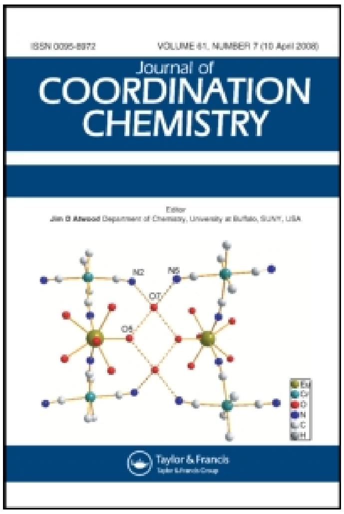

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Structural investigation of lead(II) fluorine-substituted <i>β</i>-diketonates

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Structural investigation of lead(II) fluorine-substituted *β*-diketonates

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Lead(II) 2,9-dimethyl-1,10-phenanthroline complexes with anionic (L = 4,4,4-trifluoro-1-phenyl-1,3-butandionate (tfpb) and thenoyltrifluoroacetonate (ttfa)) ligands, $[Pb_2(dmp)_2(\mu\text{-}L)_2(L)_2]$, have been synthesized and characterized by elemental analysis and IR, ^{1}H NMR, and ^{13}C NMR spectroscopy. The single-crystal structures of the compounds show the coordination number of Pb(II) to be eight with two N-donor atoms from a "dmp" ligand and six O-donors from the anionic ligands. Self-assembly of these complexes is realized by C–H $\cdots$ F–C, C–F $\cdots$ F–C and π–π stacking interactions.

Keywords: Crystal structure; Lead(II) complexes; *β*-Diketone; Weak interactions

1. Introduction

Supramolecular metal complexes formed by self-assembly are a frontier in research because of their potential applications in catalysis, molecular recognition, molecular electronics photonic materials, etc. Weak forces such as hydrogen bonding, π-stacking, dipole–dipole attractions and van der Waals forces can assemble molecular components selectively into complex structural motifs [1–3]. Fluorous materials, essentially compounds in which CH bonds have been completely or partially replaced by CF, have recently become the subject of considerable interest as "green" solvents and as catalysts with novel properties [4, 5]. Computational studies [6–9] indicated that fluorocarbon/hydrocarbon and π–π stacking interaction energies may be quite significant, with the mode of interaction dependent upon other substituents within the molecules. The F-based intermolecular interactions are rather weak, and the importance of the C–F bond in hydrogen bonding has been debated intensely in recent years [10], particularly with respect to the hydrogen bond of the C–F $\cdots$ H–C type [11].

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Table 1. Crystal data and structure refinement for $[Pb_2(dmp)_2(\mu\text{-tfpb})_2(tfpb)_2]$ and $[Pb_2(dmp)_2(\mu\text{-ttfa})_2(ttfa)_2]$.

Identification code	$[Pb_2(dmp)_2(\mu\text{-tfpb})_2(tfpb)_2]$	$[Pb_2(dmp)_2(\mu\text{-ttfa})_2(ttfa)_2]$
Empirical formula	$C_{68}H_{48}F_{12}N_4O_8Pb_2$	$C_{60}H_{40}F_{12}N_4O_8Pb_2S_4$
Formula weight	1691.48	1715.58
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	11.873(2)	11.923(2)
b	12.653(2)	12.663(2)
c	13.0054(9)	12.694(2)
α	103.320(10)	104.90(2)
β	106.940(10)	116.72(2)
γ	115.980(10)	105.18(2)
Volume (Å^3)	1527.6(4)	1487.8(4)
Z	1	1
Density (calculated) (Mg m^{-3})	1.839	1.915
Absorption coefficient (mm^{-1})	5.601	5.888
$F(000)$	820	828
Crystal size (mm^3)	0.52 × 0.48 × 0.25	0.46 × 0.37 × 0.24
θ range for data collection	2.04 to 27.97°	2.05 to 23.99°
Index ranges	$0 \le h \le 15$, $-16 \le k \le 15$, $-17 \le l \le 16$	$0 \le h \le 13$, $-14 \le k \le 13$, $-14 \le l \le 12$
Reflections collected	7946	5045
Independent reflections	7703 [$R_{(int)} = 0.0130$]	4910 [$R_{(int)} = 0.0053$]
Completeness to θ	99.9%	99.7%
Max. and min. transmission	1.00 and 0.70	1.00 and 0.55
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	7703/108/511	4910/26/503
Goodness-of-fit on F^2	1.152	1.123
Final R indicate [$I > \sigma(I)$]	$R_1 = 0.0287$, $wR_2 = 0.0789$	$R_1 = 0.0585$, $wR_2 = 0.1386$
R indices (all data)	$R_1 = 0.0384$, $wR_2 = 0.0934$	$R_1 = 0.0646$, $wR_2 = 0.1501$
Largest diff. Peak, hole (e Å^{-3})	0.811 and −1.467	4.131 and −4.196

