

Thermal, structural and solution studies of a new lead(II) coordination polymer with η^4 Pb–C interactions

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ABSTRACT

A new Pb(II) one-dimensional coordination polymer $\{[\text{Pb}(\text{PAA})_2]_n$ (**1**), PAA^- = phenylacetate) was synthesized by the reaction of $\text{Pb}(\text{CH}_3\text{COO})_2 \cdot 3\text{H}_2\text{O}$ and ligand phenyl acetic acid. Compound **1** was structurally characterized by single-crystal X-ray diffraction. The crystal structure of this compound consists of one-dimensional polymeric units of $[\text{Pb}(\text{PAA})_2]$ and the coordination number of Pb^{II} ions is six. The lead atoms have irregular coordination sphere containing stereo-chemically active lone pair and tetra-hapto (η^4) interactions, thus attaining a total hapticity of 10 with environment $\text{C}_4\text{O}_6\text{Pb}$. The thermal stability of compound **1** was studied by thermal gravimetric (TG) and differential thermal analyses (DTA). The results of studies of the stoichiometry and formation of complex **1** in methanol, ethanol and acetonitrile solutions were found to be in support of their solid state stoichiometry.

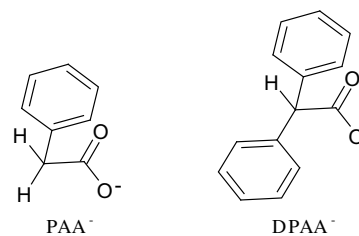
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1. Introduction

The design of crystal structures and control of molecular arrangements of coordination polymers has attracted much attention in recent years [1,2]. So far, extended systems of a variety of metals have been characterized providing very interesting information about supramolecular structures. The lead(II) complexes are interesting and frequently discussed in considering the coordination and stereo-activity of heavy metals is that of the 'stereo-chemical activity' of valence shell electron lone pairs [3–6].

The phenylacetate (PAA^-) anion is an interesting ligand, with an aromatic group and because of its ability for forming of polyhapto may also be a very good candidate for the investigation of the "stereo-chemical activity" of valence shell electron lone pairs in the lead(II) polymeric and supramolecular compounds.

In our last works, we reported the coordination polymer of diphenylacetate (DPAA^-) with thallium(I) [7] and silver(I) [8]. In the present study, we report on the synthesis and crystal structure determination of a lead(II) coordination polymer with PAA^- and solution studies of this compound.



2. Experimental

2.1. Materials and physical techniques

All chemicals were of reagent grade and were used as commercially obtained without further purification. IR spectra were recorded using Perkin–Elmer 597 and Nicolet 510P spectrophotometers and pressed potassium bromide (KBr) disks were used for transmission spectroscopy of compound. Microanalyses were carried out using a Heraeus CHN–O– Rapid analyzer. Melting points were measured on an Electrothermal 9100 apparatus and are uncorrected. The thermal behavior was measured with a PL–STA 1500 apparatus. All UV–Vis. spectra were recorded on a computerized double-beam Shimadzu 2550 spectrophotometer, using two matched 10-mm quartz cells. Crystallographic

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Table 1
Crystal data and structure refinement for compound $[Pb(PAA)_2]_n$ (**1**)

Identification code	1
Empirical formula	$C_{16}H_{14}O_4Pb$
Formula weight	477.46
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$C2/c$
Unit cell dimensions	
a (Å)	17.0900(11)
b (Å)	10.9833(10)
c (Å)	7.9716(5)
α (°)	90.00
β (°)	103.880(5)
γ (°)	90.00
Volume (Å ³)	1452.61(19)
Z	4
D_{calc} (g cm ⁻³)	2.183
Absorption coefficient (mm ⁻¹)	11.627
$F(000)$	896
Crystal size (mm ³)	0.52 × 0.37 × 0.24
Theta range for data collection (°)	2.22–27.99
Index ranges	$-22 \leq h \leq 22$, $-14 \leq k \leq 14$, $-10 \leq l \leq 10$
Reflections collected	1747
Independent reflections ($R(int)$)	1675 (0.0568)
Absorption correction	Integration
Maximum and minimum transmission	0.0653 and 0.0095
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	1747/0/97
Goodness-of-fit on F^2	1.093
Final R indices [$I > 2 \sigma(I)$]	$R_1 = 0.0188$ $wR_2 = 0.0454$
R indices (all data)	$R_1 = 0.0202$ $wR_2 = 0.0459$
Largest difference peak and hole (e Å ⁻³)	0.849 and -0.510

