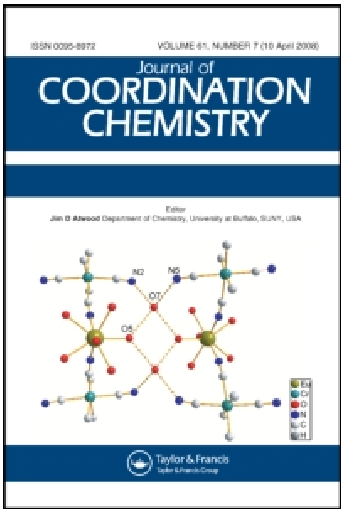

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Synthesis and crystal structure of a three-dimensional network coordination polymer: $[\mathrm{Pb}(\mathrm{C_5H_4NCOO})_2(\mathrm{H_2O})]$<b><i>n</i>

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Synthesis and crystal structure of a three-dimensional network coordination polymer: $[Pb(C_5H_4NCOO)_2(H_2O)]_n$

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A new coordination polymer $[Pb(C_5H_4NCOO)_2(H_2O)]_n$ has been prepared by reaction of $Pb(NO_3)_2$ with isonicotinic acid in the presence of equimolar NaOH. Single-crystal X-ray diffraction analysis reveals that the coordination geometry of each lead(II) centre in $[Pb(C_5H_4NCOO)_2(H_2O)]_n$ is a distorted square antiprism comprised of five O atoms and one N atom from three distinct isonicotinate ligands, and two water molecules. The complex displays a three-dimensional network structure, in which isonicotinate ligands adopt two different bridging coordination modes.

Keywords: Crystal structure; Lead; Isonicotinate

1. Introduction

Metal-organic polymeric frameworks containing metal ions and organic bridging ligands have developed in recent years due to their particular beauty and intriguing architectural diversity and crystal packing motifs along with potential applications as functional materials [1, 2]. In particular, the rational selection of multifunctional organic ligands containing appropriate coordination sites plays a role in adjusting the coordination frameworks, and the nature of the donors may lead to formation

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of unique networks with desired properties and functions [3]. Isonicotinic acid is an excellent multidentate bridging ligand which has been extensively employed to synthesize a variety of metal coordination polymers because the N and O donors on opposite sites of the pyridine ring can make isonicotinic acid a linear ligand. Examples of these polymers are the 1-D rare earth polymer $[Ln(C_5H_4NCOO)_3(H_2O)_2]_n$ (Ln = Nd, Gd) [4], a T-shaped 1-D chain polymer $[Cd(C_5H_4NCOO)(C_5H_5NCOO)(NO_3)(H_2O)]_n$ [5], 2-D network polymer $[Cd_4(C_5H_4NCOO)_8(H_2O)_4]_n$ [6] and 3-D extended frameworks $[Fe(C_5H_4NCOO)_2]_n$ [7]. However, most of the reported structures are transition metal complexes; complexes with Pb(II) ions as main group metal have been seldom reported [8]. Herein the crystal structure of a three-dimensional lead(II) coordination polymer, $[Pb(C_5H_4NCOO)_2(H_2O)]_n$, is reported.

2. Experimental

Isonicotinic acid (C_5H_4NCOOH), NaOH, CH_3CH_2OH and $Pb(NO_3)_2$ were used as received commercially without further purification. IR spectra were recorded on a Nicolet FT-IR Spectrophotometer with KBr pellets (range: 4000–400 cm^{-1}) and elemental analysis for C, H and N was determined on a Varlo ERBA1106EL, analyzer.

2.1. *Synthesis of* $[Pb(C_5H_4NCOO)_2(H_2O)]_n$

A mixture of $Pb(NO_3)_2$ (1.0 mmol), isonicotinic acid (2.0 mmol), NaOH (2.0 mmol), ethanol (12 mL) and H_2O (6 mL) was sealed in a 26 mL stainless-steel reactor with a Teflon liner, heated to 423 K for 5 days, and then cooled to room temperature, obtaining yellow crystals of $[Pb(C_5H_4NCOO)_2(H_2O)]_n$ in 56% yield (based on Pb). Anal. Found: C, 30.53; H, 2.43; N, 5.82. Calcd for $C_{12}H_{10}N_2O_5Pb$: C, 30.68; H, 2.13; N, 5.96%. IR (KBr pellets, cm^{-1}): 3408(s), 3053(w), 2856(w), 1694(v), 1625(m), 1547(s), 1303(s), 1259(s), 1026(m), 991(w), 914(w), 756(m).

2.2. *X-ray crystallography*

The diffraction data were collected on a Siemens P4 diffractometer in the range $2.20 \leq \theta \leq 25.49°$ for $[Pb(C_5H_4NCOO)_2(H_2O)]_n$ at 296(2) K with graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). A total of 2817 reflections were collected, of which 2491 were unique. The structures were solved by direct methods (SHELXS-97) [9] and refined by full-matrix least-squares calculations on F^2 (SHELXL-97) [10]. All non-hydrogen atoms were located with successive difference Fourier syntheses and refined anisotropically, while H atoms on C atoms were positioned geometrically and allowed to ride on their parent atoms, with C–H distances of 0.93 Å, and $U_{iso}(H) = 1.2U_{eq}(C)$. Coordination water H atoms were located in a difference map and refined, subject to an O–H restraint of 0.821(10) Å. The absolute structure which has been determined is in accord with the selected setting (Flack χ parameter is $-0.04(2)$) [11]. The crystal data and details of crystal structure determinations are summarized in table 1 and selected bond lengths and bond angles are listed in table 2.

Table 1. Crystal data and structure refinement details for $[Pb(C_5H_4NCOO)_2(H_2O)]_n$.

