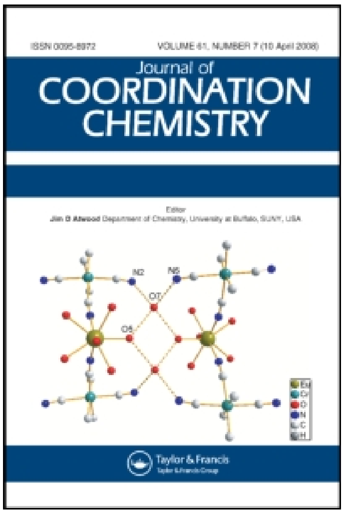

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Fluorine-substituted β-diketonate Pb^{II} complexes, $[Pb(phen)(TFPB)_2]$ and $[Pb(2,2'\text{-}bipy)(TFPB)_2]$

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Fluorine-substituted *β*-diketonate Pb^{II} complexes, [Pb(phen)(TFPB)$_2$] and [Pb(2,2′-bipy)(TFPB)$_2$]

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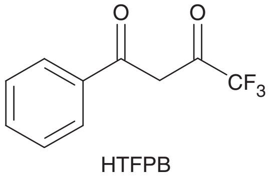
Lead(II) 4,4,4-trifluoro-1-phenyl-1,3-butandionate ($TFPB^-$) complexes with 1,10-phenanthroline (phen) and 2,2′-bipyridine (2,2′-bipy), [Pb(L)(TFPB)$_2$], have been synthesized and characterized by elemental analysis, IR-, ^1H NMR spectroscopy and studied by X-ray crystallography. The self-assembly of [Pb(L)(TFPB)$_2$] complexes, (L = phen or 2,2′-bipy) is caused by C–H ⋯ F–C, C–H ⋯ O–C and π–π stacking interactions. The thermal stabilities of compounds were studied by thermal gravimetric (TG) and differential thermal analyses (DTA).

Keywords: Lead; 4,4,4-Trifluoro-1-phenyl-1,3-butandionate; 2,2′-Bipyridine; 1,10-Phenanthroline

1. Introduction

Design and syntheses of new lead(II) compounds to study stereochemically active lone pair electrons ($6s^2$) is a goal. Complexes of bidentate ligands such as 1,10-phenanthroline (phen) and 2,2′-bipyridine (2,2′-bipy) with lead(II) complexes containing nitrate, perchlorate, thiocyanate anions and multifunction coordination anions such as *β*-dicarbonyls have not been well studied [1–11]. *β*-Dicarbonyl ligands [12, 13] are versatile exhibiting a variety of coordination modes [14]. Equilibrium mixtures of the tautomeric keto and enol forms of *β*-diketones could be affected by replacement of the terminal groups with electron-withdrawing or electron-releasing substituents [15]. Determination of the structures Pb^{II}(phen) and Pb^{II}(bipy) with 4,4,4-trifluoro-1-phenyl-1,3-butandionate ($TFPB^-$) anion provide new lead(II) compounds involving CH ⋯ F–C, CH ⋯ O–C interactions.



HTFPB

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2. Experimental

2.1. *Physical measurements*

IR spectra were recorded 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. ^{1}H NMR spectra were measured with a BRUKER DRX-500 AVANCE spectrometer at 500 MHz. Crystallographic measurements were made at 293(2) and 273(2) K using a Siemens *R*3m/V diffractometer for **1** and **2**, respectively. The structures were solved by direct methods and refined by full-matrix least-quares techniques on F^2. The molecular structure plots were prepared by using ORTEPIII [16] and mercury [17].

2.2. *Preparation of [Pb(2,2′-bipy)(TFPB)$_2$] (1)*

2,2′-Bipyridine (0.156 g, 1 mmol) was placed in one arm of a branched tube and lead(II) acetate (0.36 g, 1 mmol) and "HTFPB" (0.432 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 2 days, crystals had deposited in the cooler arm which were filtered off, washed with acetone and ether, and air dried, yield: 75%, m.p. 185°C. Anal. Calcd for $C_{30}H_{20}F_6N_2O_4Pb$: C 45.39, H 2.52, N 3.53%; found: C 45.72, H 2.65, N 3.56%.

