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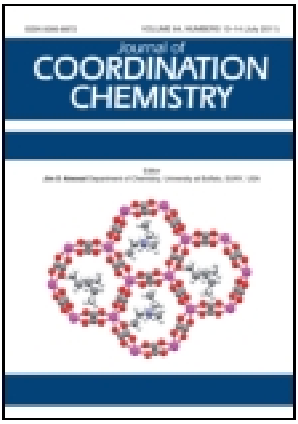

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Sonochemical synthesis and characterization of a nanostructured 3-D lead(II) coordination polymer with 4-methoxybenzoyltrifluoroacetone

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Nanoparticles of a 3-D coordination polymer, $[Pb_2(mbtfa)_4]_n$ (**1**) (Hmbtfa = 4-methoxybenzoyltrifluoroacetone), have been synthesized by a sonochemical method. The nanomaterial was characterized by scanning electron microscopy, X-ray powder diffraction, IR spectroscopy, and elemental analyses. Compound **1** was structurally characterized by single-crystal X-ray diffraction. The structure of **1** shows the compound is triclinic and consists of 3-D polymeric units.

Keywords: Coordination polymer; Nanostructure; Sonochemical

1. Introduction

Metal coordination polymers have been widely studied as an important interface between synthetic chemistry and materials science with specific structures, properties, and reactivities that are not found in mononuclear compounds. The synthesis of metal coordination polymers is often guided by a quest to understand how molecules can be organized and how functions can be achieved [1–10]. Lead(II) contains a $6s^2$ lone-pair, which can cause distortion in a coordination sphere and is frequently discussed in considering ‘‘stereo-chemical activity’’ according to directed ligands classified as holodirected and hemidirected [11–23]. In continuation of our previous studies on Pb(II) supramolecular compounds [23–26], we report a coordination polymer from Pb(II) ion with 4-methoxybenzoyltrifluoroacetone (Hmbtfa) and focus on a simple synthetic preparation of a nanostructure of the 3-D polymer $[Pb_2(mbtfa)_4]_n$ (**1**).

Sonochemistry is an area in which molecules undergo reaction owing to an application of powerful ultrasound radiation (20 kHz–10 MHz) [27]. The efficiency of

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heterogeneous reactions involving solids dispersed in liquids will depend upon available reactive surface area and mass transfer. The mass transport of ultrasonic energy is thought to be due to two transient processes: (i) bubble collapse at or near the solid–liquid interface with microjetting directed toward the surface and (ii) bubble motion near or within a diffusion layer of the surface. From an inorganic chemistry point of view, most of the effects of interest regarding ultrasonication are related to cavitation. Cavitation causes solute thermolysis along with the formation of highly reactive radicals and reagents [28, 29]. In addition, if a solid is present in solution, the sample size of the particles is diminished by solid disruption, thereby increasing the total solid surface in contact with the solvent [30–35].

2. Experimental

2.1. *Materials and physical techniques*

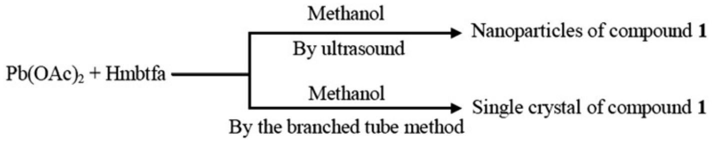
All reagents for the synthesis and analysis were commercially available from Merck Company and used as received. Ultrasonic generation was carried out on a SONICA-2200 EP, input: 50–60 Hz/305W. Melting points were measured on an Electrothermal 9100 apparatus. Microanalyses were carried out using a Heraeus CHN-O-Rapid analyzer. IR spectra were recorded using Perkin-Elmer 597 and Nicolet 510P spectrophotometers. A simulated X-ray diffraction (XRD) powder pattern based on single-crystal data was prepared using Mercury software [36]. XRD measurements were performed using a Philips X'pert diffractometer with monochromated Co-Kα radiation ($\lambda = 1.78897$ Å). The samples were characterized by a scanning electron microscope (SEM) (Philips XL 30 and S-4160) with gold coating.

