Three-Dimensional Supramolecular Network Directed by Intermolecular Interactions in $[\text{Pb}_2(\text{dmp})_2(\text{hfacac})_4]$

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Abstract: To investigate the interactions between noncovalent bond donor and acceptor giving rise to three dimensional networks, compound $[\text{Pb}_2(\text{dmp})_2(\text{hfacac})_4]$ (**1**) (dmp = 2,9-dimethyl-1,10-phenanthroline and Hhfacac = hexafluoroacetylacetonate) has been prepared and characterized by elemental analysis, IR, ^1H NMR, and ^{13}C NMR spectroscopy and its crystal structures was investigated. The single crystal structure 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. The supramolecular structure of **1** is realized by weak directional C–H $\cdots$ O–C, C–F $\cdots$ F–C and π – π stacking interactions.

Keywords: Crystal structure, Lead(II) complex, Intermolecular interactions

Introduction

Control of the supramolecular solid state organization of individual molecules is one of the most important ways to develop novel functional materials. In this field the use of molecular self-organization processes for the development of self-assembled and self-organized structures has attracted attention both in biology and in materials chemistry¹. Understanding of charge assisted non-covalent interactions such as hydrogen bonding, π – π stacking, dipole–dipole, hydrophobic interactions, *etc.*, collectively constitute a promising field of persistent research interest². Molecular organization into one-, two-, or three-dimensional networks is mainly driven by noncovalent interactions, of which hydrogen bonding (of both the strong and the weak variations) plays an important role^{3,4}. Weak hydrogen bonding can play a role in enzymatic reactions because it is capable of modulating the bonding situation in

catalytic sites to a significant degree, thus influencing catalytic properties^{3b}. The construction of metallo-supramolecular systems based on these types of intermolecular interactions is becoming of wide interest nowadays. Recently in an effort to explore weak interactions in complexes, the lead(II) complexes with β -diketonate and neutral diimine chelating ligands have been synthesized and determined by X-ray crystal structure⁵⁻⁸. In this paper we report the synthesis and crystal structures of $[\text{Pb}_2(\text{dmp})_2(\text{hfacac})_4]$ **1** (dmp and hfacac are the abbreviations of 2,9-dimethyl-1,10-phenanthroline and hexafluoroacetylacetonate ligands, respectively, which have the potential to generate intermolecular interactions).

Experimental

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 NMR spectra were measured with a BRUKER DRX-500 AVANCE spectrometer at 500 MHz.

*Preparation of $[\text{Pb}_2(\text{dmp})_2(\text{hfacac})_4]$ (**1**)*

2,9-Dimethyl-1,10-phenanthroline (0.217 g, 1 mmol) was placed in one arm of a branched tube⁹ and lead(II)acetate (0.36 g, 1 mmol), and "Hhfacac" ligand (0.416 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 3 days, crystals had deposited in the cooler arm which were filtered off, washed with acetone and ether and air dried. Yield: 75%, m.p.= 230 °C. (Found, C: 34.80, H: 1.80, N: 3.30%. calculated for $\text{C}_{24}\text{H}_{14}\text{F}_{12}\text{N}_2\text{O}_4\text{Pb}$: C: 34.73, H: 1.70, N: 3.38%). IR (cm^{-1}): 701m, 763m, 1018m, 1149s, 1280vs, 1473s, 1533s¹⁰, 2990m and 3070w. ¹H NMR (DMSO, δ): 2.79(s, 6H), 5.40(s, 2H), 7.64(m, 2H), 7.86(d, 2H), 8.23 (m, 2H) ppm. ¹³C NMR (DMSO, δ): 25.38, 83.74, 124.12, 126.02, 127.24, 137.13, 145.13, 145.07, 158.88, 177.72.