IR (selected signals, cm^{-1}): 701m, 763m, 1018m, 1155s, 1283vs, 1485s, 1573s, 1625vs, and 3065w.

^{1}H NMR (DMSO, δ): 8.70 (m, 2H, Py–H), 8.40m, 2H, (Py–H), 7.93 (m, 2H, Py–H), 7.47 (m, 2H, Py–H), 7.40 (d, 2H, Ph–H), 7.90 (t, 2H, Ph–H), 8.65 (t, 1H, Ph–H), 6.15 (s, =CH–).

2.3. *Preparation of [Pb(phen)(TFPB)$_2$] (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 "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 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. 196°C. Anal. Calcd for $C_{32}H_{20}F_6N_2O_4Pb$: C 46.96, H 2.44, N 3.42%; found: C 46.80, H 2.65, N 3.56%.

IR (selected signals, cm^{-1}): 701m, 763m, 1018m, 1149s, 1280vs, 1473s, 1573s, 1619vs, and 3070w.

^{1}H NMR (DMSO, δ): 7.40 (m, 2H, phen-H), 7.70 (m, 2H, phen-H), 8.05 (m, 2H, phen-H), 8.15 (m, 2H, phen-H), 7.70 (d, 2H, Ph–H), 8.00 (t, 2H, Ph–H), 8.65 (t, 1H, Ph–H), 5.95 (s, 1H, =CH–).

Table 1. Crystal data and structure refinement for [Pb(2,2′-bipy)(TFPB)$_2$] (**1**) and [Pb(phen)(TFPB)$_2$] (**2**).

Identification code	**1**	**2**
Empirical formula	$C_{30}H_{20}F_6N_2O_4Pb$	$C_{32}H_{20}F_6N_2O_4Pbb$
Formula weight	793.68	817.69
Temperature (K)	273(2)	293(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Triclinic	Tetragonal
Space group	$P\bar{1}$	$I4_1/a$
Unit cell dimensions (Å, °)		
a	10.8194(11)	28.9393(18)
b	11.5539(12)	28.9393(18)
c	11.7830(12)	14.1581(17)
α	79.709(2)	90
β	85.422(2)	90
γ	73.171(2)	90
Volume (Å^3)	1386.6(2)	11857.2(18)
Z	2	16
Density (Calculated) (Mg m^{-3})	1.901	1.832
Absorption coefficient (mm^{-1})	6.164	5.770
$F(000)$	764	6304
Crystal size (mm^3)	0.38 × 0.17 × 0.15	0.23 × 0.25 × 0.43
θ range for data collection (°)	1.76–25.30	1.41–26.00
Index ranges	$-12 \le h \le 12$, $-7 \le k \le 13$, $-14 \le l \le 13$	$-35 \le h \le 35$, $-35 \le k \le 34$, $-17 \le l \le 17$
Reflections collected	4949	45,557
Independent reflections	4521 [$R_{\text{int}} = 0.0155$]	5835 [$R_{\text{int}} = 0.0828$]
Completeness to θ	98.3%	100.0%
Max. and min. transmission	0.4583 and 0.2029	0.3504 and 0.1905
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	4521/0/388	5835/0/406
Goodness-of-fit on F^2	1.608	1.070
Final R indicate [$I > 2\sigma(I)$]	$R_1 = 0.1153$, $wR2 = 0.3389$	$R_1 = 0.0436$, $wR_2 = 0.0886$
R indices (all data)	$R_1 = R_1 = 0.1202$, $wR_2 = 0.3492$	0.0716, $wR_2 = 0.0977$
Largest diff. peak, hole (e Å^{-3})	5.149, −1.710	2.285, −1.096

