Synthesis and Characterization of Lead(II) Complexes with the 4-Methoxybenzoyltrifluoroacetonate Ligand

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To investigate the intermolecular interactions of ligands in lead(II) complexes featuring stereochemical activity of the lone electron pair and noncovalent donor-acceptor interactions giving rise also to multidimensional networks, the compounds $[Pb_2(phen)_2(mbtfa)_4]$ (**1**) and $[Pb_2(dmp)_2(mbtfa)_4]$ (**2**) (phen, dmp and $mbtfa^-$ for 1,10-phenanthroline, 2,9-dimethyl-1,10-phenanthroline and 4-methoxybenzoyltrifluoroacetonate ligands, respectively) have been prepared and characterized by elemental analysis and their crystal structures investigated. The structures show the coordination number of Pb(II) to be seven and eight, respectively. Supramolecular structures of **1** and **2** are realized by weak directional intermolecular interactions.

Key words: Lead(II), Crystal Structure, Intermolecular Interactions

Introduction

The Pb^{2+} cation has a $[Xe]4f^{14}5d^{10}6s^2$ electronic configuration and exhibits an especially versatile character with respect to the HSAB theory [1] for which it appears as a borderline acid, able to bind to wide families of ligands [2] within very flexible coordination modes [3]. The coordination chemistry of Pb(II) is mainly determined by two factors: (i) its large size (ionic radius 1.32 Å [4], covalent radius 1.54 Å [4], van der Waals radius 2.00 Å [5]), which permits coordination numbers that range from quasi-one [6] to twelve [7], and (ii) its 6*s* electron pair, which may or may not play a role in the stereochemistry of lead(II) complexes [8]. The lone pair activity can depend on (1) hard or soft ligands, (2) attractive or repulsive interactions among ligands, and (3) the number of electrons (charge) transferred from the ligands to the metal atom [3a]. It has been proposed that holodirected structures do not necessarily exclude an inactive lone pair [9]. Recently, in an effort to explore the role of weak intermolecular interactions among ligands in the stereochemical activity of valence shell electron lone pairs, the lead(II) complexes with fluorinated β-diketonate and neutral aromatic diamine chelating ligands have been synthesized and characterized by X-ray crystal structure determination [10]. Fluorinated β-diketonate

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

Compound	**1**	**2**
Empirical formula	$C_{68}H_{48}F_{12}$-$N_4O_{12}Pb_2$	$C_{72}H_{56}F_{12}$-$N_4O_{12}Pb_2$
Formula weight	1755.48	1811.59
Temperature, K	210(2)	180(2)
Wavelength, Å	0.71073	0.71073
Crystal size, mm^3	$0.23 \times 0.19 \times 0.16$	$0.49 \times 0.11 \times 0.014$
Crystal system	triclinic	triclinic
Space group	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)
a, Å	11.2342(9)	10.9573(9)
b, Å	11.9459(8)	12.2169(10)
c, Å	13.5133(10)	14.8803(12)
α, deg	100.361(8)	98.411(6)
β, deg	109.481(9)	104.334(6)
γ, deg	100.996(9)	114.111(6)
Volume, Å^3	1619.2(2)	1691.2(2)
Z	1	1
Density (calcd.), g cm^{-3}	1.800	1.779
$\mu(MoK_\alpha)$, mm^{-1}	5.293	5.070
$F(000)$, e	852	884
θ range, deg	2.6 – 26.0	1.9 – 26.0
Index ranges	$-13 \le h \le 13$	$-13 \le h \le 13$
	$-13 \le k \le 13$	$-13 \le k \le 15$
	$-16 \le l \le 16$	$-18 \le l \le 18$
Reflections coll. / indep.	13210 / 5945	14298 / 6551
R_{int}	0.026	0.058
Completeness to θ_{max}	93.5%	98.6%
Data / ref. parameters	5945 / 442	6551 / 467
$R1$ / $wR2$ [$I \ge 2\sigma(I)$]	0.0209 / 0.0406	0.0338 / 0.0766
$R1$ / $wR2$ (all data)	0.0300 / 0.0418	0.0433 / 0.0790
Goodness-of-fit on F^2	1.031	0.974
$\Delta\rho_{fin}$ (max / min), e Å^{-3}	0.54 / −0.43	1.55 / −1.41