Most of the previously reported studies of C–F ··· H–C hydrogen bonds have been limited to C, H, and F compounds in the absence of competing acceptors [12]. In addition to steric and electrostatic factors, two other aspects could determine the fluorine substitution effect. The first is the nature of the fluorine atom that increases the acidity of close hydrogen atoms, thus enhancing their capacity to participate in hydrogen bonding, and the second is the particular ability of the fluorine atom to take part in weak interactions. The latter aspect may be particularly relevant, and although the weak F-based interactions are easily overridden by the stronger heteroatom-based intermolecular interactions, at least one situation has been reported in which the crystal structure is controlled by weak interactions of the type C–H ··· F–C and C–F ··· F–C [13]. Experimentally, one method of obtaining information on these modes is by crystal structure determinations for appropriate materials [6, 9, 14] and the present work is an exploration of the value of this approach using readily crystallised derivatives of lead(II) complexes. These derivatives involve the neutral diimine chelate, 2,9-dimethyl-1,10-phenanthroline (dmp), and the anionic fluorine-substituted β-diketonate ligands which have the potential to generate intermolecular attractions.

Table 2. Selected bond lengths (Å) and angles (°) for the $[Pb_2(dmp)_2(\mu\text{-tfpb})_2(tfpb)_2]$ complex.

