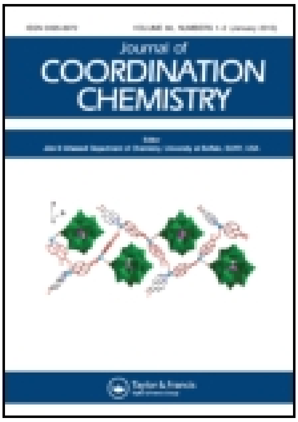
This article was downloaded by: [Renmin University of China]
On: 13 October 2013, At: 10:26
Publisher: Taylor & Francis
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gcoo20

Synthesis and characterization of lead(II) complexes with substituted 2,2′-bipyridines, trifluoroacetate, and furoyltrifluoroacetonate

Farzin Marandi [a] , Zahra Nikpey [a] , Maryam Khosravi [a] , Saeideh Hosseini [b] , Hoong-Kun Fun [c] & Madhukar Hemamalini [c]

[a] Chemistry Department , Payame Noor University , 19395-4697 Tehran , I. R. of Iran

[b] Chemistry Department , Islamic Azad University , Karaj Branch, Karaj , I. R. of Iran

[c] X-ray Crystallography Unit, School of Physics, Universiti Sains Malaysia , 11800 USM, Penang , Malaysia

Published online: 07 Sep 2011.

To cite this article: Farzin Marandi , Zahra Nikpey , Maryam Khosravi , Saeideh Hosseini , Hoong-Kun Fun & Madhukar Hemamalini (2011) Synthesis and characterization of lead(II) complexes with substituted 2,2′-bipyridines, trifluoroacetate, and furoyltrifluoroacetonate, Journal of Coordination Chemistry, 64:17, 3012-3021, DOI: 10.1080/00958972.2011.609593

To link to this article: http://dx.doi.org/10.1080/00958972.2011.609593

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the “Content”) contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing,

Journal of Coordination Chemistry
Vol. 64, No. 17, 10 September 2011, 3012–3021

Taylor & Francis
Taylor & Francis Group

Synthesis and characterization of lead(II) complexes with substituted 2,2′-bipyridines, trifluoroacetate, and furoyltrifluoroacetonate

FARZIN MARANDI*†, ZAHRA NIKPEY†, MARYAM KHOSRAVI†,
SAEIDEH HOSSEINI‡, HOONG-KUN FUN§ and MADHUKAR HEMAMALINI§

†Chemistry Department, Payame Noor University, 19395-4697 Tehran,
I. R. of Iran
‡Chemistry Department, Islamic Azad University, Karaj Branch, Karaj, I. R. of Iran
§X-ray Crystallography Unit, School of Physics, Universiti Sains Malaysia,
11800 USM, Penang, Malaysia

(*Received 11 April 2011; in final form 8 July 2011*)

Two substituted 2,2′-bipyridine lead(II) complexes, $[Pb(5,5'\text{-dm-}2,2'\text{-bpy})(tfac)_2]_n$ (**1**) (5,5′-dm-2,2′-bpy = 5,5′-dimethyl-2,2′-bipyridine and tfac = trifluoroacetate) and $[Pb_2(4,4'\text{-dmo-}2,2'\text{-bpy})_2(ftfa)_4]$ (**2**) (4,4′-dmo-2,2′-bpy = 4,4′-dimethoxy-2,2′-bipyridine and ftfa = furoyltrifluoroacetonate), have been synthesized and characterized by elemental analysis, IR, ^1H NMR, and ^{13}C NMR spectroscopies, thermal behavior, and X-ray crystallography. Complexes **1** and **2** are 1D coordination polymer and dinuclear complex, respectively. The supramolecular features in these complexes are guided by weak directional intermolecular interactions.

Keywords: Lead(II); Substituted 2,2′-bipyridine; Intermolecular interactions

1. Introduction

Research on supramolecular chemistry has developed rapidly to produce new materials with interesting structural features and potential applications, one of the most active branches in current coordination chemistry [1, 2]. By self-assembly of well-designed organic ligands and metal ions under appropriate conditions, a variety of metallosupramolecular architectures have been achieved. Hydrogen bonds also have been used to organize coordination compounds; however, π–π interactions have been scarcely studied in the design of crystals of coordination compounds [1, 2]. Shimoni and Glusker [3], however, have pointed out that although C–H $\cdots$ F–C interactions are weak compared to C–H $\cdots$ O–C interactions, their contributions cannot be ignored in determining molecular packing in complexes and crystals. A number of studies have been carried out to explore the different modes of interactions involving the C–F group [4]. Row *et al.* [5] have been involved in investigation of interactions of organic fluorine in different chemical environments and have demonstrated that fluorine provides

---

*Corresponding author. Email: f.marandi@gmail.com

ISSN 0095-8972 print/ISSN 1029-0389 online
DOI: 10.1080/00958972.2011.609593

different types (F ··· F, C–H ··· F, and C–F ··· π) of directional interactions to build crystal structures. Fluorine-substituted β-diketonate compounds are an important class of ligands [6, 7], versatile, and exhibit a variety of coordination modes [8]. β-Diketonate could be favored by replacement of terminal groups by electron-withdrawing or electron-releasing substituents [9]. Recently in an effort to explore weak interactions in complexes, metal(II) complexes with β-diketonate and neutral diimine chelating ligands have been synthesized and determined by X-ray crystal structure [10]. We report here the preparation and crystal structures of two substituted 2,2′-bipyridine adducts of lead(II) trifluoroacetate and furoyltrifluoroacetonate. The ligands employed in this work are given in scheme 1.