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

Pb1–O2	2.242(7)	O4–Pb1–O1	101.1(3)
Pb1–O4	2.256(8)	O3–Pb1–O1	169.0(3)
Pb1–O3	2.268(8)	O2–Pb1–N2	167.5(3)
Pb1–O1	2.283(8)	O4–Pb1–N2	87.6(3)
Pb1–N2	2.348(9)	O3–Pb1–N2	99.7(3)
Pb1–N1	2.349(10)	O1–Pb1–N2	91.3(3)
O2–Pb1–O4	103.1(3)	O2–Pb1–N1	100.5(3)
O2–Pb1–O3	88.7(3)	O4–Pb1–N1	154.4(3)
O4–Pb1–O3	80.4(3)	O3–Pb1–N1	90.2(3)
O2–Pb1–O1	80.3(3)	O1–Pb1–N1	92.7(3)
		N2–Pb1—N1	70.4(3)

3. Results and discussion

Reaction between 2,2′-bipy and phen with lead(II) acetate and 4,4,4-trifluoro-1-phenyl-1,3-butandione (HTFPB) provided crystalline materials analyzing as [Pb(2,2′-bipy)(TFPB)$_2$] (**1**) and [Pb(phen)(TFPB)$_2$] (**2**). The structures of **1** and **2** were determined by X-ray crystallography (Table 1 and 2). Single X-ray crystal analysis reveals that **1** and **2** crystallize in triclinic and tetragonal space groups of

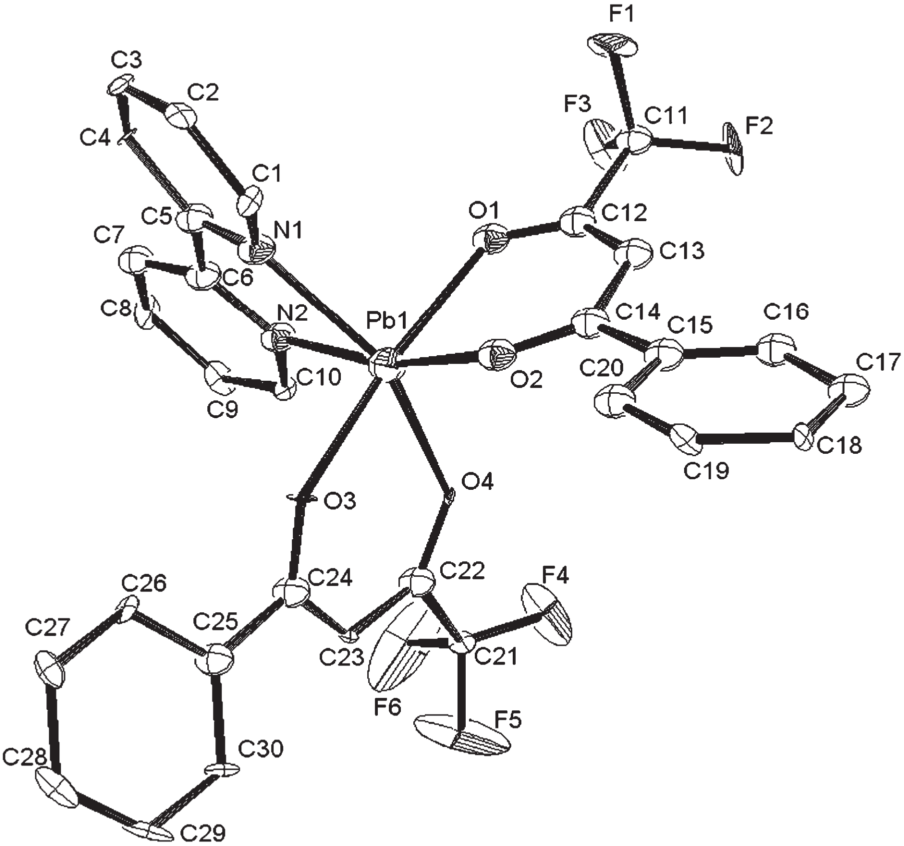

Figure 1. X-ray crystal structure (ORTEP representation) of [Pb(2,2′-bipy)(TFPB)$_2$] (**1**) ellipsoids 30% probability. C–H hydrogens are omitted for clarity.