Pb(1)–O(5)	2.509(10)	Pb(1)–O(6)	2.607(12)
Pb(1)–N(1)	2.665(15)	Pb(1)–O(7)	2.673(12)
Pb(1)–O(8)	2.713(12)	Pb(1)–O(3)	2.729(14)
Pb(1)–N(2)	2.768(14)	Pb(1)–O(4)	3.170(18)
Pb(2)–O(8)	3.226(15)	Pb(2)–O(2)	2.516(13)
Pb(2)–O(1)	2.535(9)	Pb(2)–N(3)	2.618(13)
Pb(2)–N(4)	2.658(12)	Pb(2)–O(3)	2.702(11)
Pb(2)–O(4)	2.774(13)	Pb(2)–O(7)	2.778(12)
Pb(1)–Pb(2)	3.9033(7)		
O(6)–Pb(1)–N(1)	129.2(5)	O(5)–Pb(1)–O(7)	126.8(4)
O(6)–Pb(1)–O(7)	161.1(3)	N(1)–Pb(1)–O(7)	68.0(4)
O(5)–Pb(1)–O(8)	166.4(4)	O(6)–Pb(1)–O(8)	100.6(4)
N(1)–Pb(1)–O(8)	110.6(4)	O(7)–Pb(1)–O(8)	62.5(4)
O(5)–Pb(1)–O(3)	99.9(4)	O(6)–Pb(1)–O(3)	76.2(4)
N(1)–Pb(1)–O(3)	152.2(4)	O(7)–Pb(1)–O(3)	89.1(4)
O(8)–Pb(1)–O(3)	68.9(4)	O(5)–Pb(1)–N(2)	111.1(5)
O(6)–Pb(1)–N(2)	88.0(4)	N(1)–Pb(1)–N(2)	63.9(4)
O(7)–Pb(1)–N(2)	95.1(4)	O(8)–Pb(1)–N(2)	75.3(4)
O(3)–Pb(1)–N(2)	136.9(4)	O(5)–Pb(1)–O(4)	79.2(4)
O(6)–Pb(1)–O(4)	115.7(4)	N(1)–Pb(1)–O(4)	97.8(4)
O(7)–Pb(1)–O(4)	62.8(3)	O(8)–Pb(1)–O(4)	99.6(5)
O(3)–Pb(1)–O(4)	56.3(4)	N(2)–Pb(1)–O(4)	156.3(4)
O(2)–Pb(2)–N(3)	113.8(5)	O(1)–Pb(2)–N(3)	95.4(4)
O(2)–Pb(2)–N(4)	84.5(4)	O(1)–Pb(2)–N(4)	135.0(4)
N(3)–Pb(2)–N(4)	61.4(4)	O(2)–Pb(2)–O(3)	125.3(4)
O(1)–Pb(2)–O(3)	155.5(3)	N(3)–Pb(2)–O(3)	94.7(4)
N(4)–Pb(2)–O(3)	69.1(4)	O(2)–Pb(2)–O(4)	164.2(4)
O(1)–Pb(2)–O(4)	99.0(4)	N(3)–Pb(2)–O(4)	77.5(4)
N(4)–Pb(2)–O(4)	111.1(4)	O(3)–Pb(2)–O(4)	61.7(4)
O(2)–Pb(2)–O(7)	97.9(4)	O(1)–Pb(2)–O(7)	70.2(4)
N(3)–Pb(2)–O(7)	138.5(4)	N(4)–Pb(2)–O(7)	152.2(4)
O(3)–Pb(2)–O(7)	87.5(4)	O(4)–Pb(2)–O(7)	67.2(4)
O(2)–Pb(2)–O(8)	77.4(4)	O(1)–Pb(2)–O(8)	109.7(3)
N(3)–Pb(2)–O(8)	154.9(3)	N(4)–Pb(2)–O(8)	99.3(4)
O(3)–Pb(2)–O(8)	61.8(3)	O(4)–Pb(2)–O(8)	96.9(5)
O(7)–Pb(2)–O(8)	54.9(3)	O(2)–Pb(2)–O(1)	69.7(3)

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. ^1H and ^{13}C NMR spectra were measured with a BRUKER DRX-500 AVANCE spectrometer at 500 and 125 MHz, respectively.

2.2. *Preparation of $[Pb_2(dmp)_2(\mu\text{-tfpb})_2(tfpb)_2]$ (1)*

2,9-Dimethyl-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 4,4,4-trifluoro-1-phenyl-1,3-butandione(Htfpb) (0.432 g, 2 mmol) in the other. Ethanol was carefully added to fill both arms, the tube sealed and the ligand-containing arm immersed in a bath at

Table 3. Selected bond lengths (Å) and angles (°) for the [$Pb_2(dmp)_2(\mu\text{-ttfa})_2(ttfa)_2$] complex.

