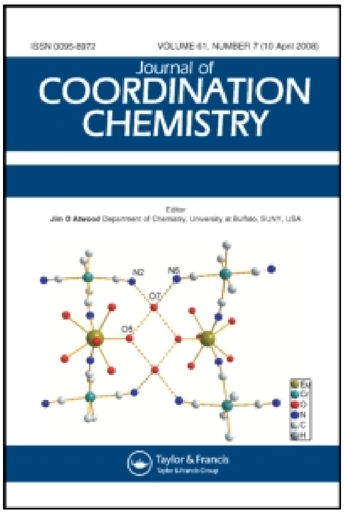

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Pb^{II} 4,4,4-trifluoro-1-naphthyl-1,3-butanedione complexes of 1,10-phenanthroline and 2,2'-bipyridine ligands

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Pb^{II} 4,4,4-trifluoro-1-naphthyl-1,3-butanedione complexes of 1,10-phenanthroline and 2,2′-bipyridine ligands

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Lead(II) 4,4,4-trifluoro-1-naphthyl-1,3-butanedione (Htfnb) complexes of 1,10-phenanthroline (phen) and 2,2′-bipyridine (bpy), $[Pb_2(bpy)_2(tfnb)_2]$ (**1**) and $[Pb_2(phen)_2(tfnb)_2]$ (**2**), have been synthesized and characterized by elemental analysis, IR, spectroscopy and X-ray crystallography. The self-assembly of **1** and **2** is likely to be caused by C–H···F–C, C–H···O and π–π stacking interactions.

Keywords: Lead(II); 4,4,4-Trifluoro-1-naphthyl-1,3-butanedione; Weak interaction

1. Introduction

Designing new materials requires the manipulation of intermolecular interactions to achieve the desired solid-state structure, and therefore the desired physical or chemical properties [1]. This necessitates understanding of the nature of weak non-covalent interactions, which dictate conformational and packing features in crystalline solids. There are a rich variety of such intermolecular interactions, which serve as tools in engineering such as molecular assemblies [2]. H-bonds are amongst the most studied of such intermolecular interactions [3], although other, weaker molecular interactions have been identified such as halogen–halogen interactions [4], electrostatic forces [5], and π–π stacking [6]. However, H-bonds [7, 8] are still the most important and decisive element in crystal engineering because the interactions involving hydrogen bonds are of a highly directional nature and the strength depends on the electronegativity of the element that accepts the hydrogen atom. Some of the well-known interactions involving hydrogen bonds are O–H···N, N–H···O, C–H···O, C–H···N, C–H···π and C–H···X [9], which provide well-defined molecular frameworks in crystalline lattices. Interactions involving halogens, especially Cl and Br, have been analyzed both in terms of their directional preferences and in terms of the strength of their interactions [10]. In recent literature, the importance of interactions involving fluorine in crystal engineering has

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been explored in greater detail [11, 12]. Recently in an effort to explore weak interactions in complexes, lead(II) complexes with β-diketonate and neutral diimine chelating ligands have been synthesized and determined by X-ray crystal structures [13–16]. In this paper we report the synthesis and crystal structures of $[Pb_2(bpy)_2(tfnb)_4]$ (**1**) and $[Pb_2(phen)_2(tfnb)_4]$ (**2**) ("bpy", "phen" and "tfnb" are the abbreviations of 2,2′-bipyridine, 1,10-phenanthroline and 4,4,4-trifluoro-1-naphthyl-1,3-butanedionate ligands, respectively). These ligands have the potential to generate $C–H \cdots F$, $C–H \cdots O$, and π-stacking interactions in the solid state.

2. Experimental

2.1. *Physical measurements*

IR spectra were recorded as nujol mulls using Perkin-Elmer 597 and Nicolet 510P spectrophotometers. Microanalyses were carried out using a Heraeus CHN-O- Rapid analyzer. Melting points were measured on an Electrothermal 9100 apparatus and are uncorrected.