$P\bar{1}$ and $I4_1/a$, respectively. The crystal structure of **1** consists of monomeric units of [Pb(2,2′-bipy)(TFPB)$_2$] (figure 1). Each lead is chelated by 2,2′-bipy and the oxygen atoms of two "TFPB$^-$" anions. The coordination number in this complex is six (two from "bipy" and four from "TFPB$^-$" anions). The crystal structure of **2** consists of dimeric units of [Pb(phen)(TFPB)$_2$] (figure 2). Each lead is chelated by the phen and the oxygen atoms of two "TFPB$^-$" anions. The coordination number in this complex is also six; weak interaction of lead(II) with one of oxygen atoms of neighboring "TFPB$^-$" anions produce dimers in the solid state. Each Pb in this structure, in addition to six normal bonds, forms one "weak" Pb···O bond, yielding the Pb_2O_2 rhomb, and the Pb1–O2^i (i: $-x+1/2$, $-y+1/2$, $-z+1/2$) distance is 3.132(5) Å (table 3).

The arrangement of O-, and N-atoms in **1** do not suggest a gap in coordination geometry around the Pb coordination sphere (figure 3a), whereas in **2** a gap possibly occupied by a 'stereo-active' electron lone pair exists. Hence, the coordination geometry of Pb in **2** is caused by the coordinated O-, and N-atoms, and by the influence of a stereochemically 'active' electron lone pair. The geometry of Pb in **1** is holodirected; **2** is hemidirected (figure 3a and b) [18].

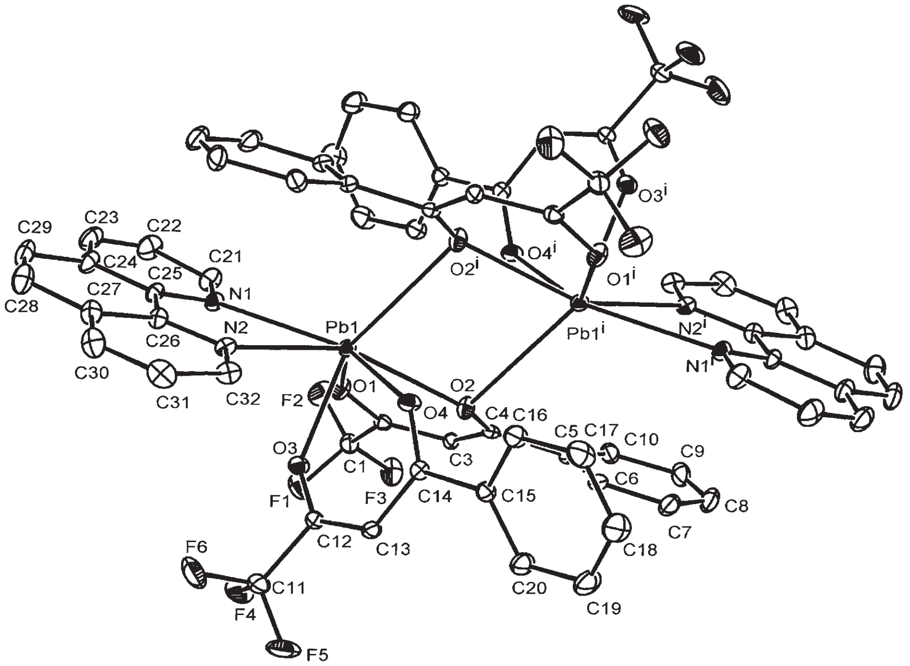

Figure 2. X-ray crystal structure (ORTEP representation) of $[Pb(phen)(TFPB)_2]_2$ (**2**) ellipsoids 30% probability. C–H hydrogens are omitted for clarity.