Pb(1)–O(2)	2.482(18)	Pb(1)–N(1)	2.58(2)
Pb(1)–O(1)	2.619(18)	Pb(1)–N(2)	2.65(2)
Pb(1)–O(5)	2.73(2)	Pb(1)–O(5)	2.769(18)
Pb(1)–O(6)	2.823(18)	Pb(1)–O(4)	3.44(2)
Pb(2)–O(7)	2.533(15)	Pb(2)–O(8)	2.55(2)
Pb(2)–O(4)	2.59(2)	Pb(2)–O(3)	2.638(15)
Pb(2)–O(5)	2.66(2)	Pb(2)–N(4)	2.70(2)
Pb(2)–N(3)	2.80(3)	Pb(2)–O(6)	3.27(3)
Pb(1) – Pb(2)	3.984(7)		
O(2)–Pb(1)–N(1)	114.5(7)	O(2)–Pb(l)–O(1)	68.6(5)
N(1)–Pb(1)–O(1)	92.5(7)	O(2)–Pb(1)–N(2)	85.6(6)
N(1)–Pb(1)–N(2)	60.9(6)	O(1)–Pb(1)–N(2)	131.4(6)
O(2)–Pb(1)–O(5)	124.5(6)	N(1)–Pb(1)–O(5)	96.7(6)
O(1)–Pb(1)–O(5)	157.7(5)	N(2)–Pb(1)–O(5)	70.4(6)
O(2)–Pb(1)–O(3)	98.0(7)	N(1)–Pb(1)–O(3)	139.4(6)
O(1)–Pb(1)–O(3)	76.8(6)	N(2)–Pb(1)–O(3)	149.6(5)
O(5)–Pb(1)–O(3)	83.0(6)	O(2)–Pb(1)–O(6)	163.0(6)
N(1)–Pb(1)–O(6)	78.5(7)	O(1)–Pb(1)–O(6)	101.1(5)
N(2)–Pb(1)–O(6)	110.9(6)	O(5)–Pb(1)–O(6)	61.3(6)
O(3)–Pb(1)–O(6)	65.8(6)	O(2)–Pb(1)–O(4)	78.7(6)
N(1)–Pb(1)–O(4)	153.6(6)	O(1)–Pb(1)–O(4)	113.8(6)
N(2)–Pb(1)–O(4)	99.6(6)	O(5)–Pb(1)–O(4)	58.3(6)
O(3)–Pb(1)–O(4)	52.4(5)	O(6)–Pb(1)–O(4)	94.2(7)
O(7)–Pb(2)–O(8)	69.0(7)	O(7)–Pb(2)–O(4)	100.3(7)
O(8)–Pb(2)–O(4)	168.7(6)	O(7)–Pb(2)–O(3)	160.6(6)
O(8)–Pb(2)–O(3)	124.3(7)	O(4)–Pb(2)–O(3)	65.0(7)
O(7)–Pb(2)–O(5)	76.1(7)	O(8)–Pb(2)–O(5)	101.3(6)
O(4)–Pb(2)–O(5)	71.5(6)	O(3)–Pb(2)–O(5)	86.8(6)
O(7)–Pb(2)–N(4)	130.9(7)	O(8)–Pb(2)–N(4)	81.7(6)
O(4)–Pb(2)–N(4)	109.0(6)	O(3)–Pb(2)–N(4)	68.0(6)
O(5)–Pb(2)–N(4)	150.3(6)	O(7)–Pb(2)–N(3)	89.9(7)
O(8)–Pb(2)–N(3)	111.7(7)	O(4)–Pb(2)–N(3)	71.1(7)
O(3)–Pb(2)–N(3)	96.5(6)	O(5)–Pb(2)–N(3)	136.7(6)
N(4)–Pb(2)–N(3)	64.9(6)	O(7)–Pb(2)–O(6)	114.3(6)
O(8)–Pb(2)–O(6)	78.8(6)	O(4)–Pb(2)–O(6)	103.0(7)
O(3)–Pb(2)–O(6)	60.7(5)	O(5)–Pb(2)–O(6)	55.8(6)
N(4)–Pb(2)–O(6)	96.7(6)	N(3)–Pb(2)–O(6)	155.8(6)