2.2. *Crystallography*

Crystallographic data were collected at 100 K with the Oxford Cyrosystem Cobra low-temperature attachment. The data were collected using a Bruker SMART APEXII CCD diffractometer with graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) at a detector distance of 5 cm and with APEXII software [37]. The collected data were reduced using SAINT [37] and the empirical absorption corrections were performed using SADABS [37]. The structures were solved by direct methods and refined by least-squares using the Shelxtl software package [38]. All non-hydrogen atoms were refined anisotropically and hydrogen atoms were located and included at their calculated positions. Materials for publication were prepared using SHELXTL [38] and ORTEPIII [39].

2.3. *Synthesis of $[Pb(mbtfa)_2]_n$ (1)*

4-Methoxybenzoyltrifluoroacetone, Hmbtfa (0.460 g, 2 mmol), and lead(II) acetate (0.379 g, 1 mmol) were placed in separate arms of a branched tube [40]. Methanol was carefully added to fill both arms, the tube was sealed and the ligand-containing arm was immersed in a bath at 60°C while the other was at ambient temperature. After 10 days,



Scheme 1. Materials produced and synthetic methods.

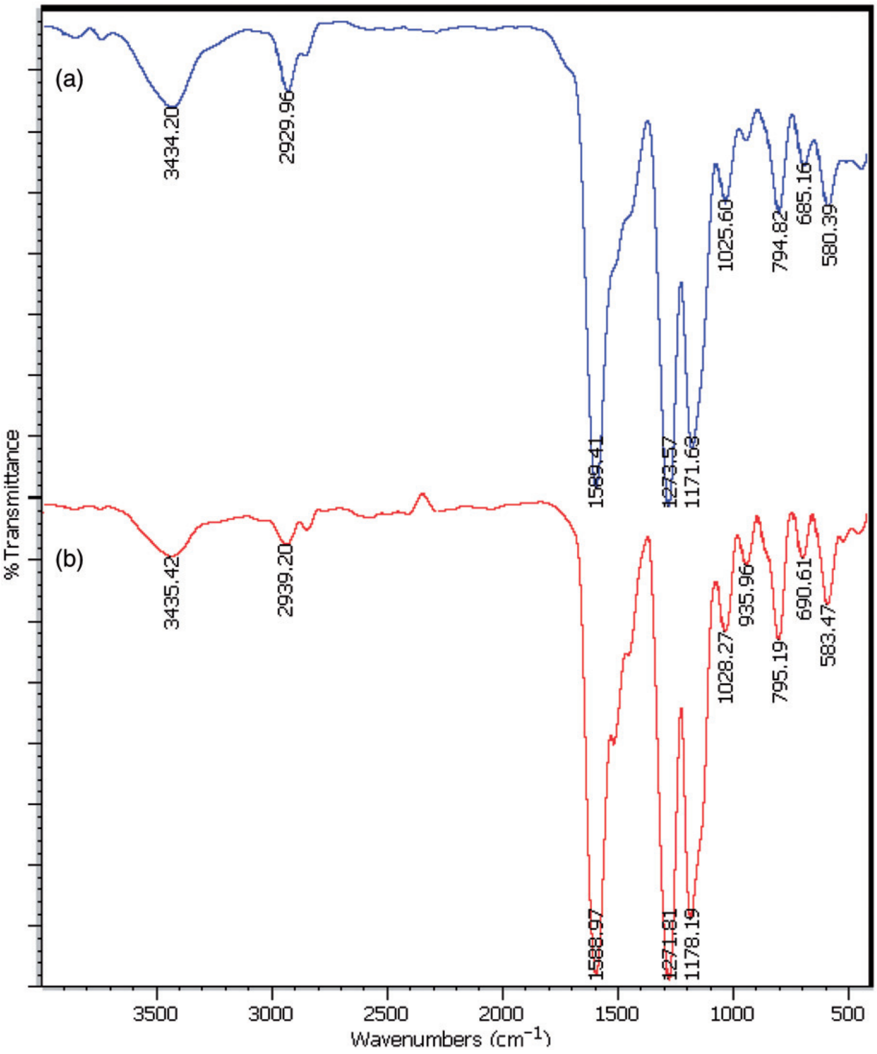


Figure 1. IR spectra of (a) bulk materials as synthesized of **1** and (b) nanoparticles of **1** produced by the sonochemical method.