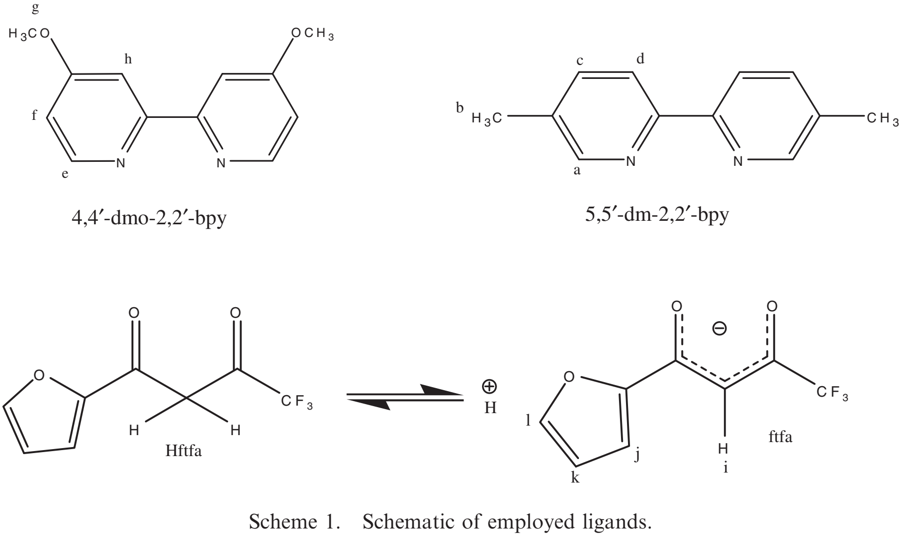
2. Experimental

2.1. *Material and measurements*

All chemicals were of reagent grade and used without purification. FT-IR spectra were collected on a Mattson 1000 spectrophotometer using KBr pellets from 4000 to 450 cm^{-1}. Elemental analyses (CHN) were performed using a Carlo ERBA model EA 1108 analyzer, ^{1}H NMR spectra were obtained with a Bruker spectrometer at 250 MHz in DMSO-d_6. Thermal analyses were carried out on a Perkin-Elmer instrument (Seiko Instruments).

2.2. *Preparation of [Pb(5,5′-dm-2,2′-bpy)(tfac)$_2$]$_n$ (1)*

5,5′-Dimethyl-2,2′-bipyridine (0.184 g, 1 mmol) was placed in one arm of a branched tube [11] and lead(II) acetate (0.190 g, 0.5 mmol) and “Hftfa” (0.206 g, 1 mmol) in the other. Methanol and ethanol ratio (1 : 3) was carefully added to fill both arms, the tube



4,4′-dmo-2,2′-bpy

5,5′-dm-2,2′-bpy

Hftfa

ftfa

Scheme 1. Schematic of employed ligands.

sealed, and the ligand-containing arm immersed in a bath at 60°C while the other was at ambient temperature. After 3 days, crystals had deposited in the cooler arm which were filtered off, washed with acetone and ether, and dried in air, yield: 56%; m.p. 260°C. Analysis: found: C (%): 31.54, H: 1.20, N: 4.44 Calcd for $C_{16}H_6F_6N_2O_4Pb$ (%): C: 31.43, H: 0.98, N: 4.58. IR (cm^{-1}) selected bands: 650(vs), 838(vs) (C–H), 927(m), 1043(s), 1143(s), 1202(vs, C–F), 1400, 1480, 1535(s, aromatic ring), 1661(vs, C=O), 2945(w, C–H aliphatic), 3047(w, C–H aromatic) (figure 1S). ^{1}H NMR (DMSO, δ): 8.48 (d, 2H, a), 8.21 (s, 2H, d), 7.70 (d, 2H, c), 2.33 (s, 6H, b) ppm. ^{13}C NMR (DMSO, δ): 18.47(1), 120.16(7), 133.7(5), 138.1(2), 149.9(4), 153.2(3), 165.1(6), 181.7(8) ppm (scheme 1S).