2.2. *Preparation of [Pb$_2$(bpy)$_2$(tfnb)$_4$] (1)*

2,2′-bipyridine (0.156 g, 1 mmol) was placed in one arm of a branched tube [17] and lead(II) acetate (0.36 g, 1 mmol), and "Htfnb" ligand (0.532 g, 2 mmol) in the other. Methanol was carefully added to fill both arms, the tube sealed and the ligand-containing arm immersed in a bath at 60°C while the other was at ambient temperature. After 3 days, crystals deposited in the cooler arm were filtered off, washed with acetone and ether, and air dried, yield: 0.580 g, 65%, m.p. = 185°C. (Found C, 51.30; H, 2.65; N, 3.26; calculated for $C_{76}H_{48}F_{12}N_4O_8Pb_2$: C, 51.02; H, 2.68; N, 3.13%).

IR (cm^{-1}): 632(m), 709(m), 809(m), 1133(s), 1187(s), 1288(vs), 1473(s), 1535(s), 1612(vs), and 3062(w).

2.3. *Preparation of [Pb$_2$(phen)$_2$(tfnb)$_4$] (2)*

1,10-phenanthroline (0.2 g, 1 mmol) was placed in one arm of a branched tube and lead(II) acetate (0.36 g, 1 mmol), and "Htfnb" (0.532 g, 2 mmol) in the other. Methanol was carefully added to fill both arms, the tube sealed and the ligand-containing arm immersed in a bath at 60°C while the other was at ambient temperature. After 3 days, crystals deposited in the cooler arm were filtered off, washed with acetone and ether, and air dried, yield: 0.642 g, 70%, m.p. 215°C. (Found C, 52.10; H, 2.75; N, 3.26; calculated for $C_{80}H_{48}F_{12}N_4O_8Pb_2$: C, 52.30; H, 2.61; N, 3.05%).

IR (cm^{-1}): 721(m), 758(m), 1025(m), 1160(s), 1288(vs), 1465(s), 1573(s), 1621(vs), and 3065(w).

Table 1. Crystal data and structure refinement for **1** and **2**.

Identification code	**1**	**2**
Empirical formula	$C_{76}H_{48}F_{12}N_4O_8Pb_2$	$C_{80}H_{48}F_{12}N_4O_8Pb_2$
Formula weight	1787.56	1835.60
Temperature (K)	298(2)	298(2)
Wavelength (Å)	0.71069	0.71069
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
Unit cell dimensions (Å, °)		
a	11.5360(18)	10.347(2)
b	12.129(2)	13.229(2)
c	12.492(2)	14.053(3)
α	81.62(2)	106.51(2)
β	82.57(2)	90.18(2)
γ	73.41(2)	105.46(2)
Volume (Å^3)	1650.1(5)	1771.1(6)
Z	1	1
Density (calculated) (Mg m^{-3})	1.799	1.721
Absorption coefficient (mm^{-1})	5.191	4.839
$F(000)$	868	892
Crystal size (mm^3)	$0.45 \times 0.41 \times 0.23$	$0.38 \times 0.25 \times 0.20$ mm^3
Theta range for data collection (°)	1.76–20.40	1.52–20.40
Index ranges	$-11 \le h \le 11$, $-11 \le k \le 11$, $-11 \le l \le 11$	$-9 \le h \le 10$, $-12 \le k \le 12$, $-13 \le l \le 13$
Reflections collected	6666	7048
Independent reflections	5673 [R(int) = 0.0613]	6005 [R(int) = 0.0501]
Completeness to theta	93.3%	93.6%
Refinement method Full-matrix least-squares on F^2 Full-matrix least-squares on F^2		
Data/restraints/parameters	5673/22/540	6005/5/486
Goodness-of-fit on F^2	1.157	1.211
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0584$, $wR_2 = 0.1439$	$R_1 = 0.0502$, $wR_2 = 0.1390$
R indices (all data)	$R_1 = 0.0614$, $wR_2 = 0.1476$	$R_1 = 0.0573$, $wR_2 = 0.1539$
Largest diff. peak, hole (e Å^{-3})	1.240 and −3.286	1.251 and −1.567

2.4. *Crystallography*

The structure was solved by direct methods, SHELXS-97 [18], and refined by full matrix least squares using SHELXL-97 [19]. SHELX operations were automated using OSCAIL, which was also used to obtain the drawings [20]. The xcad program WITHIN Oscail was used for data reduction and the data were corrected for Lorentz and polarization effects. An absorption correction was applied using the PSI scans method [21]. Hydrogen atoms were included in calculated positions with thermal parameters 30% larger than the atom to which they were attached. The lead atoms and those of their coordination spheres were refined anisotropically. All calculations were performed on a Pentium PC.