60°C while the other was at ambient temperature. After 2 days, crystals had deposited in the cooler arm, which were filtered off, washed with acetone and ether, and air dried, yield: 80%, m.p. 178°C. (Found: C: 47.90, H: 2.65, N: 3.56%, calculated for $C_{68}H_{48}F_{12}N_4O_8Pb_2$: C: 48.28, H: 2.84, N: 3.31%). IR (cm^{-1}) selected bonds: 701(m), 763(m), 1018(m), 1149(s), 1280(vs), 1473(s), 1573(s), 1619(vs), 2990(m) and 3070(w). ^{1}H NMR (DMSO, δ): 2.80 (s, 6H), 5.95 (s, 2H), 7.35 (m, 6H), 7.65 (m, 2H), 7.75 (m, 2H), 7.45 (d, 2H), 7.85 (m, 2H), 8.35 (d, 2H).[13] ^{1}H NMR (DMSO, δ): 25.36, 91.66, 122.19, 123.95, 125.94, 127.16, 127.58, 128.75, 131.90, 136.97, 140.03, 145.14, 158.80, 168.70, 169.18, 177.83 and 186.72 ppm.

2.3. *Preparation of [$Pb_2(dmp)_2(\mu\text{-ttfa})_2(ttfa)_2$] (2)*

The above procedure was repeated with thenoyltrifluoroacetonate (Httfa; 1 mmol) substituted for Htfpb. Again, after 2 days, crystals had deposited in the cooler arm which were filtered off, washed with acetone and ether, and air dried, yield.

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

C–H ··· F–C	H ··· F (Å)	C ··· F (Å)	C–H ··· F (°)
1			
(dmp, aliphatic) C–H ··· F	2.568	3.503	164
	2.637	3.430	140.17
(dmp, aromatic) C–H ··· F	2.662	3.589	175
(Phenyl, bridging anion) C–H ··· F (bridging anion)	2.530	3.181	127
(Phenyl) C–H ··· F (bridging anion)	2.584	3.487	164.19
2			
(dmp, aliphatic) C–H ··· F	2.562	3.399	145.47
(dmp, aromatic) C–H ··· F	2.659	3.560	162.67
(Thenoyl, bridging anion) C–H ··· F (bridging anion)	2.487	3.201	133.12
(Thenoyl, bridging anion) C–H ··· F (bridging anion)	2.656	3.207	118.62
(Thenoyl) C–H ··· F (bridging anion)	2.627	3.355	135.86

80%, m.p. 180°C. (Found: C: 41.90, H: 2.55, N: 3.56%, calculated for $C_{60}H_{40}F_{12}N_4O_8Pb_2S_4$, C: 42.00, H: 2.33, N: 3.26%). IR (cm^{-1}) selected bonds: 701(m), 763(m), 1018(m), 1149(s), 1280(vs), 1473(s), 1573(s), 1619(vs), 2990(m) and 3070(w). ^{1}H NMR (DMSO, δ): 2.88 (dmp-H), 8.35 (dmp-H), 7.85 (dmp-H), 7.75 (thienyl-H), 7.70 (dmp-H), 7.65 (thienyl-H), 7.10 (thienyl-H), 5.95 (s, =CH–). ^{13}C–{^{1}H} NMR (DMSO, δ): 24.36, 91.26, 122.12, 123.94, 124.85, 126.94, 127.58, 129.45, 132.65, 138.12, 145.14, 147.66, 152.20, 177.70 and 179.18 ppm.

2.4. *Crystallography*

The structure was solved by direct methods, SHELXS-97 [15], and refined by full matrix least squares using SHELXL-97 [16]. SHELX operations were automated using OSCAIL, which was also used to obtain the drawings [17]. 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 [18]. 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 coordination sphere 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. Intermolecular interactions in crystals are given in table 4. 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 1–4.