2.3. *Preparation of [Pb_2(4,4′-dmo-2,2′-bpy)$_2$(ftfa)$_4$] (2)*

Complex **2** was synthesized in the same way as **1** using 4,4′-dimethoxy-2,2′-bipyridine in place of 5,5′-dimethyl-2,2′-bipyridine, yield: 67%; m.p. 197°C. Analysis: found: C (%): 40.54, H: 2.52, N: 3.32. Calcd for $C_{56}H_{40}F_{12}N_4O_{16}Pb_2$ (%): C: 40.30, H: 2.40, N: 3.36. IR (cm^{-1}) selected bands: 671(m, C–H), 938(m), 769(s), 1037, 1090(s), 1290(vs, C–F), 1338, 1407, 1550(s, aromatic ring), 1621(vs, C=O), 2979(w, C–H aliphatic), 3121(w, C–H aromatic) (figure 2S). ^{1}H NMR (DMSO, δ): 8.50 (d, 2H, e), 8.18 (d, 2H, h), 7.80 (d, 2H, f), 7.91 (dd, 2H, k), 7.04 (d, 2H, j), 6.59 (d, 2H, l), 5.89 (s, 2H, i), 3.91 (s, 6H, g) ppm (figure 3S). ^{13}C NMR (DMSO, δ): 55.88(9), 91.07(17), 106.7(20), 111.2(11), 112.9(21), 114.7(13), 117.05-125(15), 146.2(l), 150.9(19), 154.3(12), 157.2(14), 158.4(10), 168.7(16), 175.8(18) ppm (figure 4S, scheme 1S).

2.4. *Crystallography*

Crystallographic data were collected at 100 K with an 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 [12]. The collected data were reduced using SAINT [12] and the empirical absorption corrections were performed using SADABS [12]. The structures were solved by direct methods and refined by least-squares using the SHELXTL software package [13]. All non-hydrogen atoms were refined anistropically and hydrogens were located and included at their calculated positions. Materials for publication were prepared using SHELXTL [13] and ORTEPIII [14]. Six figures and one scheme, plus selected intermolecular interactions are given as supplementary information.

3. Results and discussion

3.1. *Spectroscopic studies*

Reactions between lead(II) acetate and furoyltrifluoroacetone with 5,5′-dimethyl-2,2′-bipyridine and 4,4′-dimethoxy-2,2′-bipyridine yielded crystalline materials formulated as [Pb(5,5′-dm-2,2′-bpy)(tfac)$_2$]$_2$ (**1**) and [Pb(4,4′-dmo-2,2′-bpy)(ftfa)$_2$]$_2$ (**2**), respectively. IR spectra display characteristic absorption bands for substituted 2,2′-bipyridines, "tfac$^-$" and "ftfa$^-$". The relatively weak absorptions at 3121 and 3047 cm^{-1} are from C–H modes involving aromatic ring hydrogens. C–H modes involving aliphatic hydrogens were revealed at 2945 and 2979 cm^{-1}. Absorptions with variable intensity at 1400–1580 cm^{-1} correspond to aromatic ring vibrations of the substituted 2,2′-bipyridines and "ttfa$^-$". Absorptions with variable intensity at 1661, 1621 cm^{-1} and 1100–1350 cm^{-1} correspond to COO and C–F vibrations of "tfac$^-$" and "ftfa$^-$" [15]. The ^{1}H NMR spectrum in DMSO of **1** and **2** displays three different protons of py groups of the substituted 2,2′-bipyridines at 6.59–8.51 ppm. In **2**, three distinct peaks at 6–8 ppm were assigned to the furan ring. The proton of methine, =CH–, is a singlet at 5.89 ppm for **2**. The ^{1}H NMR spectra show bands at 2.33 for **1** and 3.91 ppm for **2** assigned to $-CH_3$ of substituted 2,2′-bipyridines. The ^{13}C NMR spectra of **1** and **2** have six distinct bands assigned to aromatic carbons of py of bipyridines. Two and eight distinct bands in ^{13}C NMR spectrum at 85–180 ppm have been assigned to carbons of "tfac$^-$" and "ftfa$^-$", respectively. The ^{13}C NMR spectra of **1** and **2** display other bands at 18.47 and 55.88 ppm assigned to carbons of methyl and methoxy groups of the bipyridines.

3.2. *Thermal studies*

To study the stability of the compounds, thermogravimetric analyses (TGA) for these complexes were performed on polycrystalline samples under nitrogen. Complexes **1** and **2** are thermally stable at 210°C, demonstrating that the compounds were retained to this temperature. The thermal decomposition of **1** follows a one-step mechanism at 210–280°C corresponding to exothermic decomposition of the ligands. The TGA curve of **2** (figure 5S) shows neither weight loss nor structural change to 215°C then follows a two-step mechanism from 215–320°C for exothermic decomposition of the ligands. The solid residue formed at the end of the decomposition at 300°C is suggested to be $Pb(bpy)_2O$ with total mass loss of 51% for **2** (Calcd 48%). The weight loss (23% (Calcd 26%)) at 320–560°C is equivalent to loss of two coordinated substituted 2,2′-bipyridines with exothermic effects. The mass loss calculations as well as microanalyses of the solid residues suggest that the residue left as a final decomposition product of the complexes at 600°C is PbO with total mass loss of 35.10% for **1** (Calcd 36.47%) and 28.26% for **2** (Calcd 27.12%), agreeing with the proposed structures. It is possible that these compounds are potential source precursors for lead oxides.