Crystal data and structure refinement parameters are given in table 1. Selected bond lengths and angles are given in tables 2 and 3. Anisotropic thermal parameters, observed and calculated structure factors, full lists of bond distances, bond angles and torsion angles are given in the supplementary material. ORTEX diagrams and perspective views of the packing in the crystal are shown in figures 1 to 4.

Table 2. Selected bond lengths (Å) and angles (°) for **1**.

Pb1–O1	2.36(2)	Pb1–O2	2.49(2)
Pb1–O3	2.50(2)	Pb1–O4	2.52(2)
Pb1–N1	2.69(3)	Pb1–N2	2.72(3)
Pb2–O5	2.33(2)	Pb2–O8	2.44(2)
Pb2–O6	2.48(2)	Pb2–O7	2.53(2)
Pb2–N4	2.67(2)	Pb2–N3	2.69(2)
O1–Pb1–O2	73.9(6)	O1–Pb1–O3	71.8(8)
O2–Pb1–O3	131.0(7)	O1–Pb1–O4	82.3(6)
O2–Pb1–O4	72.9(6)	O3–Pb1–O4	68.8(7)
O1–Pb1–N1	91.0(7)	O2–Pb1–N1	137.3(8)
O3–Pb1–N1	77.1(8)	O4–Pb1–N1	145.7(8)
O1–Pb1–N2	83.0(7)	O2–Pb1–N2	81.8(7)
O3–Pb1–N2	126.3(8)	O4–Pb1–N2	153.4(6)
N1–Pb1–N2	56.4(9)	O5–Pb2–O8	75.9(7)
O5–Pb2–O6	69.1(7)	O8–Pb2–O6	132.7(7)
O5–Pb2–O7	83.0(7)	O8–Pb2–O7	72.0(7)
O6–Pb2–O7	73.0(7)	O5–Pb2–N4	81.8(7)
O8–Pb2–N4	126.6(7)	O6–Pb2–N4	79.0(8)
O7–Pb2–N4	151.4(6)	O5–Pb2–N3	95.1(7)
O8–Pb2–N3	72.8(7)	O6–Pb2–N3	139.6(8)
O7–Pb2–N3	144.1(6)	N4–Pb2–N3	61.6(7)

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

Pb1–O1	2.37(2)	Pb1–O2	2.51(2)
Pb1–N1	2.62(2)	Pb1–N2	2.63(3)
Pb1–O3	2.64(2)	Pb1–O4	2.67 (2)
Pb2–O7	2.28(2)	Pb2–O5	2.42(2)
Pb2–O8	2.49 (2)	Pb2–N3	2.62(2)
Pb2–N4	2.64(2)	Pb2–O6	2.64(2)
O1–Pb1–O2	73.8(7)	O1–Pb1–N1	81.3(8)
O2–Pb1–N1	78.7(8)	O1–Pb1–N2	83.1(8)
O2–Pb1–N2	135.8(8)	N1–Pb1–N2	60.7(8)
O1–Pb1–O3	75.2(9)	O2–Pb1–O3	129.7(7)
N1–Pb1–O3	133.4(7)	N2–Pb1–O3	76.8(8)
O1–Pb1–O4	93.4(8)	O2–Pb1–O4	73.3(7)
N1–Pb1–O4	151.8(7)	N2–Pb1–O4	146.5(7)
O3–Pb1–O4	70.1(7)	O7–Pb2–O5	77.0(7)
O7–Pb2–O8	72.9(7)	O5–Pb2–O8	124.7(7)
O7–Pb2–N3	79.1(6)	O5–Pb2–N3	136.2(7)
O8–Pb2–N3	81.0(7)	O7–Pb2–N4	82.8(7)
O5–Pb2–N4	77.7(6)	O8–Pb2–N4	140.1(7)
N3–Pb2–N4	63.3(7)	O7–Pb2–O6	88.8(8)
O5–Pb2–O6	67.0(7)	O8–Pb2–O6	67.1(7)
N3–Pb2–O6	148.1(7)	N4–Pb2–O6	144.7(7)

