Evaluation of the relative importance of Ti–Cl···H–N hydrogen bonds and supramolecular interactions between perfluorophenyl rings in the crystal structures of $[Ti(NR)Cl_2(NHMe_2)_2]$ (R = ⁱPr, C₆H₅ or C₆F₅)[†]

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The three closely-related compounds [Ti- $(N^{i}Pr)Cl_2(NHMe_2)_2$] 1, [Ti(NC_6H_5) $Cl_2(NHMe_2)_2$] 2 and [Ti(NC_6F_5) $Cl_2(NHMe_2)_2$] 3 all crystallize in the space group *C*2/*c* with the titanium atoms lying on two-fold axes at (0, *y*, 1/4); in compounds 1 and 2 the molecules are linked in one-dimensional infinite chains by intermolecular Ti-Cl···H-N hydrogen bonds along the direction of the crystallographic *c* axis, whereas in 3 offset face-to-face interactions between the C₆F₅ rings break down the hydrogen bonded chains.

The importance of non-covalent interactions between hydrogen-substituted arene rings in supramolecular chemistry is now well-recognised.1 Arene-perfluoroarene interactions represent a special case and are, for instance, responsible for the 24 °C melting point of the 1:1 benzene-perfluorobenzene complex (while those of neat benzene and perfluorobenzene are 5.5 and 4 °C, respectively).² Such mixed arene-perfluoroarene interactions have recently attracted renewed attention in a range of supramolecular contexts.³ More recently, reports of the possible importance of supramolecular interactions between pairs of perfluoroarene rings in organic and inorganic/organometallic contexts have appeared.⁴ Hunter and Sanders were the first to propose a simple model for the interpretation of intermolecular π -interactions between aromatic molecules.⁵ Also recently, Dance and coworkers⁶ reported density funtional calculations on the gas-phase dimers $(\hat{C}_6H_6)_2$ and $(\hat{C}_6F_6)_2$ and concluded that (i) intermolecular interactions between perfluorinated aromatic rings are slightly more attractive than those of the hydro analogues (due mainly to an increased van der Waals component); (ii) calculated intermolecular potentials for offset face-toface (off) interactions between pairs of C_6F_6 rings are twice as favourable as edge-to-face or vertex-to-face interactions; and that (iii) there are no major differences between the supramolecular embraces adopted by poly-phenyl and poly-fluorophenyl systems. Despite these recent, promising indicators of such supramolecular interactions, no clear-cut, 'head-to-head' study has been reported showing the relative importance of fluoroarene-fluoroarene interactions in comparison with possible arene-arene or other (e.g. hydrogen bonded) supramolecular motifs. Here we report the molecular and supramolecular structures of a series of closely related compounds that further demonstrate the importance of fluoroarene-fluoroarene interactions in crystal engineering.

As part of our research programme in transition metal imido chemistry⁷ we found that the reaction of a very wide range of primary amines RNH₂ (R = alkyl or aryl) with [TiCl₂(NMe₂)₂] in benzene leads to the highly air- and moisture-sensitive imidobis(dimethylamino) titanium complexes [Ti(NR)Cl₂(NHMe₂)₂] in good to excellent yields.⁸ In this communication we focus on the molecular and supramolecular structures of three of these compounds, namely where $R = {}^{i}Pr \mathbf{1}$, $C_6H_5 \mathbf{2}$ or $C_6F_5 \mathbf{3}$.†‡ The solid state molecular structures are fully consistent with the solution ${}^{1}H$ and ${}^{13}C-\{{}^{1}H\}$ NMR and solid state IR (Nujol mull) spectra given as ESI.†

The molecular structures of $[Ti(NR)Cl_2(NHMe_2)_2]$ (R = ⁱPr **1**, C₆H₅ **2** or C₆F₅ **3**) are presented in Fig. 1.‡ All adopt approximately trigonal bipyramidal geometries (equatorial NR and Cl groups) with linear or near-linear Ti=N–R linkages; the intramolecular distances and angles in **1**–**3** are unexceptional in comparison with other titanium imido complexes.⁹ Hydrogens were placed in calculated positions (N–H 0.87 Å, C–H 1.00 Å). The structures are approximately isomorphous, with all three compounds crystallizing in the space group *C*2/*c* and the Ti atoms lying on crystallographic two-fold axes (passing through the Ti=N bond) at (0, *y*, 1/4) or a symmetry-equivalent position. While the molecular structures of **1**, **2** and **3** are very similar, their supramolecular structures differ significantly.