measurements were made at 293(2) K using a STOE-IPDS 2 diffractometer. The intensity data were collected within the range $2.22^\circ \leq \theta \leq 27.89^\circ$ using graphite monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å). The structure has been solved by direct methods and refined by full-matrix least-squares techniques on F^2 using SHELXTL [9]. Crystallographic data and details of the data collection and structure refinements are listed in Table 1. The observed anisotropic thermal parameters, the calculated structure factors, and full lists of bond distances, bond angles and torsion angles are given in the supplementary material.

2.2. Synthesis of $[Pb(PAA)_2]_n$ (**1**)

The ligand phenylacetic acid (1 mmol, 0.136 g) and lead(II) acetate (1 mmol, 0.36 g) were placed in the bottom of main of a branched tube. Methanol was carefully added to fill both arms, the tube sealed and the main arm immersed in oil bath at 60 °C while the branched arm was at ambient temperature. After 5–10 days, very suitable single crystals had deposited in the cooler arm which was filtered off, washed with acetone and air dried. d.p. = 320 °C, Yield: 0.112 g (35%). IR (selected bands; in cm⁻¹): 607m, 701s, 834m, 929w, 1202m, 1414s, 1444m, 1525vs, 1559m, 3020w. Anal. calc. for $C_{16}H_{14}O_4Pb$: C, 40.21; H, 2.93; Pb, 43.35. Found: C, 40.50; H, 2.84; Pb, 43.60%.