3. Results and discussion

Reaction between "bpy" or "phen" with mixtures of lead(II) acetate with "Htfnb" provided crystalline materials that analyzed as $[Pb_2(bpy)_2(tfnb)_4]$ **1** and $[Pb_2(phen)_2(ttfa)_4]$ **2**, respectively. Single X-ray crystal analysis reveals that **1** and **2** crystallize in the triclinic space group P1. The structures of these complexes can be considered as dimers of lead(II) coordinated by the two "bpy" or "phen" ligands and four "$tfnb^-$" anions, respectively (figures 1 and 2). The coordination number of lead in

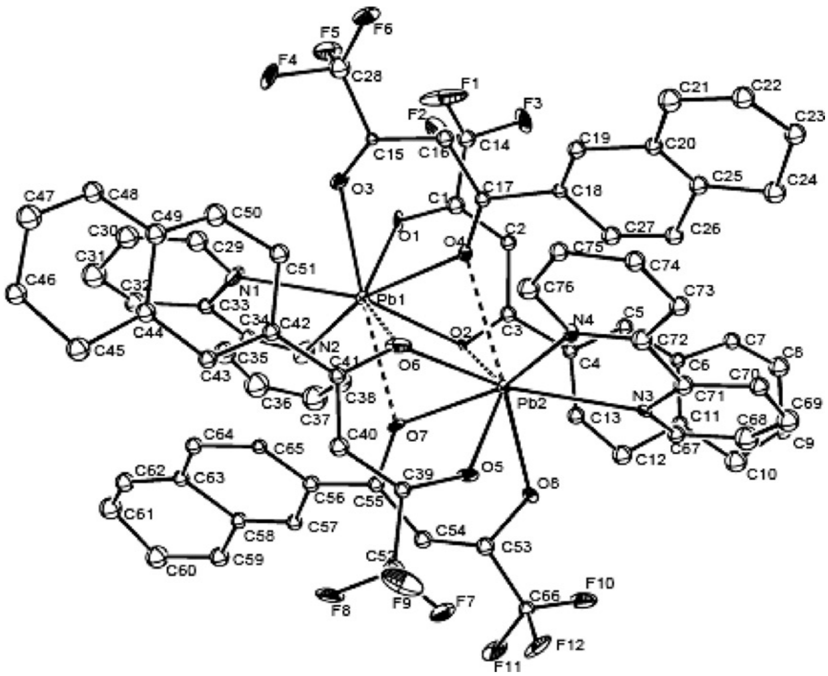

Figure 1. ORTEX diagram of **1**; hydrogen atoms are omitted for clarity.

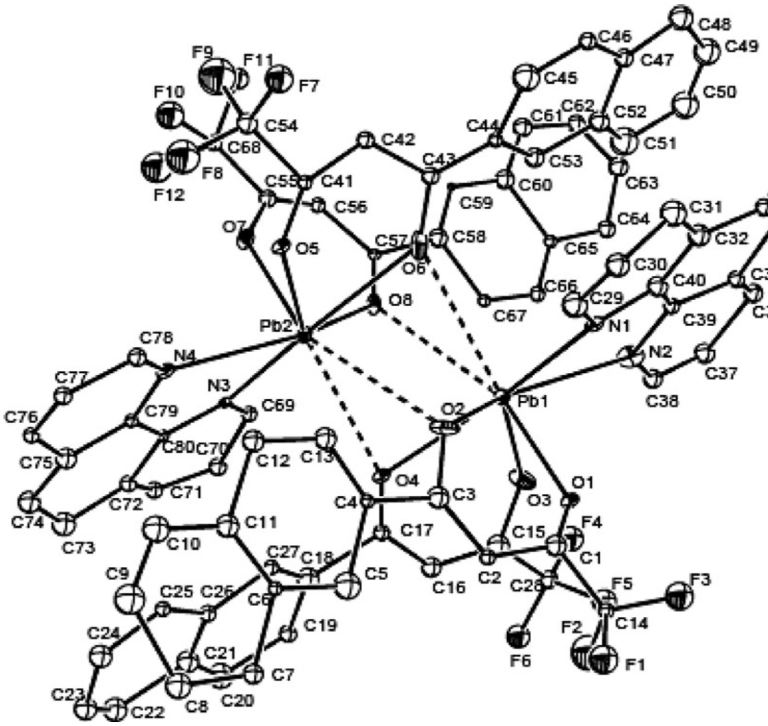

Figure 2. ORTEX diagram of **2**; hydrogen atoms are omitted for clarity.