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

Pb–O3	2.338(5)
Pb–O4	2.497(5)
Pb–O1	2.498(5)
Pb–O2	2.523(5)
Pb–N2	2.708(6)
Pb–N1	2.721(5)
Pb1–O2^i	3.132(5)
O3–Pb–O4	75.06(16)
O3–Pb–O1	75.55(18)
O4–Pb–O1	131.54(16)
O3–Pb–O2	85.29(18)
O4–Pb–O2	68.96(17)
O1–Pb–O2	71.00(16)
O3–Pb–N2	71.48(17)
O4–Pb–N2	80.04(17)
O1–Pb–N2	124.50(17)
O2–Pb–N2	145.24(17)
O3–Pb–N1	89.77(18)
O4–Pb–N1	140.43(18)
O1–Pb–N1	76.34(17)
O2–Pb–N1	147.18(17)
N2–Pb–N1	60.43(18)

i: $-x+1/2$, $-y+1/2$, $-z+1/2$.

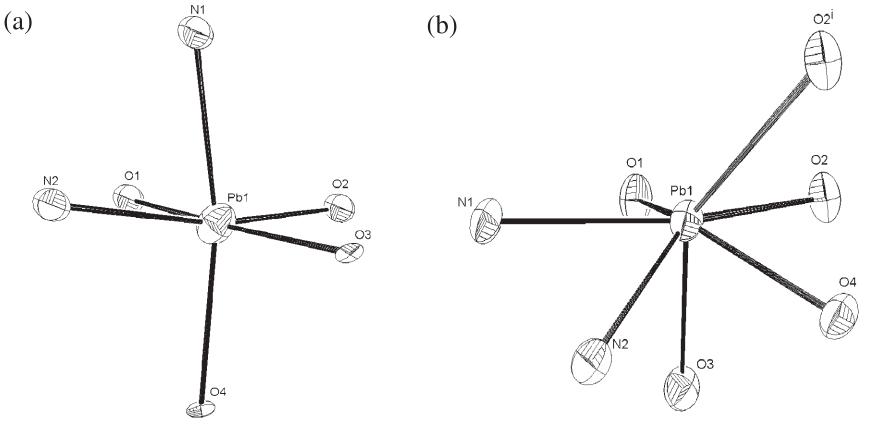

Figure 3. Schematic representation of two different types of Pb^{II} environments (a) for **1** with no hole in the sphere and (b) for **2** containing a gap in the sphere.

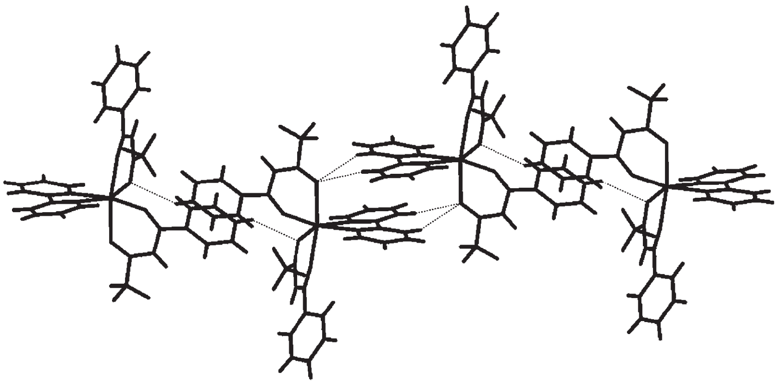

Figure 4. The O···HC interactions in the packing of **1**.