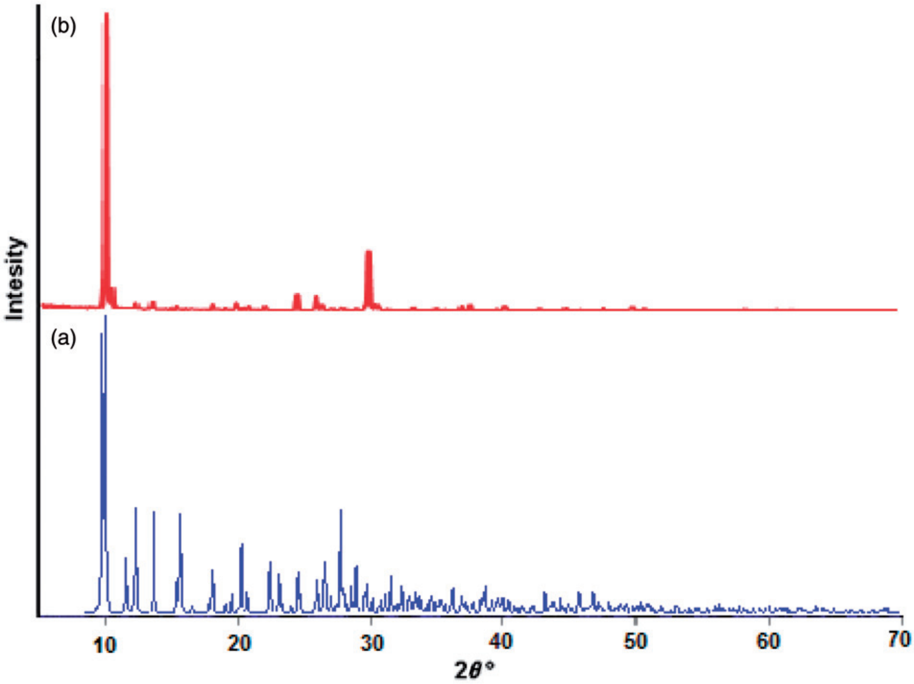


Figure 2. XRD patterns: (a) simulated pattern based on single-crystal data of **1** and (b) nanoparticles of **1** prepared by sonochemical process.

crystals deposited in the cooler arm. The crystals were filtered off, washed with ether, and air dried. Yield: 70%, m.p. 285°C. Analysis found (%): C, 37.65; H, 2.10; Pb, 29.34. Calculated for $C_{22}H_{16}F_6O_6Pb$ (%): C, 37.84; H, 2.29; Pb, 29.68. IR (cm^{-1}) selected bands: 580(m), 685(m), 794(m), 1025(m), 1178(vs), 1273(vs), 1589(vs).

2.4. *Synthesis of [Pb(mbtfa)$_2$]$_n$ (1) nanostructure by sonochemical method*

To prepare nano-sized $[Pb(mbtfa)_2]_n$ (**1**), 20 mL solution of lead(II) acetate ($0.05\,molL^{-1}$) in methanol was positioned in a high-density ultrasonic probe that was operated at 50 Hz with a maximum power output of 305 W. Into this solution a 20 mL solution of the ligand 4-methoxybenzoyltrifluoroacetone ($0.05\,molL^{-1}$) and sodium hydroxide ($0.05\,molL^{-1}$) were added dropwise. Resulting precipitates were filtered, washed with methanol, and then dried in air. M.p. 27°C. Found (%): C, 36.74; H, 2.41; Pb, 29.32. IR (cm^{-1}) selected bands: 583(m), 690(m), 795(m), 1028(m), 1171(vs), 1271(vs), 1588(vs).