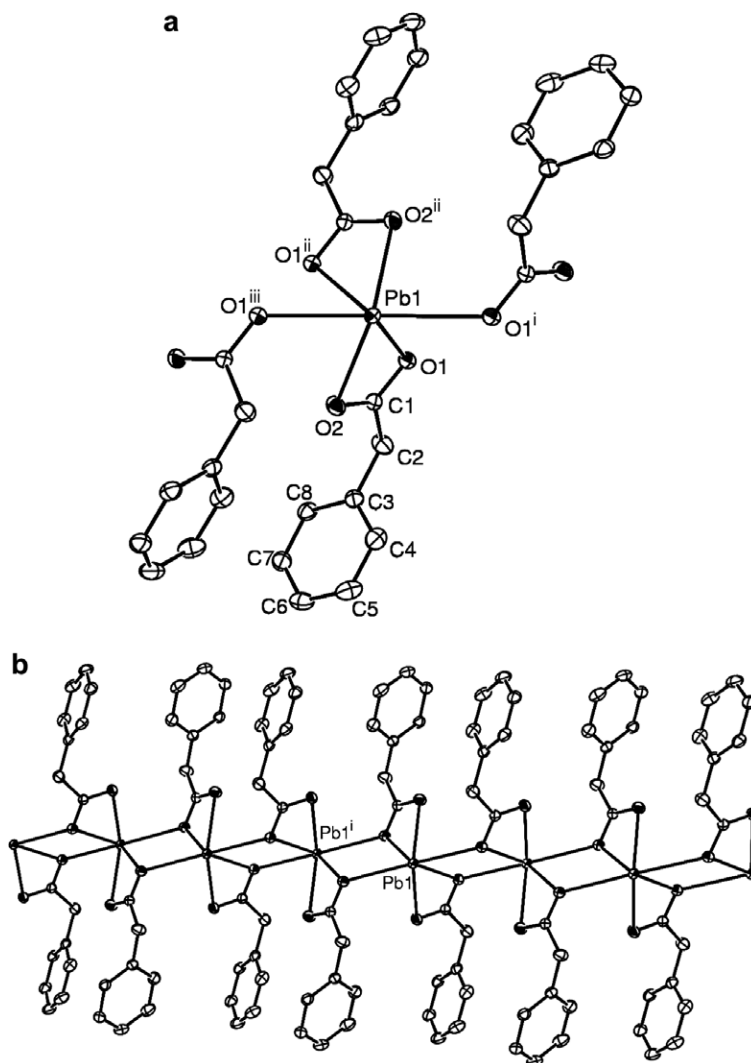


Fig. 1. (a) ORTEP diagram and (b) a fragment of the one-dimensional chain in compound $[Pb(PAA)_2]_n$ (**1**). i: $-x, y, -z + 1/2$; ii: $-x, -y, -z$; iii: $x, -y, z + 1/2$.

3. Results and discussion

The reaction between phenylacetate (PAA^-) and $\text{Pb}^{\text{II}}(\text{CH}_3\text{COO})$ provided crystalline materials of the general formula $[\text{Pb}(\text{PAA})_2]_n$ (**1**). The IR spectrum of compound **1** shows characteristic absorption bands for the PAA^- ligand. The absorption bands with variable intensity in the frequency range $1400\text{--}1580\text{ cm}^{-1}$ correspond to ring vibrations of the pH moiety of the PAA^- ligand, and symmetric and asymmetric vibrations of the carboxylate group are observed

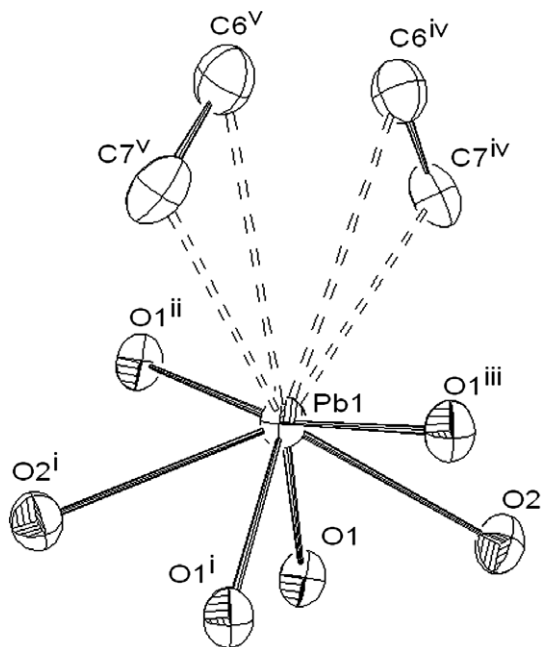


Fig. 2. Showing of $\text{Pb}\cdots\text{C}$ interactions in compound $[\text{Pb}(\text{PAA})_2]_n$ (**1**) after extending the bonding limit: i: $-x, y, -z + 1/2$; ii: $-x, -y, -z$; iii: $x, -y, z + 1/2$; iv: $-x + 1/2, y + 1/2, -z + 1/2$; v: $x + 1/2, y + 1/2, z$.

at 1414 and 1559 cm^{-1} . The $\Delta(\nu_{\text{asym}} - \nu_{\text{sym}})$ value of 145 cm^{-1} indicates that the carboxylate groups coordinate to the lead(II) centers in a bridging mode [10].

Determination of the structure of the compound **1** by X-ray crystallography (Table 1) showed the complex to be a new one-dimensional polymer (Fig. 1) and the lead atoms can be considered to be six-coordinate. Each PAA^- anion acts as a three-connecting ligand, connecting two Pb^{II} ions. The carboxylate groups of the PAA^- ligand act as both bidentate chelating, and bridging group where two oxygen atoms of the carboxylate group coordinate to a lead(II) ion, also one of this oxygen atoms bridge to other lead atom (Fig. 1).