Crystallography

The structure was solved by direct methods and refined by full matrix least squares using SHELXL-97^{11,12}. SHELX operations were automated using ORTEX, which was also used to obtain the drawings¹³. Data were corrected for Lorentz and polarization effects but not for absorption. Hydrogen atoms were included in calculated positions with thermal parameters 30% larger than the atom to which they were attached. The non hydrogen atoms were refined anisotropically. All calculations were performed on a Pentium PC.

Results and Discussion

Determination of the structure of $[\text{Pb}_2(\text{dmp})_2(\text{hfacac})_4]$ by X-ray crystallography (Table 1) showed the complex to be dinuclear in the solid state. The crystallographic unit of $[\text{Pb}_2(\text{dmp})_2(\text{hfacac})_4]$ is illustrated in the ORTEP-3 plot Figure 1 and it consists of two lead(II) ions coordinated to two dmp molecules and four "hfacac" ligands. The coordination number of Lead(II) ions in $[\text{Pb}_2(\text{dmp})_2(\text{hfacac})_4]$ is eight (two of bidentate "dmp", two of bidentate "hfacac" anions and four of two bridging "hfacac" ligands). Distances of Pb-O bonds with terminal "hfacac" ligands are less than bridging "hfacac" ligands Table 2. It is possible, nonetheless, to view the Pb atoms of asymmetric units as linked *via* Pb_2O_2 rhombs, structurally a feature of many Pb(II) complex structures^{6,8b,14-16}, involving these four hfacac-O atoms and which may be indicative of very weak Pb...Pb bonding¹⁷ aided by the O-donor-atom bridging. The Pb atom with a coordination number of 8 possesses a stereo-chemically 'inactive' lone pair, and the coordination sphere is holodirected¹⁸ (Figure 1).

Table 1. Crystal data and structure refinement details for [Pb₂(dmp)₂(hfacac)₄].

Empirical formula	C ₂₄ H ₁₄ F ₁₂ N ₂ O ₄ Pb
Formula weight	829.56
Temperature	298(2) K
Wavelength	0.71069 Å
Crystal system	Triclinic
Space group	P1
Unit cell dimensions	a = 11.108(1) Å α = 99.07(2) deg b = 12.614(2) Å β = 110.68(2) deg c = 11.312(1) Å γ = 109.92(2) deg
Volume	1322.7(4) Å ³
Z	1
Density (calculated)	2.083 Mg/m ³
Absorption coefficient	6.497 mm ⁻¹
F(000)	788
Crystal size	0.43 x 0.35 x 0.32 mm
Theta range for data collection	1.81 to 22.98 deg.
Index ranges	-10 ≤ h ≤ 10; -11 ≤ k ≤ 10; -12 ≤ l ≤ 12
Reflections collected	5268
Independent reflections	4492 [R(int) = 0.0275]
Reflections observed, >2σ	4304
Data Completeness	0.663
Absorption correction	PSI-Scans
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	4492 / 93 / 536
Goodness-of-fit on F ²	1.229
Final R indices, I>2σ(I)	R ₁ = 0.0348 wR ₂ = 0.0907
R indices (all data)	R ₁ = 0.0361 wR ₂ = 0.0916
Absolute structure parameter	0.0(18)
Largest diff. peak and hole	0.690 and -0.962 e.Å ⁻³

Table 2. Selected bond lengths / Å and angles / ° for [Pb₂(dmp)₂(hfacac)₄].

Pb1-N3	2.32(2)	Pb1-N4	2.56(2)
Pb1-O3	2.67(2)	Pb1-O5	2.85(3)
Pb1-O6	2.86(3)	Pb1-O7	2.90(3)
Pb1-O8	2.71(3)	Pb1-O4	2.92(2)
Pb2-N2	2.39(2)	Pb2-N1	2.57(3)
Pb2-O2	2.70(2)	Pb2-O6	2.70(2)
Pb2-O1	2.72(2)	Pb2-O5	2.88(2)
Pb2-O3	2.83(2)	Pb2-O4	2.97(3)
N3-Pb1-O8	119.8(8)	O3-Pb1-O8	83.7(7)
N4-Pb1-O5	61.0(7)	O7-Pb1-O4	72.6(7)
N3-Pb1-O4	103.7(7)	O6-Pb1-O4	70.6(7)
N4-Pb1-O8	82.7(8)	N2-Pb2-O1	87.2(8)
N1-Pb2-O2	91.6(7)	O2-Pb2-O4	116.4(5)
O1-Pb2-O3	123.3(7)	O1-Pb2-O5	77.0(7)
N2-Pb2-O3	63.6(9)