3. Results and discussion

Reaction of 4-methoxybenzoyltrifluoroacetone (Hmbtfa) with lead(II) acetate leads to the formation of a lead(II) 3-D coordination polymer $[Pb(mbtfa)_2]_n$ (**1**). Nanoparticles

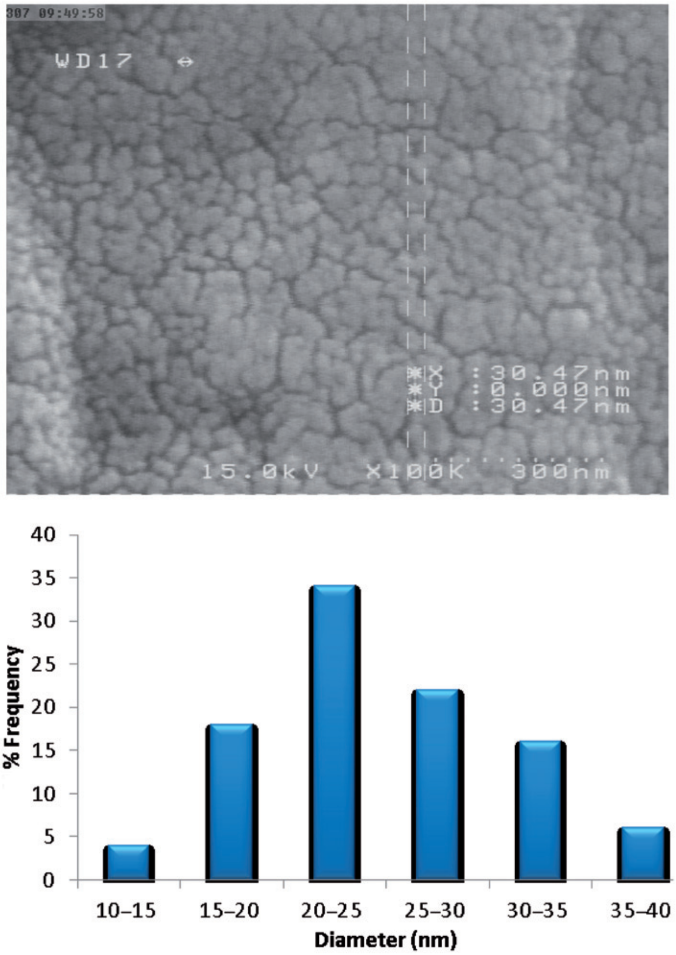


Figure 3. SEM image and the corresponding particle size distribution histogram of **1** nanoparticles prepared by sonochemical process.

of **1** were obtained in aqueous solution by ultrasonic irradiation, while single crystals of **1** were obtained using a heat gradient applied to an aqueous solution of the reagents (i.e., ''branched tube method''). Scheme 1 gives an overview of the methods used for the synthesis of $[Pb(mbtfa)_2]_n$ (**1**) using the two different routes. Elemental analyses and IR spectra of the nanostructures generated by the sonochemical method and the bulk material produced by the branched tube method are comparable (figure 1). Figure 2 shows the simulated XRD pattern from single-crystal X-ray data of **1** (figure 2a) in comparison with the XRD pattern of the typical sample of **1** prepared by the sonochemical process (figure 2b). Acceptable matches, with slight differences in 2θ, were observed between the simulated and experimental powder XRD patterns. This indicates that the compound obtained by the sonochemical process as nanoparticles is identical to that obtained by single-crystal diffraction. The significant broadening of the peaks indicates that the particles are of nanometer dimensions. The reaction between 4-methoxybenzoyltrifluoroacetone (Hmbtfa) and lead(II) acetate provided a crystalline

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

Identification code	$[Pb_2(mbtfa)_4]_n$
Empirical formula	$C_{22}H_{16}F_6O_6Pb$
Formula weight	697.54
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions (Å, °)	
a	9.5933(3)
b	10.8985(4)
c	11.2463(4)
α	99.4500(10)
β	109.6780(10)
γ	96.8910(10)
Volume (Å^{-3}), Z	1072.52(6), 2
Calculated density (Mg m^{-3})	2.160
Absorption coefficient (mm^{-1})	7.956
$F(000)$	664
Crystal size (mm^3)	$0.635 \times 0.171 \times 0.084$
θ range for data collection (°)	3.27–37.47
Index ranges	$-12 \le h \le 12$; $-14 \le k \le 14$; $-14 \le l \le 14$
Reflections collected	16,276
Independent reflections	4787 [R(int) = 0.0254]
Completeness to θ (%)	97.0
Refinement method	Full-matrix least squares on F^2
Data/restraints/parameters	4787/0/318
Goodness-of-fit on F^2	1.077
Final R [$I > 2\sigma(I)$]	$R_1 = 0.0182$ $wR_2 = 0.0445$
R indices (all data)	$R_1 = 0.0194$ $wR_2 = 0.0466$
Largest difference peak and hole (e Å^{-3})	1.83 and −0.78

material of general formula $[Pb(mbtfa)_2]_n$ (**1**). The morphology and size of **1** prepared by the sonochemical method was characterized by SEM, showing that it is composed of particles with sizes of about 24 nm. Figure 3 shows the SEM and the corresponding particle size distribution histograms of **1** produced by the sonochemical method.