3.3. *Crystal structures of 1 and 2*

According to single crystal X-ray diffraction analysis, **1** forms a coordination polymer, crystallizing in the monoclinic space group $C2/c$ (table 1). Selected bond distances and angles are listed in table 2. Each Pb^{2+} is coordinated by two nitrogens of "5,5′-dm-2,2′-bpy" and six oxygens of four "tfac$^-$". Four oxygens of these six have bridging roles between leads. Lead in **1** is located in a special position (two-fold axis) [16]. Compound **1** is a decomposition product, arising from cleavage of "ftfa$^-$" and formation of "tfac$^-$". Examples of the cleavage of fluorinated β-diketonates to form the trifluoroacetate, by action of water during complex formation, are well-known [17]. Compound **1** is a polynuclear chain where Pb's are interconnected through bridging "tfac$^-$". The coordination number of Pb(II) in **1** is eight (figure 1) possessing a stereo-chemically

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

	1	**2**
Identification code	$[\mathrm{Pb}(5,5'\text{-dm-}2,2'\text{-bpy})(\mathrm{tfac})_2]_n$	$[\mathrm{Pb}_2(4,4'\text{-dmo-}2,2'\text{-bpy})_2(\mathrm{ftfa})_4]$
Empirical formula	$C_{16}H_6F_6N_2O_4Pb$	$C_{56}H_{40}F_{12}N_4O_{16}Pb_2$
Formula weight	611.42	1667.32
Crystal system	Monoclinic	Triclinic
Space group	$C2/c$	$P\bar{1}$
Unit cell dimensions (Å, °)		
a	11.3116(2)	10.7187(3)
b	17.8787(3)	12.0396(3)
c	13.2592(3)	12.1295(3)
α	90.00	103.458(1)
β	140.251(1)	108.499(1)
γ	90.00	94.887(1)
Volume (Å^{-3}), Z	1714.62(7), 4	1422.03(7), 1
Calculated density ($\mathrm{Mg\,m^{-3}}$)	2.369	1.947
Absorption coefficient ($\mathrm{mm^{-1}}$)	9.930	6.026
F (000)	1136	804
Crystal size ($\mathrm{mm^3}$)	$0.09 \times 0.06 \times 0.05$	$0.40 \times 0.25 \times 0.13$
θ range for data collection	2.14–35.3	1.8–32.5
Index ranges	$-18 \le h \le 18$; $-28 \le k \le 28$; $-21 \le l \le 21$	$-16 \le h \le 16$; $-18 \le k \le 18$; $-18 \le l \le 18$
Reflections collected	31,258	59,785
Independent reflections	3825[R(int) = 0.0289]	10,223 [R(int) = 0.0365]
Completeness to θ (%)	99.4	99.3
Refinement method	Full-matrix least squares on F^2	Full-matrix least squares on F^2
Data/restraints/parameters	3825/0/132	10,223/0/408
Goodness-of-fit on F^2	1.21	1.06
Final R [$I > 2\sigma(I)$]	$R_1 = 0.0284$, $wR_2 = 0.0785$	$R_1 = 0.0205$, $wR_2 = 0.0462$
R indices (all data)	$R_1 = 0.0299$, $wR_2 = 0.0792$	$R_1 = 0.0267$, $wR_2 = 0.0490$
Largest difference peak and hole ($\mathrm{e}\,\text{Å}^{-3}$)	1.93 and −2.40	1.70 and −1.18

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

1		**2**	
Pb1–N1	2.486(2)	Pb1–O5	2.363(2)
Pb1–N1^{i}	2.486(2)	Pb1–O2	2.503(2)
Pb1–O1	2.614(3)	Pb1–O6	2.524(2)
Pb1–O1^{i}	2.614(3)	Pb1–N2	2.597(2)
Pb1–O2	2.739(3)	Pb1–N1	2.600(2)
Pb1–O2^{i}	2.739(3)	Pb1–O3	2.700(2)
Pb1–O2^{ii}	2.739(3)	Pb1–O3^{i}	2.934(1)
Pb1–O2^{iii}	2.739(3)	Pb1 ··· O6^{i}	3.223(2)
N1^{i}–Pb1–O1	73.38(8)	O5–Pb1–O2	78.88(6)
N1–Pb1–O1	78.70(9)	O2–Pb1–O6	129.52(5)
O1–Pb1–O1^{i}	146.58(13)	O5–Pb1–N2	83.55(5)
N1–Pb1–O2^{iii}	147.09(9)	O6–Pb1–N1	136.59(5)
O1–Pb1–O2^{iii}	80.50(9)	N2–Pb1–O3	145.11(5)
N1–Pb1–O2^{ii}	83.60(9)	N1–Pb1–O3	146.75(5)
O1–Pb1–O2^{ii}	114.51(8)		
O2^{iii}–Pb1–O2^{ii}	128.50(14)		

Symmetry transformations used to generate equivalent atoms: for **1**, $^{i}2-x,y,3/2-z$; $^{ii}3/2-x,1/2-y,1-z$; $^{iii}1/2+x,1/2-y,1/2+z$, for **2**, $^{i}-x,-y,1-z$.