A search was made for C–H···F–C and C–H···O–C approaches in **1** and **2**. In **1** there is weak hydrogen bonding C–H···O–C between the hydrogen atoms of 2,2′-bipy and oxygen of "TFPB^{-}" of adjacent complexes, as shown in figure 4. There are two different C–H···O–C interactions with O···HC(py) distances of 2.577–2.699 Å and HC(ph)···O of 3.336–3.618 Å and ∠O···H–C = 136–196°. In **2** (figure 5), there are four different C–H···F–C interactions between fluorine atoms of "TFPB^{-}" and hydrogen atoms of "ph" and "phen" with F···HC(ph) distances of 2.703 Å {HC(ph)···F = 3.404 Å and ∠F···H–C = 132.93°}, F···HC(ph) = 2.566 Å {HC(ph)···F = 3.490 Å and ∠F···H–C = 172.40°}, F···HC (phen) = 2.631 Å {C–H(phen)···F = 3.544 Å and ∠F···H–C = 166.50°} and F···HC (phen) = 2.615 Å {C–H(phen)···F = 3.336 Å and ∠F···H–C = 134.79°}. In **2** the H···F distances range from 2.566 to 2.754 Å and the C–H···F angles from 125.80 to 172.40°, suggesting strong interactions within this class of weak noncovalent contacts [19]. In **2** there are short F···F interactions (figure 6) with the F···F distance = 2.898 Å that is less than the sum of the van der Waals radii for fluorine at 2.94 Å [20].

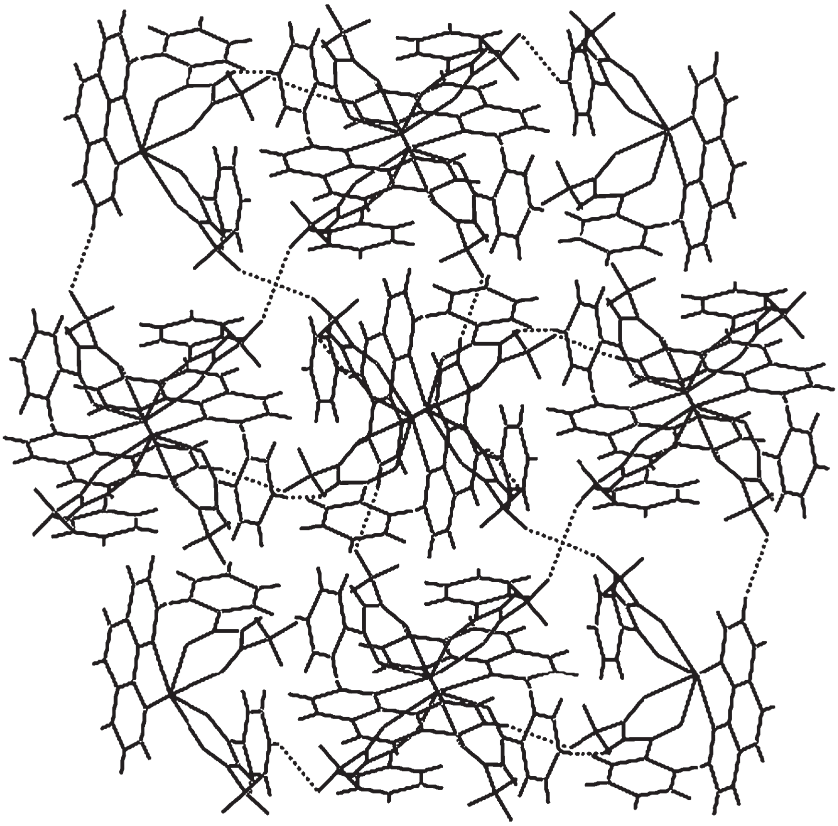

Figure 5. The F···HC and F···F interactions in the packing of **2**.