According to single-crystal structure analysis (table 1), **1** crystallized in the triclinic $P\text{ı}$ space group and forms a binuclear complex. The ORTEP diagram of the asymmetric $[Pb_2(mbtfa)_4]_n$ unit is shown in figure 4 and selected bond lengths and angles are given in table 2. Each asymmetric unit contains one Pb(II) and two 4-methoxybenzoyltrifluoroacetonates (figure 4). The coordination number of Pb(II) in **1** is six (five oxygen atoms of three bridging mbtfa anions with an additional long $Pb1 \cdots O1^{ii}$ interaction, 3.269(2) Å) (figure 4). The arrangements of the donors in **1** suggest the existence of a stereochemically active lone pair (SALP) on the open side of the coordination polyhedron of Pb [41]. This is supported by the observed shortening of the Pb–O bonds opposite to the putative location of the lone pair (2.306(2) Å) compared with the Pb–O bond with a length of 2.927(2) Å adjacent to the lone pair [42]. Hence, the geometry of the nearest coordination environment of every Pb is likely caused by geometrical constraints of the coordinated mbtfa anions and by the influence of a SALP of electrons in a hybrid orbital on the metal. Such an environment leaves space for interaction of the mbtfa anions of an adjacent

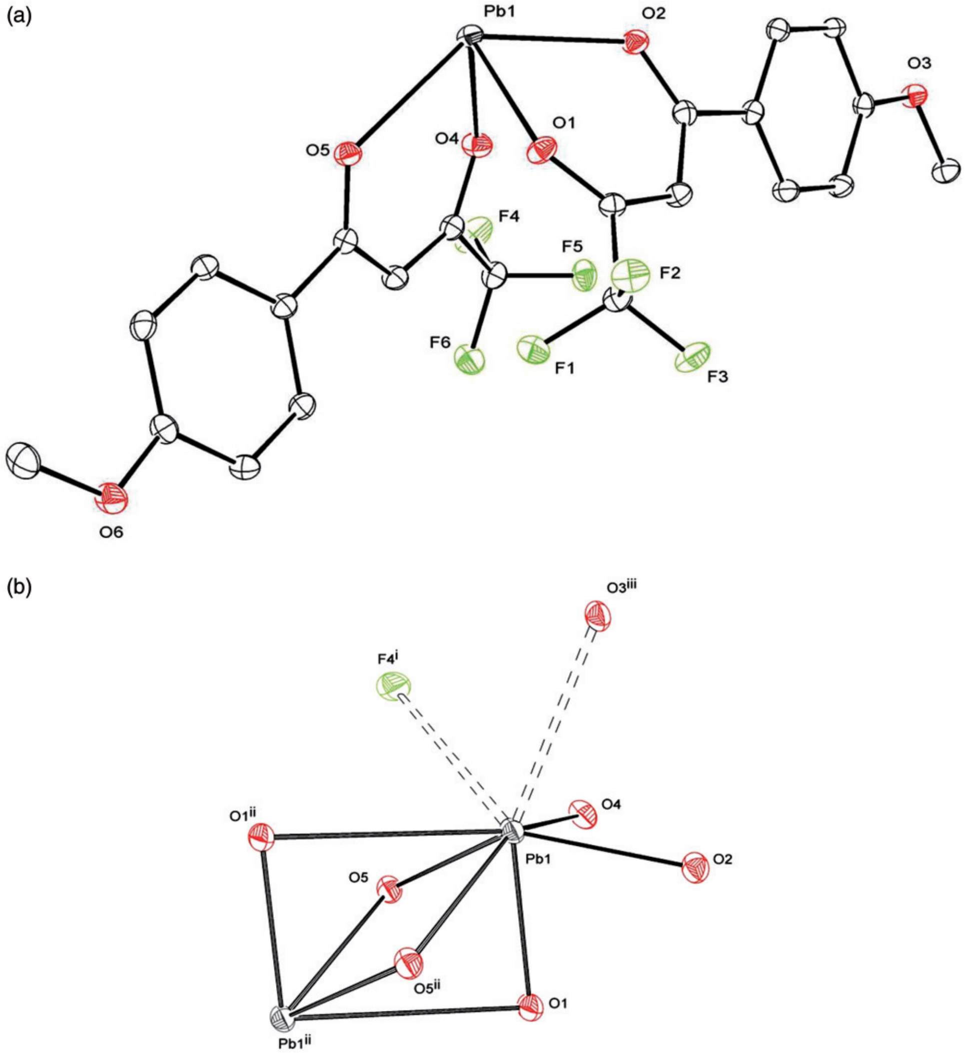


Figure 4. (a) ORTEP diagram of the asymmetric $[Pb_2(mbtfa)_4]_n$ (**1**) unit and (b) representation of the "hole" in the coordination sphere of the Pb atom in **1**.