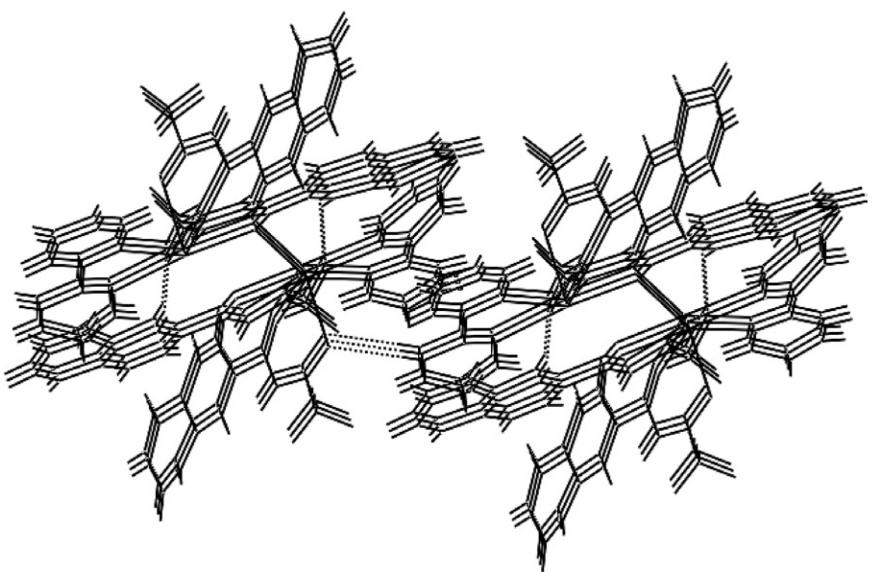

Figure 3. Packing of **1** (down a) to form a supramolecular structure *via* weak interactions.

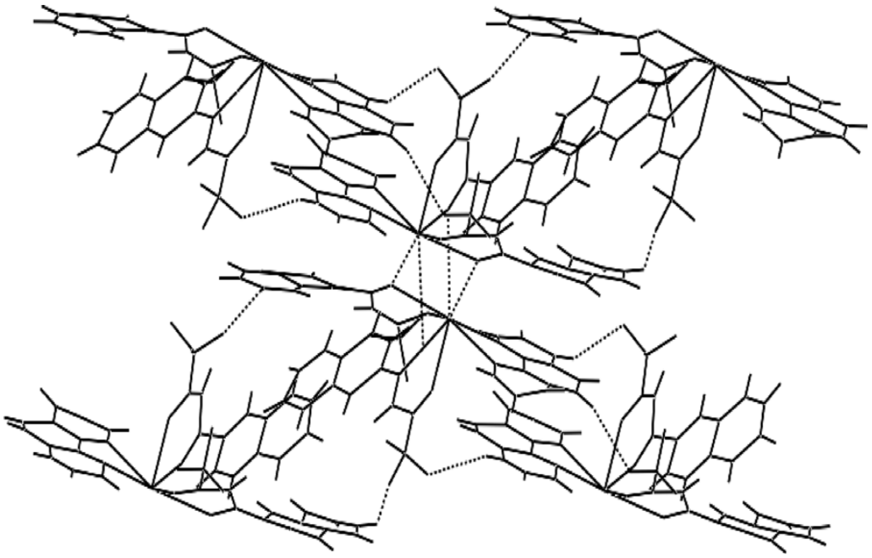

Figure 4. Packing of **2** (down a) to form a supramolecular structure *via* weak interactions.

these complexes is eight (two of "bpy" or "phen" and six of "tfnb$^-$" anions). In fact each Pb in this structure along with six normal bonds forms two "weak" Pb $\cdots$ O bonds yielding the two Pb_2O_2 rhombuses [22], with distances Pb1–O7 = 2.864 Å, Pb1–O6 = 3.924 Å, Pb2–O4 = 2.942 Å, Pb2–O2 = 3.748 Å for **1** and Pb1–O6 = 3.230 Å, Pb1–O8 = 3.330 Å, Pb2–O4 = 3.082 Å, Pb2–O2 = 3.468 Å for **2** (tables 2 and 3). The presence of a lone pair on the lead atom is apparently the reason that the bridging interactions are so long. If the stereo-chemically active lone pair [23] were not present,

Table 4. Weak interactions in crystals of **1** and **2**.