Molecules of [Ti(NiPr)Cl₂(NHMe₂)₂] 1 form hydrogen bonded chains in the solid state as shown in Fig. 2(a). Hydrogen bonds form between the N-H groups of NHMe2 ligands and Ti-Cl group hydrogen bond acceptors on neighbouring titanium complexes, and propagate in the direction of the crystallographic c axis. The $Ti-Cl\cdots H-N$ contacts of 2.51 Å may within error be considered 'short' according to Brammer and Orpen's classification¹⁰ based on a detailed analysis of crystallographic phenylimido data.9 Moving on the system to $[Ti(NC_6H_5)Cl_2(NHMe_2)_2]$ **2** [Fig. 2(b)] we encouter the same hydrogen-bonded supramolecular arrangement with experimentally comparable Ti-Cl···H-N contacts of 2.46 Å and Cl···H-N angles (158° in 2 vs. 160° in 1). There are single C- H_{arene} ...C pairwise contacts (C-H...C = 3.17 Å) between rings of one hydrogen-bonded chain of 2 and the neighbouring one. However, these are considered to be secondary consequences of the favoured Ti-Cl···H-N hydrogen bonded arrangement established for 1 (where no arene-arene interactions are possible). The *a* [16.913(1) *vs.* 16.260(1) Å] and *c* [12.044(1) vs. 11.935(1)] unit cell lengths for 1 and 2 are fairly similar while the b unit cell dimensions of 9.101(1) and 10.303(1) Å,



Fig. 1 Structures of $[Ti(NR)Cl_2(NHMe_2)_2]$ [(a) $R = {}^iPr$ 1; (b) $R = C_6H_5$ 2 and (c) $R = C_6F_5$ 3]. C-bound H atoms omitted; displacement ellipoids drawn at the 25% probablility level; H atoms drawn as spheres of arbitrary radius.

 $[\]dagger$ Electronic supplementary information (ESI) available: characterisation and crystal data for compounds 1–3. See http://www.rsc.org/suppdata/cc/ b1/b109251k/

respectively, show the greatest difference (being the direction in which the larger imido substitutent, $Pr vs. C_6H_5$, is oriented).

Turning now to the perfluorophenylimido complex $[Ti(NC_6F_5)Cl_2(NHMe_2)_2]$ **3** [Fig. 3(a)] we see immediately that the unit cell has considerably distorted to disrupt the hydrogen bonded chain and arrange the neighbouring perfluorophenyl rings in a close, offset face-to-face (*off*) arrangement. The Ti-Cl····H–N distances of 2.93 Å (associated C····H–N angles = 136°) may now be classified¹⁰ as 'long', and are approximately equal to the sum of the van der Waals radii for H (1.2 Å) and Cl



Fig. 2 Portion of the hydrogen-bonded chains of $[Ti(NR)Cl_2(NHMe_2)_2]$ [(a) $R = {}^{i}Pr$ 1; (b) $R = C_6H_5$ 2] with carbon-bound H atoms omitted and other atoms drawn as spheres of arbitrary radius.





Fig. 3 (a) Portion of the π -stacked chains of $[Ti(NC_6F_5)Cl_2(NHMe_2)_2]$ 3 with carbon-bound H atoms omitted. Intermolecular Ti–Cl···H–N distances = 2.93 Å and Cl···H–N angle = 136°. (b) Relationship between the C_6F_5 groups bonded to N(1) and N(1C). Projected strictly onto the $\{C(1),C(2),C(3),C(4),C(2B),C(3B)\}$ least-squares plane. Separation between C_6F_5 planes = 3.23 Å.

(1.75 Å).¹¹ The solid state (Nujol mull) IR spectra of **1**, **2** and **3** feature NHMe₂ ligand v(N-H) stretches of 3228, 3220 and 3275 cm⁻¹, respectively, consistent with the variations in Cl···H–N interactions determined by X-ray diffraction. While the unit cell *a* length [15.696(3) Å] in **3** is comparable to those in **1** and **2** (unsurpringly since it is perpendicular to the direction of propagation of the (formerly) hydrogen-bonded chain), there is a substantial expansion in the *b* direction [unit cell length = 15.569(1) Å] and a concomitant large contraction in the *c* unit cell length [6.7371(9) Å]. The separation between neighbouring titanium centres is c/2 = 3.365 Å which is just slightly larger than the interplanar separation of 3.23 Å between neighbouring C₆F₅ rings.

Fig. 3(b) shows in projection the *off* arrangement of two adjacent C₆F₅ rings. Each of the rings shown is involved in four close contacts to the neighbouring ring, namely two with C···C 3.264(3) Å and two with F···C 3.256(4) Å. In the π -stacked motif in crystals of **3** this gives each ring eight contacts in total (four with each of its two neigbours). The C···C and C···F contacts can be favourably compared to Dance and coworkers' calculated values of 3.19 and 3.14 Å, respectively, for gas-phase *off*-(C₆F₆)₂ (being the most stable supramolecular arrangement for this dimer).⁶

In summary, the crystal structures of the three compounds 1–3, when taken together, provide further evidence for the comparatively strong driving force of supramolecular $C_6F_5\cdots C_6F_5$ π -stacking interactions in the solid state. Such interactions appear to be at least as strong as other, well-documented examples such as M–Cl···H–N–M hydrogen bonding.¹⁰ We are continuing to investigate the supramolecular and crystal engineering roles of these types of interactions between C_6F_5 rings for both imido and non-imido systems.

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