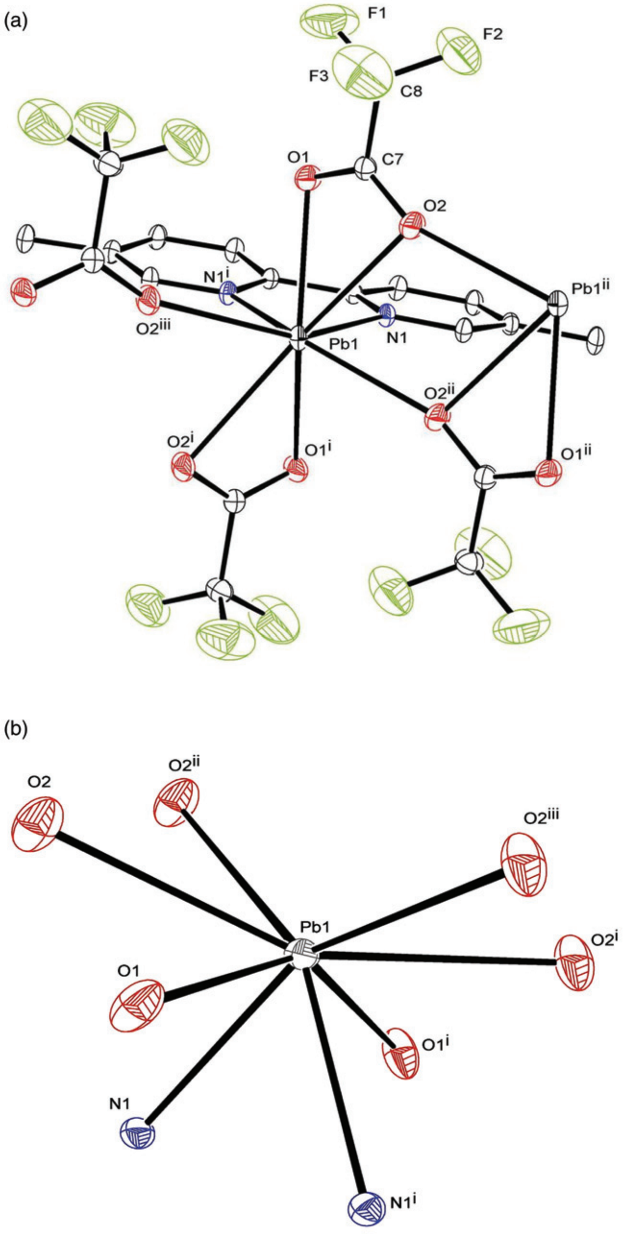


Figure 1. (a) Ortep view of the asymmetric of **1**, displacement ellipsoids are shown at the 30% probability level and (b) representation of the hole in the coordination sphere of **1**.

"active" lone pair (SALP), and the coordination sphere is hemidirected. This is supported by the observed different Pb–O and Pb–N distances (2.810 Å and 2.486 Å) [18] and the eight-coordinate polyhedron around Pb(II) is quite distorted from that of a square antiprism.

