.1°) connects the translation related molecules to furnish a hexagonal network [23] as shown in Fig. 4. 2_1-Screw related molecules in neighboring layers are further connected *via* C–H···Pt interactions (2.9 Å, 154.2°) to form a 3D network structure as shown in Fig. 5. The phenyl rings that do not participate in hydrogen bonding formation fill the voids formed in the network to avoid an open structure.

Although both forms **A** and **B** crystallize in the same space group, the conformation of **1** is different in the two polymorphs. The relative stability of the two polymorphs has not been determined. The solid state structures, however, would appear to indicate that form **A** is the lower energy form. In form **A**, most of the phenyl hydrogen donors are engaged in hydrogen bonding whereas in form **B** only fewer intermolecular interactions are present. Thus Form **A** exhibits relatively closer crystal packing (~2% denser packing) resulting in a smaller crystal volume (2579 versus 2631 $Å^3$) and hence, the calculated density of form **A** is greater than that of form **B** (2.182 versus 2.139).

4. Conclusion

To summarize, two concomitant polymorphs of **1** have been structurally characterized by low temperature single crystal X-ray diffraction studies. In both polymorphic modifications, weak hydrogen bonding mediates distinct supramolecular pillared-layer structures and hexagonal networks. In addition to being an example of concomitant polymorphism, the organometallic compound **1** also exhibits its conformational polymorphism and supramolecular isomerism. The chemical basis for the simultaneous occurrence of concomitant polymorphism and conformational polymorphism is most likely due to the comparable energy scale for these two phenomena.

Acknowledgement

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Appendix A. Supplementary material

CCDC 632382 and 632381 contain the supplementary crystallographic data for **A** and **B**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2007.02.033.

References

[1] G.R. Desiraju, Science 278 (1997) 404.
[2] J. Bernstein, Polymorphism in Molecular Crystals, Clarendon, Oxford, 2002.
[3] T.L. Threlfall, Analyst 120 (1995) 2435.
[4] M.R. Caira, Top. Curr. Chem. 198 (1998) 164.
[5] J.D. Duntiz, J. Bernstein, J. Acc. Chem. Res. 28 (1995) 193.
[6] M.U. Schmidt, J. Chem. Soc., Dalton Trans. (1996) 2077.
[7] L. Yu, J. Am. Chem. Soc. 125 (2003) 6380.
[8] T.L. Hennigar, D.C. MacQuarrie, P. Losier, R.D. Rogers, M.J. Zaworotko, Angew. Chem., Int. Ed. Engl. 36 (1997) 972.
[9] S. Dutta, D.J.W. Grant, Nat. Rev. Drug Discovery 3 (2004) 42.
[10] H.G. Brittain (Ed.), Polymorphism in Pharmaceutical Solids, Drugs and the Pharmaceutical Sciences, vol. 95, Marcel Dekker, New York, 1999.
[11] M.V. Raumer, J. Dannappel, R. Hilfiker, Chem. Today 24 (2006) 41.
[12] G.R. Desiraju, Crystal Engineering: The Design of Organic Solids, Elsevier, Amsterdam, 1989.
[13] J.A.R.P. Sarma, G.R. Desiraju, in: K.R. Seddon, M.J. Zaworotko (Eds.), Crystal Engineering, Kluwer Academic Publishers, Dordrecht, The Netherlands, 1999, pp. 325–356.
[14] V.S.S. Kumar, A. Addlagatta, A. Nangia, W.T. Robinson, C.K. Broder, R. Mondal, I.R. Evans, J.A.K. Howard, F.H. Allen, Angew. Chem., Int. Ed. 41 (2002) 3848.
[15] R.K.R. Jetti, R. Boese, J.A.R.P. Sarma, L.S. Reddy, P. Vishweshwar, G.R. Desiraju, Angew. Chem., Int. Ed. 42 (2003) 1963.
[16] V.S.S. Kumar, F.C. Pigge, N.P. Rath, New J. Chem. 27 (2003) 1554.
[17] V.S.S. Kumar, F.C. Pigge, N.P. Rath, CrystEngCommun 6 (2004) 102.

[18] J. Bernstein, R.J. Davey, J.-O. Henck, Angew. Chem., Int. Ed. 38 (1999) 3441.
[19] P.T. Cardew, R.J. Davey, Farady Soc. Discuss. 95 (1993) 160.
[20] J.H. ter Horst, H.J.M. Kramer, P.J. Jansens, Cryst. Growth Des. 2 (2002) 351.
[21] N. Blagden, R.J. Davey, Cryst. Growth Des. 3 (2003) 873.
[22] S. Chen, H. Xi, L. Yu, J. Am. Chem. Soc. 127 (2005) 17439.
[23] R.W. Lancaster, P.G. Karamertzanis, A.T. Hulme, D.K.A. Tocher, D.F. Covey, S.L . Price, Chem. Commun. (2006).
[24] B. Moulton, M.J. Zaworotko, Chem. Rev. 101 (2001) 1629.
[25] K.T. Holman, S.M. Martin, D.P. Parker, M.D. Ward, J. Am. Chem. Soc. 123 (2001) 4421.
[26] SMART and SAINT software package, Bruker Analytical X-ray Division, Madison, WI, 1999.
[27] G.M. Sheldrick, Bruker Analytical X-ray Division, Madison, WI, 1999.
[28] J. Bernstein, in: G.R. Desiraju (Ed.), Organic Solid State Chemistry, Elsevier, Amsterdam, 1987, pp. 471–518.
[29] G.R. Desiraju, T. Steiner, The Weak Hydrogen Bond in Structural Chemistry and Biology, OUP, Oxford, 1999.
[30] K.T. Holman, A.M. Pivovar, J.A. Swift, M.D. Ward, Chem. Res. 34 (2001) 107.