In compound **1**, the lone pair of lead(II) is 'active' in the solid state and the arrangement of O-atoms suggest a gap or hole in coordination geometry around the Pb^{II} coordination sphere (Figs. 1 and 2), a gap possibly occupied by a 'stereo-active' electron lone pair. Hence, the geometry of the nearest coordination environment of every Pb^{II} atoms is likely to be caused by the geometrical constraints of coordinated O-atoms and by the influence of a stereochemically 'active' electron lone pair. The observed shortening of the $\text{Pb}\text{--}\text{O}$ bond on the side of $\text{Pb}(\text{II})$ ion opposite to the putative lone pair ($\text{Pb}\text{--}\text{O1} = 2.409(3)$ compared with $\text{Pb}\text{--}\text{O1}^{\text{i}} = 2.694(3)$ Å

Table 2
Selected bond lengths (Å) and angles ($^\circ$) for compound $[\text{Pb}(\text{PAA})_2]_n$ (**1**)

$\text{Pb1}\text{--}\text{O1}$	2.409(3)	$\text{O1}\text{--}\text{Pb1}\text{--}\text{O1}^{\text{ii}}$	84.45(13)
$\text{Pb1}\text{--}\text{O2}$	2.552(3)	$\text{O1}^{\text{ii}}\text{--}\text{Pb1}\text{--}\text{O2}^{\text{ii}}$	52.13(8)
$\text{Pb1}\text{--}\text{O1}^{\text{i}}$	2.694(3)	$\text{O1}^{\text{ii}}\text{--}\text{Pb1}\text{--}\text{O2}^{\text{ii}}$	87.73(10)
		$\text{O2}\text{--}\text{Pb1}\text{--}\text{O2}^{\text{ii}}$	127.63(15)
		$\text{O1}^{\text{i}}\text{--}\text{Pb1}\text{--}\text{O1}^{\text{iii}}$	66.91(10)
		$\text{O1}\text{--}\text{Pb1}\text{--}\text{O1}^{\text{iii}}$	123.10(8)
		$\text{O2}^{\text{ii}}\text{--}\text{Pb1}\text{--}\text{O1}^{\text{iii}}$	107.85(8)
		$\text{O2}^{\text{ii}}\text{--}\text{Pb1}\text{--}\text{O1}$	77.60(8)
		$\text{O1}\text{--}\text{Pb1}\text{--}\text{O1}^{\text{i}}$	66.91(10)
		$\text{O1}^{\text{ii}}\text{--}\text{Pb1}\text{--}\text{O1}^{\text{iii}}$	168.07(12)

ⁱ $-x, y, -z + 1/2$.

ⁱⁱ $-x, -y, -z$.

ⁱⁱⁱ $x, -y, z + 1/2$.