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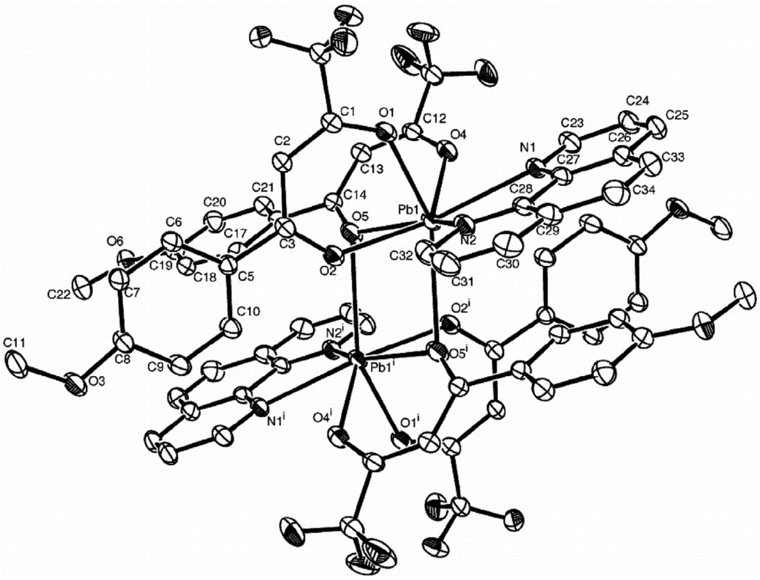

Fig. 1. ORTEP view of **1** with displacement ellipsoids shown at the 30 % probability level.

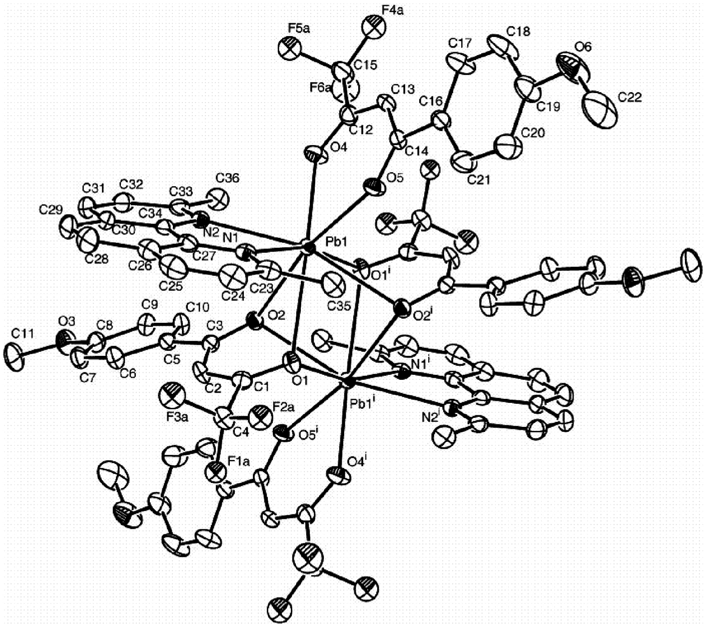

Fig. 2. ORTEP view of **2** (disordered fluorine atoms omitted for clarity; displacement ellipsoids 30 %).

ligands are very good probes because of their ability for forming intermolecular C–F$\cdots\pi$, C–H$\cdots\pi$, C–F$\cdots$H–C, C–H$\cdots$O, F$\cdots$F and $\pi\cdots\pi$ interactions. In this paper we report the synthesis and crystal structures of $[Pb_2(phen)_2(mbtfa)_4]$ (**1**) and $[Pb_2(dmp)_2(mbtfa)_4]$ (**2**), where phen, dmp and mbtfa$^-$ are the abbreviations of 1,10-phenanthroline, 2,9-dimethyl-1,10-phenanthroline and 4-methoxybenzoyltrifluoroacetonate ligands, respectively.

Results and Discussion

The single-crystal X-ray analyses revealed that **1** and **2** are dinuclear complexes, similar to other lead(II) complexes with β-diketonate anions [10b, c]. Crystal and structure refinement data are given in Table 1, and selected bond lenghts and angles are listed in Table 2. Each asymmetric unit contains one Pb(II) ion, one phen ligand in **1**, one dmp ligand in **2**, and two

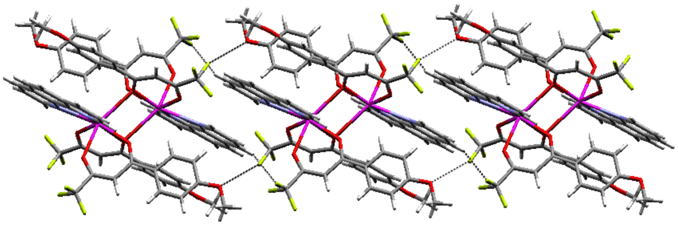

Fig. 3. Packing diagram of **1** as viewed along the crystallographic *a* axis showing the F···H, O···H and F···O interactions and π-π stacking.

