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I $\cdots \pi$ halogen-bonding in the structures of platinum–alkynyl compounds: an overlooked supramolecular interaction[†]

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The crystal structures of both a symmetric and an unsymmetric platinum–alkynyl compound with terminal iodophenyl functionalities have been determined, and found to exhibit an attractive interaction between the iodine atom and the carbon–carbon triple bond of the alkynyl ligand.

In recent years there has been a surge of interest in the use of intermolecular interactions to control crystal packing, the field of crystal engineering. With small organic molecules it is possible to do this by placing donor and acceptor groups at opposite ends of a molecule, the resulting crystal structure often displaying an interaction between the two. The orientation of the molecule in the solid state is such that this interaction is maximised, and as a result the packing of the molecule is influenced. An example of this is shown in Fig. 1, which is part of the crystal structure of 4-iodobenzonitrile.¹ There is a lone pair of electrons on the nitrogen atom, and a relatively large, lowenergy C–I σ^* orbital protruding from the iodine atom, opposite the carbon-iodine bond. A donor-acceptor interaction between the two results in the formation of a (partial) dative bond, causing the molecules to form a chain in the solid state. Pyridine groups also commonly act as the donor moiety.² A second type of interaction may also be present, of the polarisation induced dipole-dipole type. Here, the electron density of the donor species causes polarisation of the electron density on the iodine atom, thus inducing a temporary positive dipole there which is attracted to the negative dipole of the donor.3 This mechanism is responsible for the iodo-nitro interaction seen, for example, in the structure of 4-iodonitrobenzene, another case where the intermolecular donor-acceptor interaction creates linear chains of molecules.⁴ The relative magnitudes of the two interactions depend upon the precise system in question, but the two complement each other and are often discussed together under the name of 'halogen bonding'.



Fig. 1 Chains of molecules within the structure of 4-iodobenzonitrile; iodine atoms are purple and nitrogen atoms are blue.

As the interactions outlined above can be used to generate polar chains of molecules (as in Fig. 1), there has recently been interest in using them to create non-centrosymmetric crystals. Many compounds have physical properties (such as NLO activity) which are enhanced in such an environment, and this is as true for inorganic as organic species. However, whilst there have been studies towards the use of halogen-bonding in purely organic systems,⁵ there has been only one attempt⁶ to apply the effect to metal-containing molecules. Therefore, the aim of the work herein was to determine whether the principles outlined above could be applied to organometallic systems to produce

† Electronic supplementary information (ESI) available: Synthetic and characterisation details for all compounds. See http://www.rsc.org/ suppdata/dt/b5/b506025g/ such a non-centrosymmetric motif. The compounds chosen for investigation were platinum–alkynyl systems of the form *trans*-Pt(PEt₃)₂(C \equiv C-*p*-C₆H₄–I)(C \equiv C-*p*-C₆H₄–R), where the donor groups R are NO₂ (**3**) or CN (**4**), and in which the donor and acceptor ends of the desired synthon are located at 180° to each other on the ends of arylalkynyl ligands (Fig. 2). These systems, although unknown, were expected to be stable and synthetically accessible, and have a linear, relatively two-dimensional shape which thus mimics 4-iodonitrobenzene and 4-iodobenzonitrile, respectively. They also contain no other groups that seemed likely to become involved in strong intermolecular interactions that could prevent the formation of the one-dimensional pattern demonstrated by their organic analogues.



Fig. 2 Target bis-alkynyl compounds: $R = NO_2$ 3, CN 4 or I 5.

The strategy adopted for the synthesis of trans- $Pt(PEt_3)_2(C \equiv C - p - C_6H_4 - I)(C \equiv C - p - C_6H_4 - R)$ (R = NO₂ 3, CN 4) was based upon the known methodology for the synthesis of similar symmetric bis-alkynyl compounds. Starting from trans-Pt(PEt₃)₂I₂, a copper(I) iodide catalysed reaction with 1.05 equivalents of H–C=C-p-C₆H₄–R (R = NO₂ or CN) in the presence of base generates the mono-alkynyl compounds trans-Pt(PEt₃)₂(C=C-p-C₆H₄-R)I (R = NO₂ 1, CN 2) in good yield, as well as a small amount of the bis(alkynyl) compounds trans-Pt(PEt₃)₂(C \equiv C-*p*-C₆H₄-R)₂, and some unreacted diiodo starting material; the product distribution shows that replacement of the first iodide at the platinum centre is faster than the second. The three species are readily separated by column chromatography, and synthetic, spectroscopic and analytical details for all compounds are given as ESI.† Further reaction of 1 or 2 with H–C=C-p-C₆H₄–I under the same conditions generates 3 or 4, respectively. This represents the first synthesis of unsymmetrical platinum bis-alkynyl compounds from the parent alkynes; at no point has any evidence for any exchange of alkynyl ligands been observed. The crystal structure of 2 was determined by X-ray diffraction, and is reported in the ESI.†

Structural analysis[‡] of crystals of **3** revealed that there were significant intermolecular interactions within the crystal structure, but not of the envisaged $I \cdots NO_2$ variety. Rather, the major supramolecular interaction seen is between the iodine atom of one molecule and a carbon–carbon triple bond within a neighbouring molecule. This has the effect of making these two molecules perpendicular to each other, so the overall effect is to create a zigzag chain (Fig. 3).