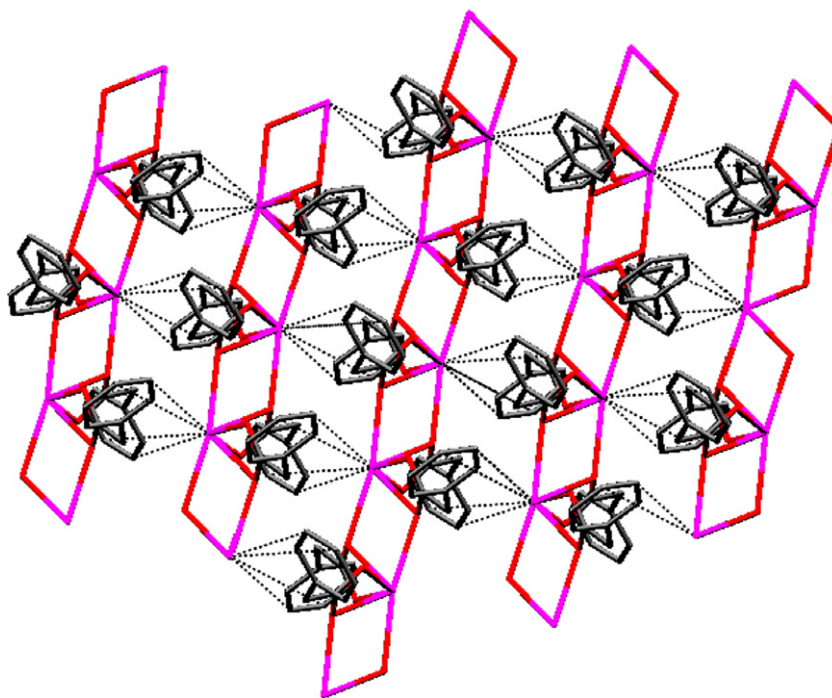


Fig. 3. Packing of the compound $[\text{Pb}(\text{PAA})_2]_n$ (**1**), showing $\text{Pb}\cdots\text{C}$ interactions.

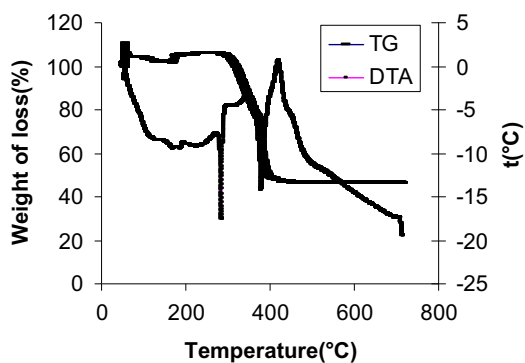


Fig. 4. Thermal behaviour of $[\text{Pb}(\text{PAA})_2]_n$ (1).

(Table 2) adjacent to the lone pair) supports the presence of this feature [11].

To find any other potential donor center, it is necessary to extend the bonding limit. A search was made generally for Pb...C approaches and it appears that Pb atom in compound **1** may also be involved in an η^4 interaction with the phenyl groups of neighboring molecules. Thus, the Pb(II) atoms are linked to four carbon atoms of phenyl groups, with distances $\text{Pb}\cdots\text{C6}^{\text{iv}} = \text{Pb}\cdots\text{C6}^{\text{v}} = 3.808$ and $\text{Pb}\cdots\text{C7}^{\text{iv}} = \text{Pb}\cdots\text{C7}^{\text{v}} = 3.504$ Å (iv: $-x + 1/2, y + 1/2, -z + 1/2$; v: $x + 1/2, y + 1/2, z$) (Figs. 2 and 3). Hence, the Pb(II) coordination sphere is completed and rather than a PbO_6 coordination sphere, the complex can be considered to contain a tetrahapto ($\text{C}_4\text{O}_6\text{Pb}$) center with an irregular ten coordination number. The reported Pb...C separations range is 3.083–4.05 Å in species $[\text{Pb}(\text{o-xylene})_2(\text{Cl}_2\text{AlCl}_2)_2]$, $[\text{Pb}(\eta^6\text{-C}_6\text{H}_6)(\text{Cl}_2\text{AlCl}_2)_2] \cdot \text{C}_6\text{H}_6$ [12] $[\text{Pb}_2\{\text{SeC}_6\text{H}_2$