3. Results and discussion

Reaction between "dmp" and mixtures of lead(II) acetate with "Htfpb" and also reaction between "dmp" and mixtures of lead(II) acetate with "Httfa" provided crystalline materials analyzed as $[Pb_2(dmp)_2([\mu\text{-tfpb})_2(tfpb)_2]$ and $[Pb_2(dmp)_2$

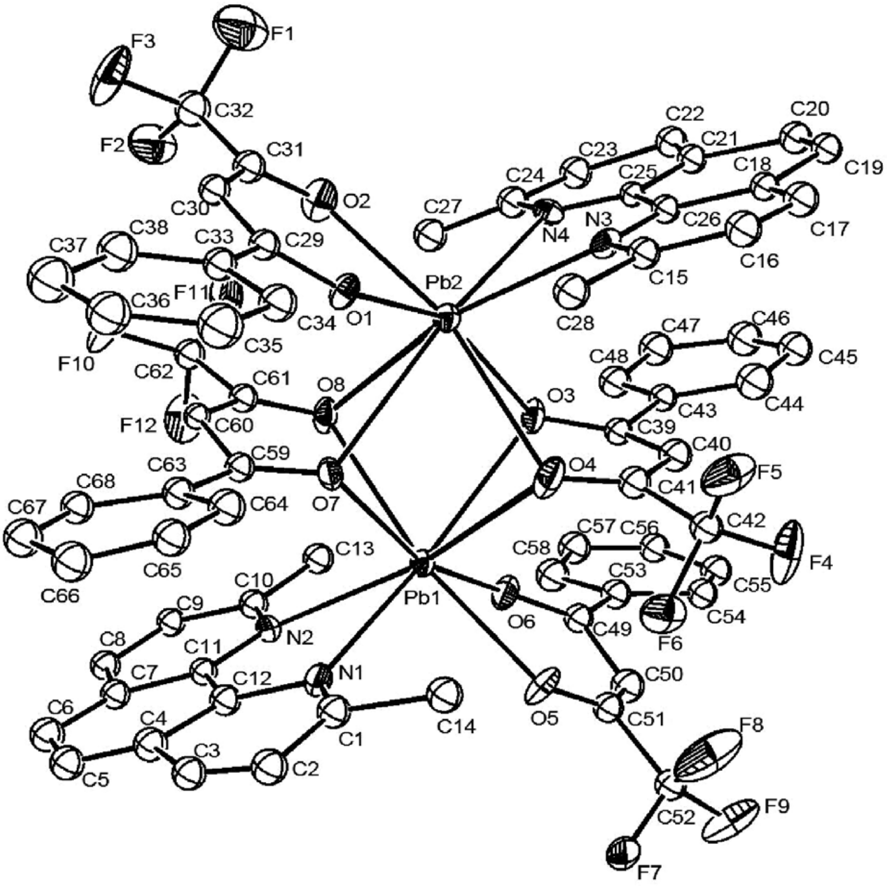

Figure 1. ORTEX diagram of $[Pb_2(dmp)_2(\mu\text{-tfpb})_2(tfpb)_2]$ complex.

$(\mu\text{-ttfa})_2(ttfa)_2]$, respectively. Single X-ray crystal analysis reveals that $[Pb_2(dmp)_2(\mu\text{-tfpb})_2(tfpb)_2]$ and $[Pb_2(dmp)_2(\mu\text{-ttfa})_2(ttfa)_2]$ crystallize in the triclinic space group P1. The structure motif of these complexes is best considered to be a dimer of lead(II) coordinated by two "dmp" ligands and four "$tfpb^-$" and "$ttfa^-$" anions, respectively (figures 1 and 2). The coordination number in these complexes is eight (two of "dmp" and six of "$tfpb^-$" and "$ttfa^-$" anions). In fact each Pb atom in this structure has six "normal" bonds and two "weak" $Pb \cdots O$ bonds, yielding the two Pb_2O_2 rhombahedrons, with distances Pb1–O4 = 3.170(18) Å, Pb2–O8 = 3.226(15) Å for **1** and Pb1–O4 = 3.44(**2**) Å, Pb2–O6 = 3.27(**3**) Å for **2** (tables 2 and 3). The presence of a lone pair on the lead is apparently the reason that the bridging interactions are so long. If the stereochemically active lone pair [19] was not present, more symmetry would be expected. In part these bond length variations may be ascribed to the bridging nature of some of the ligands and possibly to the effect of $Pb \cdots Pb$ interactions within the dimers.