molecule [43]. If a limit of 3.4 Å were to be placed upon Pb^{II}-donors in **1**, the Pb's interact with mbtfa anions with distances of $Pb1 \cdots O3^{iii} = 2.963(2)$ Å and one fluorine of mbtfa with $Pb1 \cdots F4^{i}$ distances of 3.390(2) Å. Such Pb $\cdots$ FC approaches have been observed in other systems [44] and the separation is not outside that which may be considered to signify appreciable bonding between Pb^{II} and a donor [42, 45, 46]. Consequently, Pb $\cdots$ O interactions allow the binuclear complexes to form 1-D coordination polymers (figure 5) and Pb $\cdots$ F guide the 1-D layers to form a hybrid 2-D network (figure 6). Intermolecular and intramolecular F $\cdots$ H–C, O $\cdots$ H–C, F $\cdots$ F and $\pi \cdots \pi$ stacking interactions [47–49], as well as the SALP on Pb(II), are observed in **1** and appear to be responsible for the crystal packing (figure 7 and table 3).

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

Pb1–O4	2.306(2)
Pb1–O1	2.324(2)
Pb1–O2	2.417(2)
Pb1–O5	2.441(2)
Pb1–O5^{ii}	2.927(2)
Pb1 · · · O3^{iii}	2.963(2)
Pb1 · · · O1^{ii}	3.269(2)
Pb1 · · · F4^{i}	3.390(2)
O4–Pb1–O2	75.53(7)
O1–Pb1–O2	74.30(6)
O4–Pb1–O5	75.39(7)
O1–Pb1–O5	70.87(6)
O2–Pb1–O5	135.15(6)

^{i}: $1-x$, $1-y$, $-z$; ^{ii}: $2-x$, $1-y$, $-z$; ^{iii}: $1-x$, $-y$, $-z$.

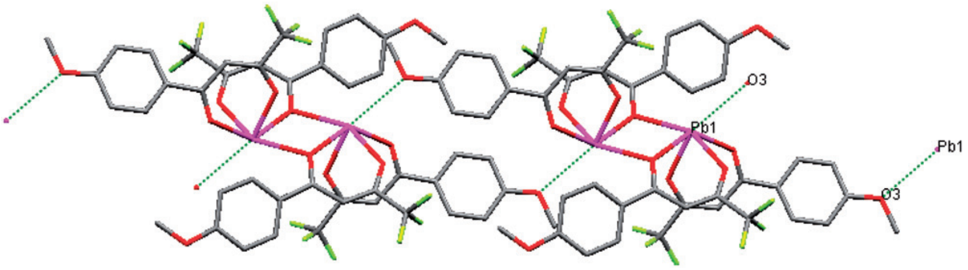


Figure 5. View of **1** resulting from Pb · · · O interactions.