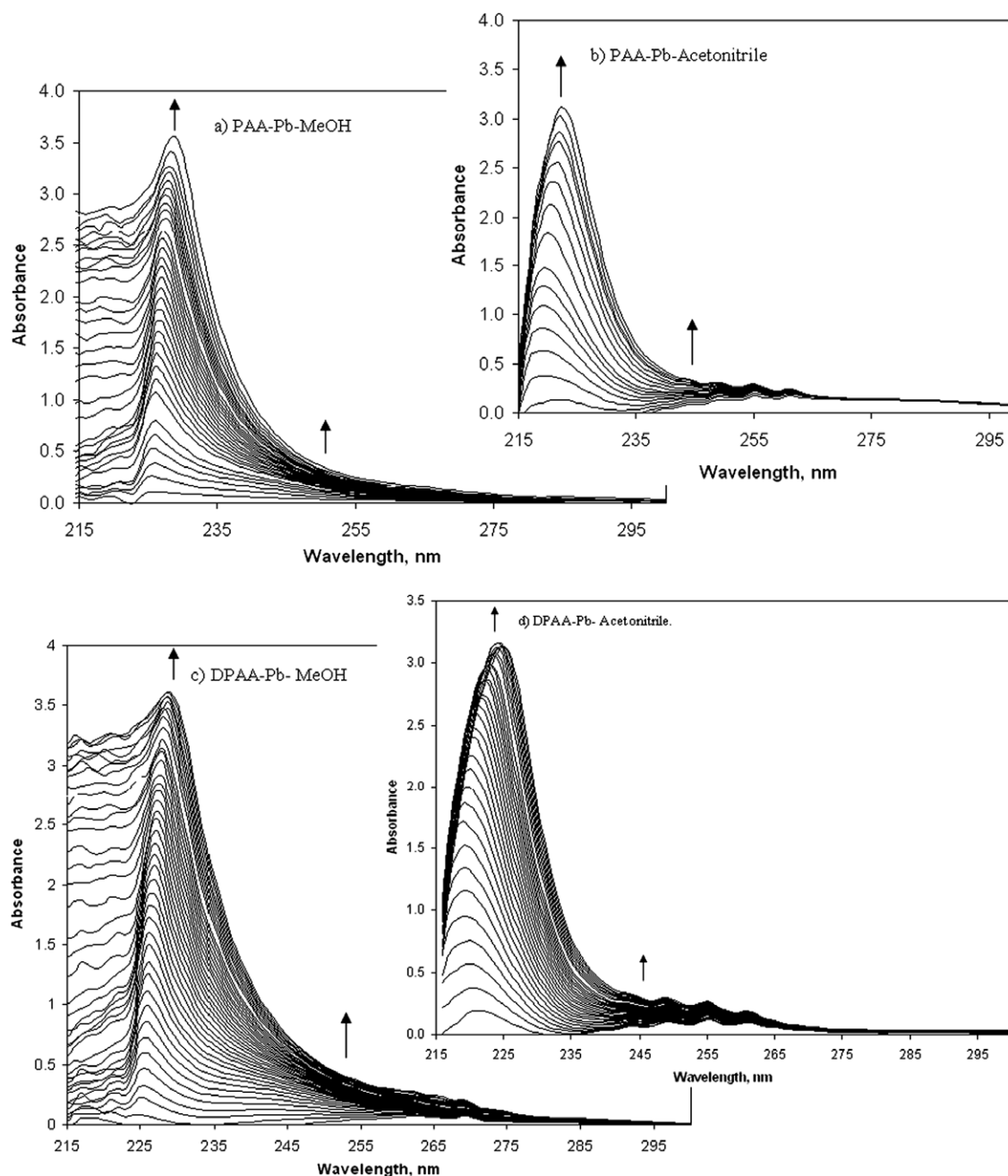


Fig. 5. Electronic absorption spectra of ligands (5.0×10^{-5} M) in the presence of increasing concentration of $\text{Pb}(\text{NO}_3)_2$ at 25 °C in different solvents.