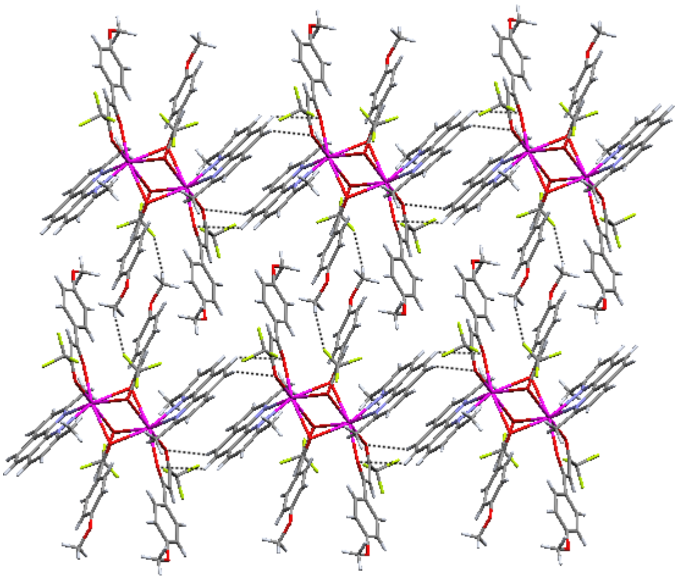

Fig. 4. Packing diagram of **2** as viewed along the *a* axis showing the F···H and O···H interactions and π-π stacking.

mbtfa$^-$ anions. The coordination number of the Pb(II) atoms in **1** is seven (four nitrogen atoms of two phen ligands and three oxygen atoms of two mbtfa$^-$ anions with an additional long Pb···O interaction) and eight in **2** (four nitrogen atoms of two dmp ligands and four oxygen atoms of two mbtfa$^-$ anions) (Figs. 1 and 2). Three bond lenghts Pb1–O5^i 2.918(5) Å in **1** and Pb1–O2 2.829(5) Å, Pb1–O1 2.874(3) Å in **2** are significantly longer than the sum of the ionic radii, but shorter than the sum of the van der Waals radii (3.54 Å) [11]. The longer Pb–O bonds were largely overlooked in previous papers [12]. These long distances are interpreted as a consequence of the position of the oxygen atoms close to the sterically active Pb(II) lone pair [3a, 13–15].

A search was made for weak directional intermolecular interactions in the crystal structure of these compounds. An interesting feature in **1** and **2** is that there are C–H···F interactions (in **1**, F2···H25^i–C25^i 2.492(4) Å and in **2**, F4A···H11b^i–C11^i 2.417(9), F1A···H11A–C11 2.585(9), F5A···H32–C32 2.622(1) and FA2···H17^i–C17^i 2.648(1) Å), O···H–C interactions (in **1**, O6···H11C–C11 2.573(5) Å, ∠O6···H11C–C11 165.17°, and in **2**, O4···H28^i–C28^i 2.705(5) Å, ∠O4···H28^i–C28^i 143.50°) and F···O(methoxy) interactions in **1**, F5···O3 2.914(4) Å (Figs. 3 and 4) [16–18]. The packing diagrams of the complexes exhibit structural topologies *via* two different types of π-π stacking (in **1**, face-to-face of aromatic rings with a distance of 3.289 Å, edge-to-edge with a distance of 3.358 Å (Fig. 3) and in **2**, face-to-face with a distance of 3.447 Å, edge-to-edge with a distance of 3.360 Å (Fig. 4) [19–21].

A useful comparison for **1** and **2** is provided by a recent structural study of the dinuclear complexes of Pb(II) with other fluorinated β-diketonates [10b, c]. The gap in the coordination sphere in **1** is larger than in **2** (Figs. 1 and 2, Table 2), therefore, the Pb(II) lone pair in **1** is stereochemically more active than in **2**.

To investigate the thermal stability of the complexes, thermogravimetric analyses (TGA) were carried out on the crystalline samples. The results have shown that compound **1** starts to decompose at 300 °C, while the decomposition of complex **2** starts at 200 °C. It seems

Table 2. Selected bond lengths (Å) and angles (deg) for **1** and **2** with estimated standard deviations in parentheses[a].