Figure 1. ORTEP diagram of $[\text{Pb}_2(\text{dmp})_2(\text{hfacac})_4]$ (**1**).

A search was made for weak directional intermolecular interactions in the crystal structure of **1**. An interesting feature is that there are $\text{C}\cdots\text{O}$ interactions with the distances of 2.64(2) Å ($\text{HC}\cdots\text{O} = 3.41$ Å and $\angle\text{O}\cdots\text{H}-\text{C} = 141.28^\circ$), 2.62(2) Å ($\text{HC}\cdots\text{O} = 3.36$ Å and $\angle\text{O}\cdots\text{H}-\text{C} = 136.21^\circ$) and 2.55(2) Å ($\text{HC}\cdots\text{O} = 3.19$ Å and $\angle\text{O}\cdots\text{H}-\text{C} = 126.37^\circ$), values¹⁹ that suggest strong interactions within this class of weak non-covalent contacts.^{20,21} There are short $\text{F}\cdots\text{F}$ interactions with the distances of 2.773(5), 2.936(3) and 2.937(3) Å which are less²² than the sum of the van der Waals radii for fluorine at 2.94 Å (Figure 2).

The packing diagram of this complex exhibits fascinating self-assembled structural topologies *via* π - π stacking (face-to-face with distance of 3.43 and 3.52 Å) (Figure 2), appreciably shorter than the normal π - π stacking^{23,24}. Consequently, the π - π stacking and $\text{F}\cdots\text{F}$ and $\text{O}\cdots\text{HC}$ interactions allow dinuclear compound to form a hybrid three dimensional network.

Figure 2. A view, down *a*, fragment of the 3D network of **1** *via* intermolecular interactions

The molecular unit of **1** is both dimensionally and structurally different from that $[\text{Pb}(\text{phen})(\text{hfacac})_2]$ **2** and $[\text{Pb}(\text{bipy})(\text{hfacac})_2]$ **3**^{8a}. **1** is a dinuclear whereas **2** and **3** are joined into polymeric chains. However **1** is similar to $[\text{Pb}(\text{bipy})_2(\text{hfacac})_2]$ **4**^{8a} and the similarity of **1** and **4** further suggests that no significant “lone pair effect” can be operative at the Pb atoms. The two structures may be regarded as having two; approximately opposed faces occupied either by aromatic (A) or by fluorinated (F) entities and this may explain the segregated nature of its lattice (Figure 2). A possible analysis of this lattice is to regard it as

being made up of undulating sheets of complex units, with the mean plane of these sheets parallel to *bc*. A view perpendicular to such a sheet (Figure 2) shows that, within the sheet, A faces confront A faces and F confront F. Accordingly, it may be concluded that dimensionally and structurally difference the between **1** on the one hand and **2** and **3** on the other is due to the methyl substituting the 1,10-phenanthroline ligand.

In conclusion, a subtle interplay among the presence of methyl groups on 1,10-phenanthroline, strong and weak interactions appears to control the packing motifs in the crystal structure of **1**. Our current results suggest that, while interactions involving “organic fluorine” have a significant influence in generating supramolecular assemblies in inorganic solids, the general use of these interactions for the a priori prediction of packing motifs is yet to be fully understood and harnessed.

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-605297 for [Pb₂(dmp)₂(hfacac)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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