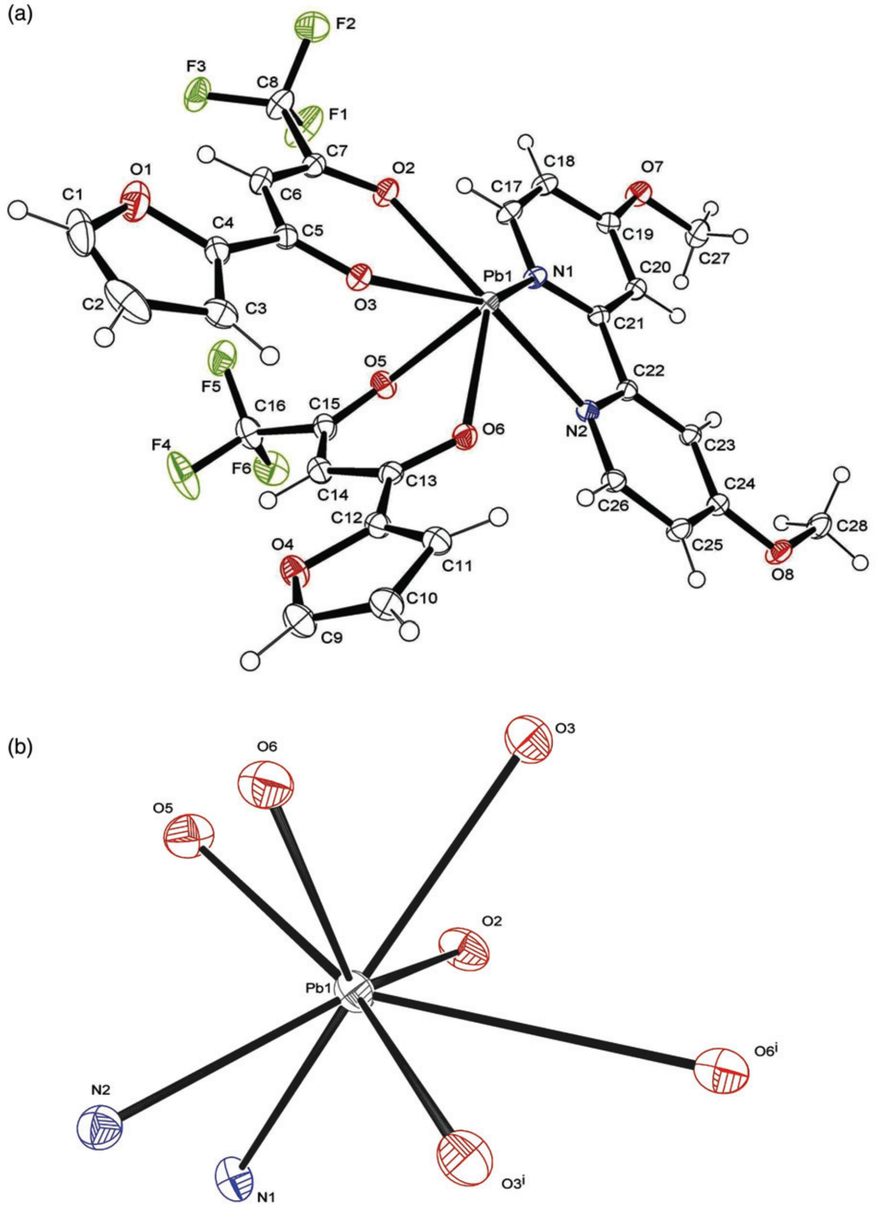


Figure 2. (a) ORTEP view of the asymmetric of **2**, displacement ellipsoids are shown at the 40% probability level and (b) representation of the hole in the coordination sphere of **2**.

X-ray structure analysis of **2** shows dimers in the triclinic space group $P\bar{1}$ (table 1). Selected bond distances and angles are listed in table 2. Each asymmetric unit contains one Pb(II), one "4,4′-dmo-2,2′-bpy" and two furoyltrifluoroacetonates (figure 2). The coordination number of Pb(II) in this complex is seven (two nitrogens of "4,4′-dmo-2,2′-bpy"ligand, five oxygens of three bridging "ftfa$^-$" (figure 2b)).

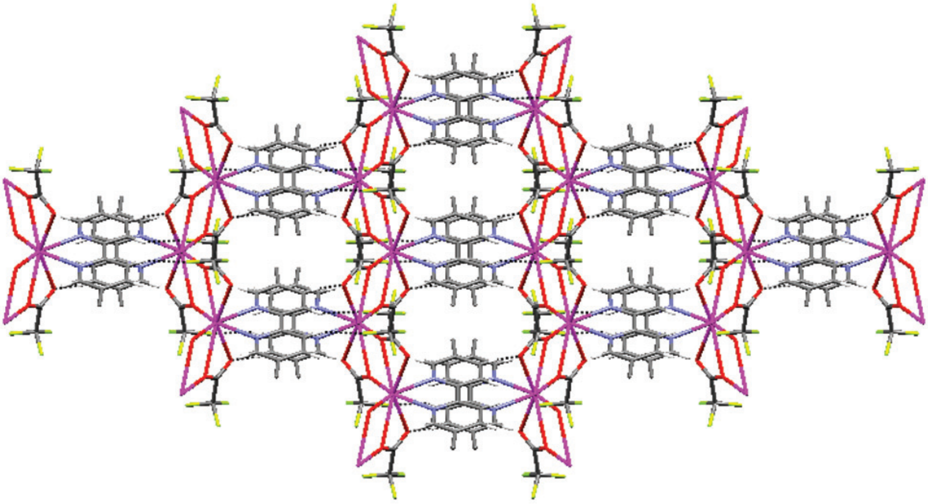


Figure 3. Packing of **1**, viewed along the *c*-axis showing non-covalent interactions and π–π stacking interactions.

One bond length (Pb1–O3^{i} = 2.934(1) Å) in **2** is longer than the sum of the ionic radii, but shorter than the sum of the van der Waals radii (3.54 Å). This longer Pb–O bond has been widely overlooked in previous reports. These long distances can be interpreted as a consequence of the position of oxygen close to the sterically active Pb(II) lone pair [11]. The arrangements of the donors in **2** suggest the existence of a stereo-chemically active lone pair on the open side of the coordination polyhedron [19]. This is supported by shortening of the Pb–O bonds on the side of the Pb(II) opposite to the putative lone pair (2.363(2) Å compared with the Pb–O bond with a length of 2.934(1) Å adjacent to the lone pair) [20].