These polar chains lie antiparallel to each other, to give a centrosymmetric two-dimensional sheet that lies parallel to the b axis of the cell. There are no short contacts involving the nitro group within the structure. There is a small amount of disorder present, with the nitro group being replaced 14% of the time by an iodine atom as the molecule is reversed within the lattice. It was not possible to grow crystals of 4 suitable for X-ray diffraction.

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Fig. 3 Solid-state packing of 3: hydrogen atoms and the ethyl groups of the PEt_3 ligands (orange) have been removed for clarity.

In order to establish whether the $I \cdots \pi$ interaction seen above is a reproducible phenomenon, we next synthesised Pt(PEt₃)₂(C \equiv C-*p*-C₆H₄–I)₂ **5**. Crystallographic analysis reveals that this structure also contains the same type of interaction, but now occurring symmetrically at both ends of the molecule (Fig. 4). The sheet of molecules thus formed have their platinum atoms lying in the (–2 0 4) plane of the cell.



Fig. 4 Solid-state packing of 5: hydrogen atoms and the ethyl groups of the PEt_3 ligands (orange) have been removed for clarity.

Within 3 and 5 the distance between the carbon atoms of the triple bond and the iodo atom is in the order of 3.4–3.7 Å, less than or equal to the sum of their van der Waals' radii (3.68 Å). The distance from the centre of the triple bond to the iodine atom is 3.60 and 3.43 Å, respectively, for 3 and 5. Clearly there is a halogen-bonding interaction between the two, in which the π -system is the electron-donor and polarising species.

A search of the Cambridge Structural Database⁷ reveals that it contains 39 structures containing both a carbon–carbon triple bond and a terminal carbon–iodine bond. The iodo– π interaction is present in three of these structures, and is thus not newly discovered but has merely been overlooked in discussions of halogen-bonding. Packing within the crystal structure of 1,2-diiodoacetylene⁸ adopts a similar motif to that seen for **5**, reflecting the disposition of iodine atoms and triple-bonds in both species; equally, the packing of 1-(ethynyl)-4-iodo-3-(methylaminocarbonyl)benzene⁹ creates a zigzag similar to **3**, as both compounds contain a single iodo group and a carbon– carbon triple bond at opposite ends of an approximately linear molecule. The third example, 1,4-bis(4-*tert*-butylphenyl)-1,2diiodobut-1-en-3-yne,¹⁰ has a different arrangement of groups, which creates a dimeric unit within the crystal.

Similarities between the recognition properties of organic iodides and terminal alkynes have been reported before,¹¹ and in this respect the iodo $\cdots \pi$ interaction discussed herein is equivalent to the \equiv CH $\cdots \pi$ synthon. As a result of this equivalence, the structures of the 4-halogenoethynylbenzenes (apart from the fluoro analogue) display the same motif as **3**,¹² and the packing of 1,4-diethynylbenzene is the same as that **Table 1** Similarities between halogen bonding motifs of terminal alkynes (left) and aryl iodides (right), showing how the $I \cdots \pi$ interaction (bottom right) might have been predicted by consideration of the similar alkynyl $\cdots \pi$ motif



of 5.¹¹ This is emphasised in Table 1, which illustrates known similarities between the recognition properties of iodo and alkyne groups and shows how the $I \cdots \pi$ interaction continues this trend.

To summarise, we report:

(i) the first straightforward synthesis of mono- and unsymmetric bis-alkynyl platinum compounds.

(ii) Identification of the $I \cdots \pi$ synthon as a halogen-bonding interaction which mimics the $\equiv CH \cdots \pi$ hydrogen bond.

(iii) That the influence of halogen-bonding on organic compounds may be reproduced in the structures of inorganic mimics.

Notes and references

‡ Crystal structure data for **2**, **3** and **5**: **2**: C₂₁H₃₄INP₂Pt, M = 684.42, triclinic, space group $P\overline{1}$ (no. 2), a = 8.609(2), b = 14.534(6), c = 19.817(9) Å, a = 95.63(3), $\beta = 90.51(3)$, $\gamma = 90.93(4)^{\circ}$, U = 2467.1(16) Å³, Z = 4, $D_c = 1.843$ g cm⁻³, $\mu = 7.074$ mm⁻¹, T = 100, 27899 reflections collected, 11193 unique data ($R_{int} = 0.0314$), R1 = 0.0363. **3**: C₂₈H₃₈I_{1.14}N_{0.86}O_{1.72}P₂Pt, M = 815.71, monoclinic, space group $P_{1/c}$ (no. 14), a = 9.897(2), b = 28.205(6), c = 10.995(2) Å, $\beta = 91.19(3)^{\circ}$, U = 3068.5(11) Å³, Z = 4, $D_c = 1.765$ g cm⁻³, $\mu = 5.844$ mm⁻¹, T = 100, 29713 reflections collected, 7040 unique data ($R_{int} = 0.0306$), R1 = 0.0385. **5**: C₂₈H₃₈I₂P₂Pt, M = 885.41, monoclinic, space group $P_{2_1/c}$ (no. 14), a = 9.4839(10), b = 15.0660(14), c = 11.1185(17) Å, $\beta = 97.685(9)^{\circ}$, U = 1574.4(3) Å³, Z = 2, $D_c = 1.868$ g cm⁻³, $\mu = 6.533$ mm⁻¹, T = 173, 17917 reflections collected, 3618 unique data ($R_{int} = 0.0209$), R1 = 0.0163. CCDC reference numbers 262633–262635. See http://www.rsc.org/suppdata/dt/b5/b506025g/ for crystallographic data in CIF or other electronic format.

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