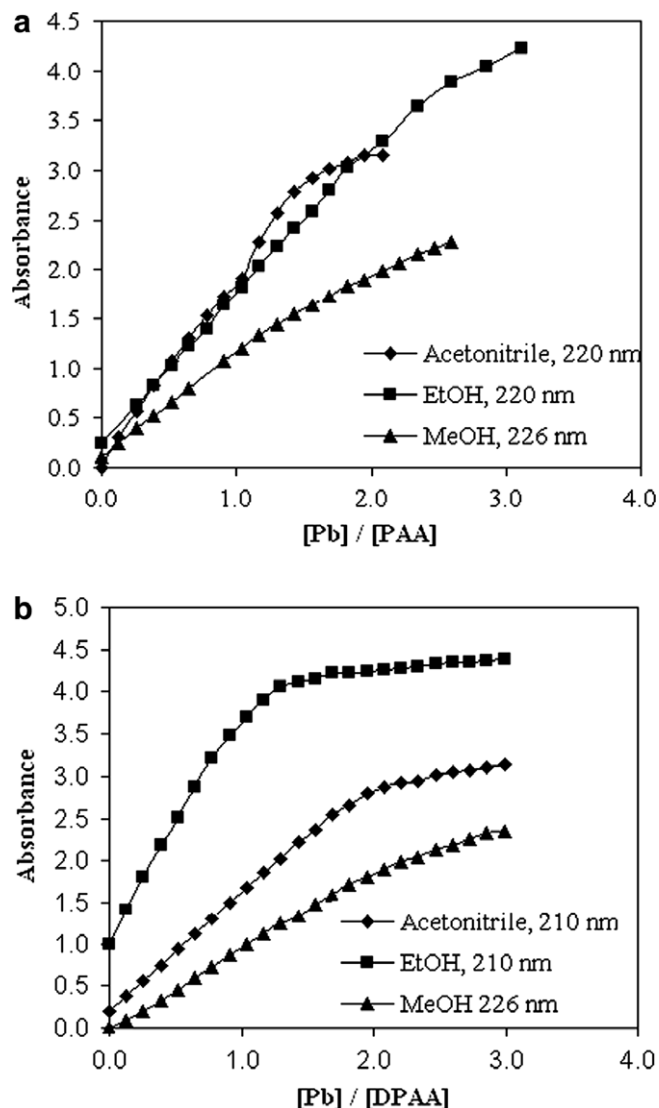


Fig. 6. Mole ratio plots of (a) PAA and (b) DPAA (5.0×10^{-5} M) with $\text{Pb}(\text{NO}_3)_2$ solution in different solvents at 25 °C.

Table 3
Formation constants of Pb-PAA and Pb-DPAA in different solvent at 25 °C

Ligands	Acetonitrile	Methanol	Ethanol
PAA	$\log k_1 = 3.73 \pm 0.04$	$\log k_1 = 4.15 \pm 0.03$	$\log k_1 = 4.02 \pm 0.06$
	$\log k_2 = 3.56 \pm 0.02$	$\log k_2 = 4.02 \pm 0.03$	$\log k_2 = 3.89 \pm 0.02$
DPAA	$\log k_1 = 2.77 \pm 0.02$	$\log k_1 = 4.31 \pm 0.01$	$\log k_1 = 4.01 \pm 0.01$
	$\log k_2 = 3.00 \pm 0.03$	$\log k_2 = 4.05 \pm 0.007$	$\log k_2 = 4.03 \pm 0.01$

$(\text{CF}_3)_3\text{C}(\text{toluene})_2$ [13] and $[\text{Pb}_2(\text{DBM})_4]$ [14]. Thus, Pb...C coordination of Pb(II) appears to be yet another factor which can make varying contributions to the stability of complexes of this metal ion and these secondary interactions grow the structure to two-dimensional coordination polymer (Fig. 3).

The thermal decomposition behavior of compound **1** was investigated in flowing nitrogen and a static atmosphere of air. It was shown that the complex exhibited similar decomposition pathways in both nitrogen and air. Compound **1** (Fig. 4) does not melt and is stable up to 322 °C at which temperature it begins to decompose. Decomposition of compound **1** takes place between 322 and

400 °C with an endothermic effect at 292 °C and an exothermic effect at 420 °C. The solid residue formed at around 420 °C is suggested to be PbO (observed 45.80, calcd.: 46.70%).

The electronic absorption spectra of PAA^- and DPAA^- with Pb^{2+} complexes in methanol and acetonitrile in the increasing concentration of $\text{Pb}(\text{NO}_3)_2$ were recorded (Fig. 5) at 25 °C. There is no isobestic point in titration of ligands with $\text{Pb}(\text{NO}_3)_2$, and it is evident that 1:1 and 1:2 (metal to ligand) complexes are formed in nitrate solution. The stoichiometry of the Pb-PAA and Pb-DPAA complexes in methanol, ethanol and acetonitrile was examined by the method of mole ratio. The resulting plots in methanol, ethanol and acetonitrile are shown in Fig. 6, and it is evident that 1:1 and 1:2 complexes are formed in nitrate solution.