Intermolecular and π–π stacking interactions are observed in these compounds, responsible for the crystal packing. An inspection of **1** and **2** for weak directional intermolecular interactions by PLATON and MERCURY, which were used for calculating supramolecular interactions, shows that there are O ··· H–C and C–H ··· F interactions [21, 22] (table 1S) (figures 3 and 6S). The H ··· O and H ··· F separations range from 2.4780 to 2.6980 Å, which is indicative of moderate-to-strong hydrogen bonds [23]. All the dimers are parallel in the crystal packing of **1** and **2**, forming a layer packing structure with an interlayer distance of 3.588 Å in **1** and 3.223 Å in **2** [24]. The centroid–centroid separations between neighboring aromatic rings exhibit typical slipped π–π stacking interactions in an offset fashion. Thus, a 3-D hydrogen-bonded and layer-packed network is constructed, as illustrated in figures 3 and 6S [25]. A comparison of this study with recent structural study of thenoyltrifluoroacetonate complex of Pb(II) with 4,4′-dmo-2,2′-bpy and other Pb(II) compounds using N-donor ligands and β-diketonates [10] considering dimer units alone show obvious differences in the relative dispositions of the chelate rings (figure 6S) and these are associated with differences in the types of contacts < 3.5 Å between atoms in separate units. These differences reflect in the interactions that can be discerned (on the basis of short atom contacts) between dimeric species (table 1S).

4. Conclusion

Four factors, lone pair activity, weak Pb–O interactions, and intermolecular and π–π stacking interactions, fluorine containing anions and 2,2′-bipyridines control the coordination sphere of these complexes. The obvious question then is whether the lone pair activity stretches coordinate bonds to result in ligand stacking or whether it is the intermolecular interaction, which has imposed a positioning of the donors for forming a gap in the coordination sphere. However, self-assembly of this complex is likely caused by lone pair activity, weak Pb–O interactions, intermolecular and π–π stacking interactions.

Supplementary material

Full crystallographic data, in CIF format, may be obtained from the Cambridge Crystallographic Data Centre (CCDC 815926 for (**1**) and 815927 for (**2**)) *via* www.ccdc.cam.ac.uk/cgi-bin/catreq.cgi

Acknowledgments

Support of this investigation by Iran National Science Foundation, INSF, is gratefully acknowledged by FM. HKF and MH thank the Malaysian Government and Universiti Sains Malaysia (USM) for the University Golden Goose Fund (Grant No. 1001/PIZIK/811012). MH thanks Universiti Sains Malaysia for a post-doctoral research fellowship.

References

[1] (a) M.W. Hosseini. *Acc. Chem. Res.*, **38**, 313 (2005); (b) S. Kitagawa, R. Kitaura, S. Noro. *Angew. Chem. Int. Ed.*, **43**, 2334 (2004); (c) L. Carlucci, G. Ciani, D.M. Proserpio. *Coord. Chem. Rev.*, **246**, 247 (2004).

[2] (a) P.J. Steel. *Acc. Chem. Res.*, **38**, 243 (2005); (b) B.H. Ye, M.L. Tong, X.M. Chen. *Coord. Chem. Rev.*, **249**, 545 (2005); (c) L. Brammer. *Chem. Soc. Rev.*, **33**, 476 (2004).

[3] L. Shimoni, J.P. Glusker. *Struct. Chem.*, **5**, 383 (1994).

[4] K. Reichenbacher, H.I. Suss, J. Hulliger. *Chem. Soc. Rev.*, **34**, 22 (2005).

[5] (a) D. Chopra, K. Nagarajan, T.N.G. Row. *J. Mol. Struct.*, **888**, 70 (2008); (b) A.R. Choudhury, R.G. Bhat, T.N.G. Row, S. Chandrasekaran. *Cryst. Growth Des.*, **7**, 844 (2007); (c) D. Chopra, T.N.G. Row. *Cryst. Growth Des.*, **6**, 1267 (2006), **5**, 1679 (2005).

[6] J.P. Fackler. Prog. *Inorg. Chem.*, **7**, 361 (1966).

[7] R.C. Mehrotra, R. Bohra, D.P. Gaur. *Metal β-Diketonates and Allied Derivatives*, Academic Press, New York (1978).

[8] S. Kawaguchi. *Coord. Chem. Rev.*, **70**, 51 (1986).

[9] S.J. Eng, R.J. Motekaitis, A.E. Martell. *Inorg. Chim. Acta*, **278**, 170 (1998).