A search was made for $C\text{–}H \cdots F\text{–}C$ approaches in complexes **1** and **2** (table 4). An interesting feature in complexes **1**–**2** is that, there are $C\text{–}F \cdots F\text{–}C$ interactions, weak hydrogen bonding, between the hydrogen atoms of "dmp" and anionic ligands and fluorine atoms belonging to "$tfpb^-$" and "$ttfa^-$" anions of adjacent

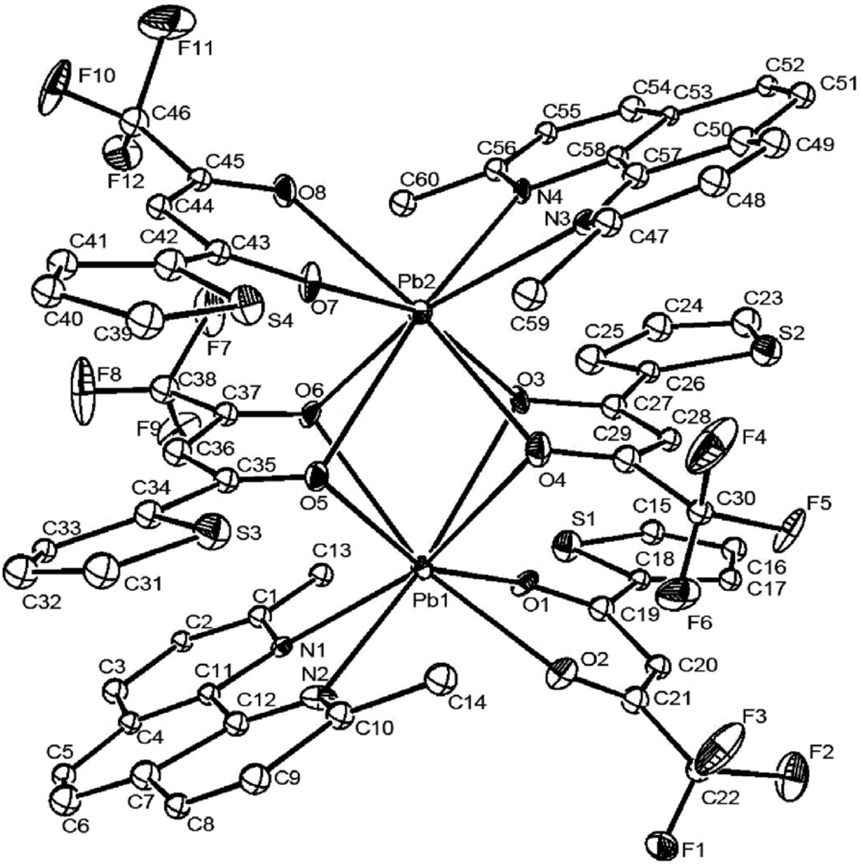

Figure 2. ORTEX diagram of [$Pb_2(dmp)_2(\mu\text{-ttfa})_2(ttfa)_2$] complex.

complexes (figures 3–4). In **1**–**2** the H ⋯ F distances range from 2.53 to 2.66 Å and the C–H ⋯ F angles from 118.62 to 175°, values that suggest strong interactions within this class of weak noncovalent contacts [9, 20]. There are short F ⋯ F interactions (figure 3 and 4) with distances of F ⋯ F = 2.897 and 2.830 Å which are less than the sum of the van der Waals radii for fluorine at 2.94 Å [21].

π–π stacking interactions exist between aromatic rings belonging to adjacent chains in complexes **1** and **2**. In the crystal packing of **1** and **2** the interplanar distance between "dmp" rings is 3.339 and 3.395 Å, respectively. Parallel arrays of the planes of the aromatic moieties in the complexes indicate that these interactions are of the slipped "face-to-face π-stacking" types. The interplanar distance range between aromatic rings in the complexes **1** and **2** are normal for π–π stacking interactions [22–24].