B–H···A	H···A/Å	B···A/Å	B–H···A/°
(**1**)			
C19–H19···F10	2.400	3.296	162.49
C57–H57···F4	2.562	3.346	142.33
C70–H70···O1	2.428	3.094	128.53
C32–H32···O5	2.634	3.451	146.95
C29–H29···O3 (Intramolecular)	2.448	3.149	132.32
C38–H38···O2 (Intramolecular)	2.523	3.226	132.52
C67–H67···O8 (Intramolecular)	2.506	3.054	117.90
C13–H13···O8 (Intramolecular)	2.505	3.292	142.63
C76–H76···O6 (Intramolecular)	2.380	3.087	132.16
(**2**)			
C77–H77···F4	2.657	3.516	153.42
C76–H76···F3	2.542	3.392	137.95
C24–H24···F11	2.564	3.362	144.39
C33–H33···F8	2.622	3.323	132.55
C49–H49···F1	2.586	3.212	124.99
C36–H36···F12	2.661	3.511	151.67
C37–H37···F7	2.595	3.446	152.47
C67–H67···O3 (Intramolecular)	2.910	3.742	149.67
C69–H69···O8 (Intramolecular)	2.572	3.290	129.38
C78–H78···O5 (Intramolecular)	2.542	3.141	122.73
C29–H29···O2 (Intramolecular)	2.499	3.156	128.39
C38–H38···O3 (Intramolecular)	2.354	3.093	136.71

this phenomenon results in more symmetry. In addition, these bond length variations may be ascribed to the bridging nature of some of the ligands and possibly to the effect of Pb···Pb interactions within the dimers.

A search was made for weak directional intermolecular interactions in the structures of **1** and **2** (table 4). There are C–H···F–C interactions and C–H···O interactions, the weak hydrogen bonding between the hydrogen of aromatic rings and fluorine and oxygen atoms belonging to "tfnb$^-$" anions of adjacent complexes. In **1** and **2**, the H···F distance ranges are 2.400 to 2.661 Å and the C–H···F angles 124.99° to 162.49°, and the H···O distances range from 2.428 to 2.634 Å and the C–H···O angles 128.53° to 146.95°, values that suggest strong interactions within this class of weak noncovalent contacts [24, 25].

There are π–π stacking interactions [26, 27] between parallel aromatic rings belonging to adjacent chains in the complexes, as shown in figures 3 and 4. The pyridyl and phenyl groups are almost parallel and separated by the expected distance. In fact, in **1**, there are five different types of noncovalent π–π stacking interactions [28, 29], "face-to-face" between pyridyl groups, slipped "face-to-face" between naphthyl groups, "face-to-face" between naphthyl and pyridyl groups (intramolecular), "edge-to-edge" between naphthyl and pyridyl groups as well as "edge-to-face" between naphthyl groups; the interplanar distances are 3.427, 3.403, 3.316, 3.740 and 3.646 Å, respectively, which are normal π–π stacking distances [30, 31]. In **2**, there are six other types of noncovalent π–π stacking interactions, "face-to-face" between "phen" groups, two "face-to-face" between naphthyl and "phen" groups, two "edge-to-face" between naphthyl groups as well as "edge-to- face" between naphthyl and "phen" groups [25, 26]; the interplanar distances are 3.161, 3.297, 3.487, 3.484, 3.402 and 3.654 Å, respectively, which are also normal π–π stacking distances [30–32].

In conclusion, a subtle interplay among lone pair activity, strong and weak interactions and π–π stacking appears to control the packing motifs in the crystal structures of **1** and **2**. Our current results suggest that while interactions involving "organic fluorine" have a significant influence in generating supramolecular assemblies in inorganic solids, the general use of these interactions for the *a priori* prediction of packing motifs is yet to be harnessed.

Supplementary material

Crystallographic data and tables of 2 and 3 of the structures reported in the paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no, CCDC-630912 for **1** and 630913 for **2**. Copies of the data can be obtained on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: +44–1223/336033; Email: deposit@ccdc.cam.ac.uk].

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