[10] (a) F. Marandi, R. Rutvand, M. Rafiee, J.H. Goh, H.-K. Fun. *Inorg. Chim. Acta*, **363**, 4000 (2010); (b) F. Marandi, Z. Nikpey, J.H. Goh, H.-K. Fun. *Z. Naturf.*, **65b**, 128 (2010); (c) F. Marandi, H. Krautscheid. *Z. Naturf.*, **64b**, 1027 (2009); (d) F. Marandi, S. Chantrapromma, H.-K. Fun. *J. Coord. Chem.*, **62**, 249 (2009); (e) F. Marandi, M. Khosravi, H.-K. Fun. *Z. Anorg. Allg. Chem.*, **634**, 2617 (2008); (f) F. Marandi, H.-K. Fun. *Z. Anorg. Allg. Chem.*, **634**, 1123 (2008); (g) F. Marandi, A. Aslani, A. Morsali. *J. Coord. Chem.*, **61**, 882 (2008); (h) F. Marandi, A. Morsali, A.A. Soudi. *Z. Anorg. Allg. Chem.*, **633**, 661 (2007); (i) F. Marandi, N. Asghari, M. Ghorbanloo, A.A. Soudi, P. Mayer. *Z. Anorg.*

Allg. Chem., **633**, 536 (2007); (j) J.M. Harrowfield, F. Marandi, A.A. Soudi. *Inorg. Chim. Acta*, **358**, 4099 (2005); (k) J.M. Harrowfield, S. Maghaminia, A.A. Soudi. *Inorg. Chem.*, **43**, 1810 (2004).

[11] (a) F. Marandi, F. Amoopour, I. Pantenburg, G. Meyer. *J. Mol. Struct.*, **973**, 124 (2010); (b) H. Sadeghzadeh, A. Morsali, V.T. Yilmaz, O. Buyukgungor. *J. Coord. Chem.*, **64**, 232 (2011); (c) Y.-L. Chen, L. Wang, L.-X. Yu, Y. Fan, J. Shi, H. Yang, J.-H. Jiang, W. Wang, P. Zhang, L.-R. Zhang. *J. Coord. Chem.*, **63**, 2079 (2010).

[12] Bruker. *APEX2 Version 1.27, SAINT Version 7.12a and SADABS Version 2004/1*, Bruker AXS Inc., Madison, Wisconsin, USA (2005).

[13] G.M. Sheldrick. *Acta Cryst.*, **A64**, 112 (2008).

[14] L.J. Farrugia. *J. Appl. Crystallogr.*, **30**, 565 (1997).

[15] K. Nakamoto. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th Edn, Wiley & Sons, New York (1986).

[16] X. Xu, X. Liu, X. Sang, E. Wang. *J. Coord. Chem.*, **63**, 3060 (2010).

[17] F. Marchetti, C. Pettinari, R. Pettinari, A. Cingolani, R. Gobetto, M.R. Chierotti, A. Drozdov, S.I. Troyanov. *Inorg. Chem.*, **45**, 3074 (2006) and references therein.

[18] H.-P. Xiao, A. Morsali. *Solid State Sci.*, **9**, 155 (2007).

[19] J. Casas, E.E. Castellano, J. Ellena, M.S. Garcıa-Tasende, A. Sanchez, J. Sordo, A. Touceda, S.V. Rodrıguez. *Polyhedron*, **26**, 4228 (2007).

[20] (a) L. Shimoni-Livny, J.P. Glusker, C.W. Brock. *Inorg. Chem.*, **37**, 1853 (1998); (b) R.D. Hancock, M.S. Shaikjee, S.M. Dobson, J.C.A. Boeyens. *Inorg. Chim. Acta*, **154**, 229 (1998); (c) A.A. Soudi, F. Marandi, A. Ramazani, E. Ahmadi, A. Morsali. *C. R. Chim.*, **8**, 157 (2005).

[21] A.C. Moro, F.W. Watanabe, S.R. Ananias, A.E. Mauro, A.V.G. Netto, A.P.R. Lima, J.G. Ferreira, R.H.A. Santos. *Inorg. Chem. Commun.*, **9**, 493 (2006).

[22] J.W. Steed, J.L. Atwood. *Supramolecular Chemistry*, Wiley & Sons, Chichester, UK (2000).

[23] (a) L.A. Barrios, G. Aromı, A. Frontera, D. Quinonero, P.M. Deya, P. Gamez, O. Roubeau, E.J. Shotton, S.J. Teat. *Inorg. Chem.*, **47**, 5873 (2008); (b) C.A. Hollis, L.R. Hanton, J.C. Morris, C.J. Sumby. *Cryst. Growth Des.*, **9**, 2911 (2009).

[24] (a) T. Dorn, C. Janiak, K. Abu-Shandi. *CrystEngComm.*, **7**, 633 (2005); (b) S. Banerjee, A. Ghosh, B. Wu, P.-G. Lassahn, C. Janiak. *Polyhedron*, **24**, 593 (2005); (c) S. Banerjee, B. Wu, P.-G. Lassahn, C. Janiak, A. Ghosh. *Inorg. Chim. Acta*, **358**, 535 (2005).

[25] (a) Z. Su, Z.-B. Wang, W.-Y. Sun. *J. Coord. Chem.*, **64**, 170 (2011); (b) C.-B. Liu, J. Wang, X.-L. Zha, X.-J. Zhang, X.-Y. Li, G.-B. Che, Y.-S. Yan. *J. Coord. Chem.*, **64**, 232 (2011).