For evaluation of the conditional formation constants, the mole ratio data obtained were fitted to the previously reported equations [15,16] using a non-linear least-squares curve fitting program KINFIT [17]. All of the $\log k_f$ values evaluated from the computer fitting of the corresponding absorbance – mole ratio data are listed in Table 3, and shown that the order of formation constant are as follow:

$$[\text{Pb}^{2+}]/[\text{PAA}] \text{ in MeOH} > [\text{Pb}^{2+}]/[\text{PAA}] \text{ in EtOH}$$

$$> [\text{Pb}^{2+}]/[\text{PAA}] \text{ in acetonitrile}$$

$$[\text{Pb}^{2+}]/[\text{DPAA}] \text{ in MeOH} > [\text{Pb}^{2+}]/[\text{DPAA}] \text{ in EtOH}$$

$$> [\text{Pb}^{2+}]/[\text{DPAA}] \text{ in acetonitrile}$$

4. Conclusions

A new Pb(II) one-dimensional coordination polymer, $\{[\text{Pb}(\text{PAA})_2]_n$ (**1**, PAA^- = phenylacetate) containing tetra-hapto (η^4) interactions was synthesized and structurally characterized by single-crystal X-ray diffraction. The thermal stability of compound **1** was studied by thermal gravimetric (TG) and differential thermal analyses (DTA). The results of studies of the stoichiometry and formation of complex **1** and diphenylacetate DPAA^- with Pb^{2+} in methanol, ethanol and acetonitrile solutions were found to be in support of their solid state stoichiometry.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2008.05.005.

References

- [1] B. Moulton, M.J. Zaworotko, Chem. Rev. 101 (2001) 1629.
- [2] D. Braga, F. Grepioni, G.R. Desiraju, Chem. Rev. 98 (1998) 1375.
- [3] J. Parr, Polyhedron 16 (1997) 551.
- [4] P. Pykkö, Chem. Rev. 88 (1988) 563.
- [5] J.M. Harrowfield, H. Miyamae, B.W. Skelton, A.A. Soudi, A.H. White, Aust. J. Chem. 49 (1996) 1165, and refs. cit. therein.
- [6] L. Shimon-Livny, J.P. Glusker, C.W. Brock, Inorg. Chem. 37 (1998) 1853.
- [7] A. Askarinejad, A. Morsali, Helvet. Chem. Acta 89 (2006) 265.
- [8] K. Akhbari, A. Morsali, M. Zeller, J. Organomet. Chem. 692 (2007) 3788.
- [9] Bruker Advanced X-ray Solutions SHELXTL (Version 6.14), Bruker AXS Inc., Madison, WI, USA, 2003.
- [10] X. Xue, X.-S. Wang, R.-G. Xiong, X.Z. You, B.F. Abrahams, C.-M. Che, H.-X. Ju, Angew. Chem., Int. Ed. 41 (2002) 2944.
- [11] R.D. Hancock, M.S. Shaikjee, S.M. Dobson, J.C.A. Boeyens, Inorg. Chim. Acta 154 (1988) 229.
- [12] A.G. Gash, P.F. Rodesiler, E.L. Amma, Inorg. Chem. 13 (1974) 2429.
- [13] D. Labahn, F.M. Bohnen, R. Herbst-Irmer, E. Pohl, D. Stalke, H.W. Roesky, Z. Anorg. Allg. Chem. 620 (1994) 41.
- [14] J.M. Harrowfield, S. Maghaminia, A.A. Soudi, Inorg. Chem. 43 (2004) 1810.
- [15] M.R. Ganjali, A. Rouhollahi, A.R. Mardan, M. Shamsipur, J. Chem. Soc., Faraday Trans. 94 (1998) 1959.
- [16] A. Fakhari, M. Shamsipur, J. Incl. Phenom. 26 (1996) 243.
- [17] V.A. Nicely, J.L. Dye, J. Chem. Educ. 49 (1971) 443.