1		**2**	
Pb1–O1	2.364(3)	Pb1–O4	2.471(4)
Pb1–O2	2.482(2)	Pb1–O5	2.528(4)
Pb1–O4	2.554(3)	Pb1–N1	2.662(4)
Pb1–O5	2.602(2)	Pb1–N2	2.663(5)
Pb1–N2	2.664(3)	Pb1–O2$^{\text{i}}$	2.720(4)
Pb1–N1	2.689(3)	Pb1–O1$^{\text{i}}$	2.760(5)
Pb1–O5$^{\text{i}}$	2.927(2)	Pb1–O2	2.829(4)
Pb···Pb	3.954(4)	Pb1–O1	2.874(3)
O1–Pb1–O2	74.89(8)	Pb···Pb	3.778(5)
O1–Pb1–O4	79.52(9)		
O2–Pb1–O4	128.69(9	O4–Pb1–O5	69.86(12)
O1–Pb1–O5	92.94(9)	O4–Pb1–N1	115.38(15)
O2–Pb1–O5	69.00(8)	O5–Pb1–N1	84.16(14)
O4–Pb1–O5	68.77(7)	O4–Pb1–N2	80.75(14)
O1–Pb1–N2	77.28(9)	O5–Pb1–N2	120.00(14)
O2–Pb1–N2	80.19(9)	N1–Pb1–N2	62.86(14)
O4–Pb1–N2	135.54(8)	O4–Pb1–O2$^{\text{i}}$	116.26(13)
O5–Pb1–N2	149.16(8)	O5–Pb1–O2$^{\text{i}}$	74.90(12)
O1–Pb1–N1	84.62(8)	N1–Pb1–O2$^{\text{i}}$	111.62(12)
O2–Pb1–N1	140.11(8)	N2–Pb1–O2$^{\text{i}}$	161.58(12)
O4–Pb1–N1	78.66(8)		
O5–Pb1–N1	147.21(8)		
N2–Pb1–N1	61.89(8)		

[a] Symmetry operation: i: $-x$, $-y$, $-z$.

reasonable to assume that the enhancement of the solid state stability in **1** is a result of stronger intermolecular interactions.

Experimental Section

*Preparation of [Pb$_2$(phen)$_2$(mbtfa)$_4$] (**1**) and [Pb$_2$(dmp)$_2$(mbtfa)$_4$] (**2**)*

The title complexes were prepared by the branched tube method: 4-methoxybenzoyltrifluoroacetone, Hmbtfa, (0.460 g, 2 mmol) was placed in one arm of the branched tube and lead(II) nitrate (0.331 g, 1 mmol) with 1,10-phenanthroline (0.18 g, 1 mmol) or 2,9-dimethyl-1,10-phenanthroline (0.210 g, 1 mmol) in the other one. Methanol was then carefully added to fill both arms, the tube was sealed and the ligand-containing arm immersed in a bath at 60 °C, while the other was left at ambient temperature. After 4 d, crystals deposited in the arm at ambient temperature, which were then filtered off, washed with acetone and ether, and dried in air. **1**: m. p. 210 °C, yield: 65 %, **2**: m. p. 190 °C, yield: 70 %. Elemental analysis: $C_{68}H_{48}F_{12}N_4O_{12}Pb_2$ (**1**): calcd. C 46.48, H 2.73, N 3.19; found C 46.68, H 2.70, N 2.75, and $C_{72}H_{56}F_{12}N_4O_{12}Pb_2$ (**2**): calcd. C 47.69, H 3.09, N 3.09; found C 47.40, H 2.90, N 3.40.

*X-Ray structure analyses of **1** and **2***

The data collections were performed on imaging plate diffractometers Stoe IPDS (**1**) and Stoe IPDS-2T (**2**) using MoK_α radiation (λ = 0.71073 Å). All intensities were corrected for Lorentz and polarization effects. A numerical absorption correction was applied to the data of **2**. The structures were solved by Direct Methods and refined by full-matrix least-squares methods on F^2 using all measured unique reflections (SHELXS/L-97 [22]). The CF_3 groups in **2** showed rotational disorder. Anisotropic displacement parameters were used for all Pb, C, N, O, and non-disordered F atoms. Hydrogen atoms were included in calculated positions. The crystallographic data are summarized in Table 1. Graphical presentations were drawn using ORTEP-3 [23].

CCDC 718040 (**1**) and 718041 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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