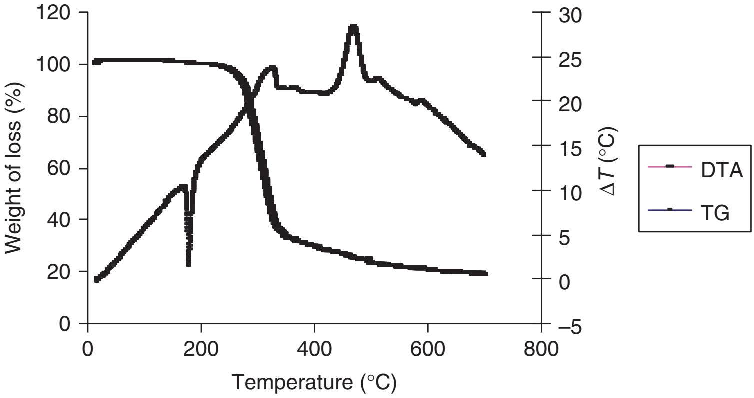

Figure 6. Thermal behaviour of **1**.

There are π–π stacking interactions between the aromatic rings of adjacent chains in **1**–**2**. In the crystal packing of **1**, interplanar distance between "py" rings of 2,2′-bipy is 3.565. In the crystal packing of **2**, the centroid···centroid distance, Cg···Cg, between phen rings and phen and phenyl rings are 3.641 and 3.324 Å.

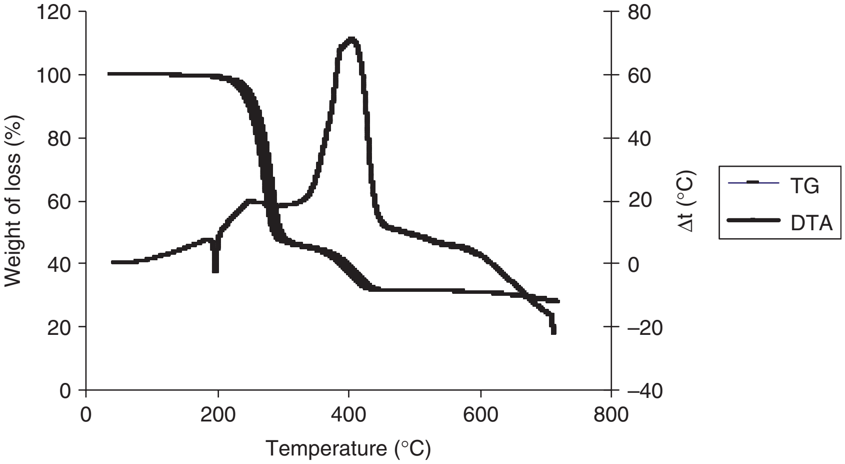

Figure 7. Thermal behaviour of **2**.

The interplanar distances between aromatic rings in **1**–**2** are normal π–π stacking interactions [21–23].

Thus in **1** and **2** two factors, C–H $\cdots$ F–C/C–H $\cdots$ O–C and π–π stacking interactions control the packing. The obvious question then is whether the C–H $\cdots$ F–C interactions stretch coordinate bonds to result in ligand stacking or whether stacking interaction impose a positioning of the donor atoms for forming the C–H $\cdots$ F–C interactions. Certainly C–H $\cdots$ F–C and C–H $\cdots$ O–C interactions play a significant and predictable structure-determining role in the fluorine-substituted β-diketonate metal ion complexes [12–14].

In order to examine the thermal stability of the compounds, thermal gravimetric (TG) and differential thermal analyses (DTA) were carried out for **1** and **2** between 30 and 700°C in air (figures 6 and 7). The TG curve of **1** indicates that it melts at 185°C and begins to decompose at 310°C. The 2,2′-bipy and TFPB$^-$ decompose at 310–415°C with two exothermic events at 355 and 410°C. The solid residue formed is PbO (observed 26.90%, Calcd 28.22%). Compound **2** does not melt and is stable up to 305°C. The TG curve of **2** indicates the decomposition of the compound takes place between 305 and 440°C with one exothermic event at 410°C (figure 7). The ligands phen and TFPB$^-$ decompose at 305–440°C. The solid residue formed is PbO (observed 26.90%, Calcd 27.40%). In summary, the thermogravimetric analysis shows that frameworks of **1** and **2** have thermal stability, decomposing above temperatures of 310 and 305°C, respectively.

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-288299 for compound **1** and 277333 for compound **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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