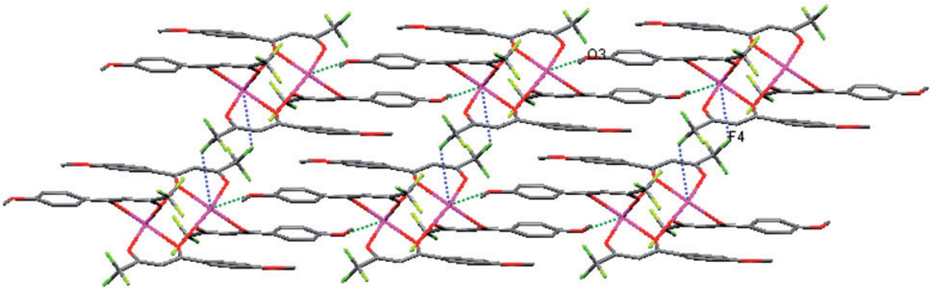


Figure 6. View of **1** showing the Pb · · · O (green) and Pb · · · F (blue) interactions down *c*.

4. Conclusion

A lead(II) coordination polymer, $[\mathrm{Pb(mbtfa)_2}]_n$ (**1**) (Hmbtfa = 4-methoxybenzoyltrifluoroacetone), has been synthesized using a thermal gradient approach. Compound **1** was structurally characterized by single-crystal XRD, X-ray powder diffraction (XRD),

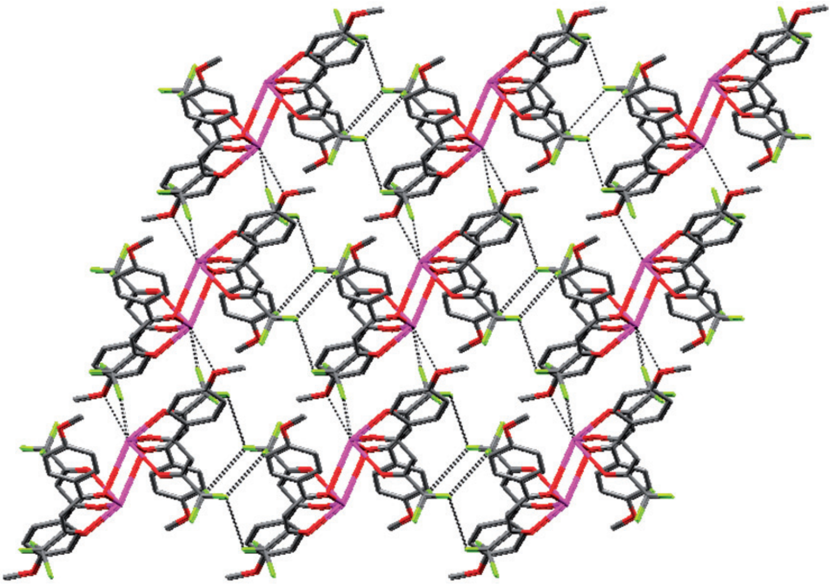


Figure 7. View of **1** showing the weak interactions down *b*.

Table 3. Intermolecular interactions in **1**.

A ··· H–B	A ··· H (Å)	A ··· B (Å)	A ··· H–B (°)
1			
F5 ··· H22A–C22 ($-1+x$, $-1+y$, z)	2.522	3.146(4)	122.62
O4 ··· H7–C7 ($1-x$, $-y$, $-z$)	2.647	3.517(3)	155.93
F2 ··· H22A–C22 (x, $-1+y$, z)	2.616	3.158(4)	116.11
O6 ··· H11C–C11 ($2-x$, $1-y$, $1-z$)	2.666	3.620(3)	172.33
F1 ··· F3 ($2-x$, $1-y$, $1-z$)		2.928(3)	
F3 ··· F6 ($2-x$, $1-y$, $1-z$)		2.919(2)	
F4 ··· O5 ($1-x$, $1-y$, $-z$)		2.872(2)	
$\pi \cdots \pi$ (slipped face-to-face)		3.351(4)	

and IR spectroscopy. The crystal structure of **1** consists of a 3-D polymer and shows the coordination number in Pb(II) is six. Nanoparticles of the compound were also synthesized by sonochemical irradiation. The method of preparation may have advantages such as shorter reaction times, better yields, and production of nano-sized particles of the coordination polymer.

Supplementary material

Full crystallographic data, in CIF format, may be obtained from the Cambridge Crystallographic Data Centre (CCDC 830981 for **1**) *via* www.ccdc.cam.ac.uk/cgi-bin/catreq.cgi.

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