Thus in **1** and **2** three factors, C–H ⋯ F–C, C–F ⋯ F–C and π–π stacking interactions, control the packing. The obvious question then is whether the C–H ⋯ F–C, C–F ⋯ F–C interactions have stretched coordinate bonds to result in ligand stacking or whether it is the stacking interaction which has imposed a positioning of the donor atoms for forming the C–H ⋯ F–C, C–F ⋯ F–C interactions in the packing. Indeed, it is now realized that C–H ⋯ F–C, C–F ⋯ F–C interactions can also

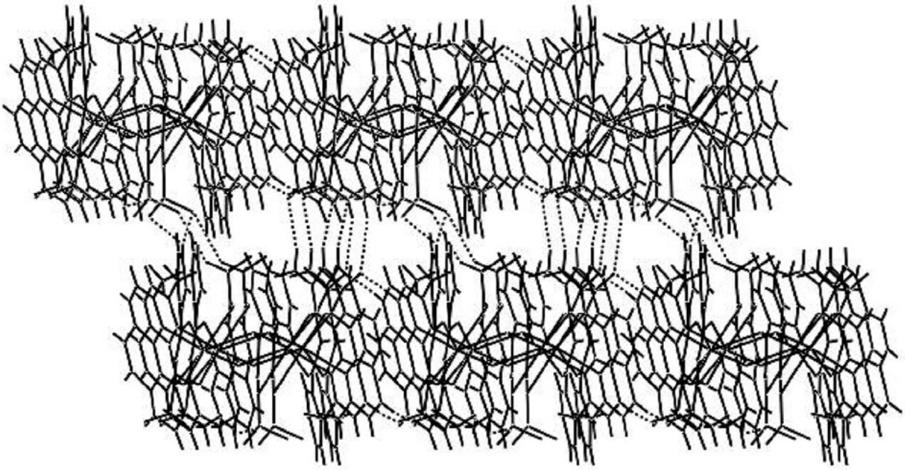

Figure 3. The weak interactions and packing of $[Pb_2(dmp)_2(\mu\text{-tfpb})_2(tfpb)_2]$ complex.

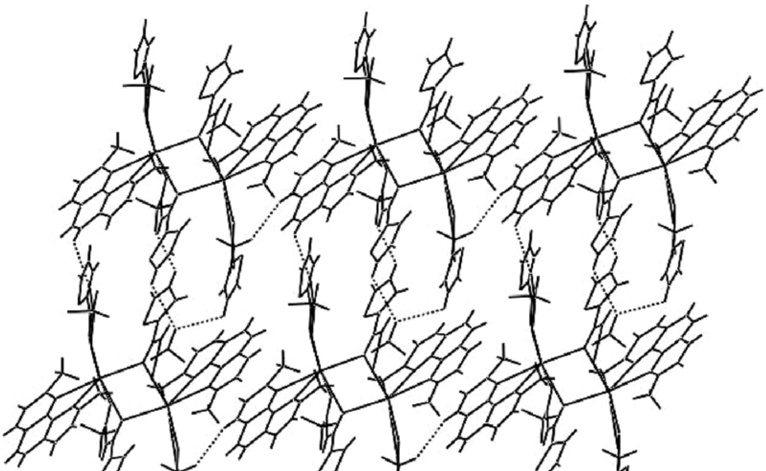

Figure 4. The weak interactions and packing of $[Pb_2(dmp)_2(\mu\text{-ttfa})_2(ttfa)_2]$ complex.

play a significant and predictable structure-determining role in the fluorine-substituted β-diketonate metal ion complexes [25–28].

Supplementary material

Crystallographic data for the structures reported in the article have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no, CCDC-605296 for $[Pb_2(dmp)_2(\mu\text{-tfpb})_2(tfpb)_2]$ and 6,05,298 for $[Pb_2(dmp)_2(\mu\text{-ttfa})_2(ttfa)_2]$. 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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