Compound	$[Pb(C_5H_4NCOO)_2(H_2O)]_n$
Empirical formula	$C_{12}H_{10}N_2O_5Pb$
Formula weight	469.41
Crystal size (mm^3)	0.46 × 0.30 × 0.16
Temperature (K)	296(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	*Cc*
a (Å)	10.915(2)
b (Å)	18.554(3)
c (Å)	7.094(1)
β (°)	111.10(1)
Volume ($Å^3$)	1340.34(34)
Z	4
D_{Calcd} ($g\,cm^{-3}$)	2.326
μ (mm^{-1})	12.608
$F(000)$	872
θ range (°)	2.20–25.49
Limiting indices	$-13 \le h \le 13$, $-22 \le k \le 22$, $-8 \le l \le 8$
Reflections collected	2817
Independent reflections	2491 ($R_{int} = 0.0335$)
Data/restraints/parameters	2491/5/185
Absorption correction	Empirical
Max. and min. transmission	0.8699, 0.2410
Refinement method	Full-matrix least-squares on F^2
Goodness-of-fit on F^2	1.000
Absolute structure parameter	−0.04(2)
Extinction coefficient	0.0030(3)
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0374$, $wR_2 = 0.0927$
R indices (all data)	$R_1 = 0.0430$, $wR_2 = 0.0942$
Max/min. $\Delta\rho$ ($e\,Å^{-3}$)	1.490/−1.618

Table 2. Selected bond lengths (Å) and angles (°) for $[Pb(C_5H_4NCOO)_2(H_2O)]_n$.

Pb–O(1)	2.431(10)	Pb–O(3)#1	2.563(13)
Pb–O(4)#1	2.628(11)	Pb–N(2)	2.68(2)
Pb–O(2)#2	2.739(10)	Pb–O(2)	2.741(11)
Pb–O(5)	2.855(13)	Pb–O(5)#2	3.001(13)
O(1)–Pb–O(3)#1	99.9(5)	O(1)–Pb–O(4)#1	81.3(4)
O(3)#1–Pb–O(4)#1	50.0(4)	O(1)–Pb–N(2)	73.6(5)
O(3)#1–Pb–N(2)	76.9(6)	O(4)#1–Pb–N(2)	115.3(5)
O(1)–Pb–O(2)#2	89.0(4)	O(3)#1–Pb–O(2)#2	147.0(4)
O(4)#2–Pb–O(2)#2	162.5(3)	N(2)–Pb–O(2)#2	75.3(5)
O(1)–Pb–O(2)	50.2(3)	O(3)#1–Pb–O(2)	128.8(4)
O(4)#1–Pb–O(2)	81.7(3)	N(2)–Pb–O(2)	118.7(5)
O(2)#2–Pb–O(2)	80.8(2)	O(1)–Pb–O(5)	115.7(4)
O(3)#1–Pb–O(5)	105.7(5)	O(4)#1–Pb–O(5)	72.9(4)
N(2)–Pb–O(5)	169.3(5)	O(2)#2–Pb–O(5)	98.7(4)
O(2)–Pb–O(5)	68.1(3)	O(1)–Pb–O(5)#2	151.8(4)
O(3)#1–Pb–O(5)#2	95.0(5)	O(4)#1–Pb–O(5)#2	126.2(4)
N(2)–Pb–O(5)#2	86.8(5)	O(2)#2–Pb–O(5)#2	66.1(3)
O(2)–Pb–O(5)#2	131.6(3)	O(5)–Pb–O(5)#2	82.6(3)

Symmetry code, #1: $x - 1/2$, $3/2 - y$, $1/2 + z$; #2: x, $1 - y$, $z - 1/2$.

3. Results and discussion

As shown in figure 1, each Pb(II) center is in a distorted square antiprism by coordinating to five O atoms and one N atom from three distinct isonicotinate ligands, and two water molecules. All Pb–O bond distances fall in the range of 2.431(10)–3.001(13) Å, within the normal range [12]. The Pb–N bond length is 2.68(2) Å, similar to that reported in [Pb(bpy)(SCN)$_2$] [13]. The isonicotinate ligand adopts two kinds of coordination modes. In type A, the ligand adopts a chelating/bridging (one oxygen atom connects two metal atoms, the other connects one metal atom, and the carboxylic group coordinates to two metal atoms) coordination mode and the pyridyl N atom is noncoordinating. The coordination mode of carboxylate is significantly different from the carboxylate of OAc, which acts as both bidentate, and bridging group in a μ-1,3 mode where oxygen atoms of the carboxylate group coordinate to a lead(II) ion and also bridge the two adjacent lead(II) ions in [Pb(phen)(O$_2$CCH$_3$)(O$_2$NO)]$_n$ [14] and [Pb(H$_2$O)(μ-OAc)(μ-sac)]$_n$ [15], and is less commonly found [16]. In type B, the ligand adopts tridentate bridging coordination (two carboxylate O atoms bind a Pb ion and a pyridyl N atom binds another Pb ion), the carboxylate group adopts chelate bidentate coordination mode, similar to the carboxylate moiety of OAc in [Pb(phen)$_2$(CH$_3$COO)](ClO$_4$) [17]. In the polymer, two such Pb(II) centers [Pb and PbB] are linked by type A and one O atom of water to give a dimeric unit with an intramolecular Pb$\cdots$Pb distance of 4.571 Å, two dimeric units and two such Pb(II) centers are further bridged by type B to form a hexanuclear macrometallacyclic unit (figure 2). The repeating hexanuclear macrometallacyclic units arrange along the a axis and expand along the *b* axis to give rise to 2D layer

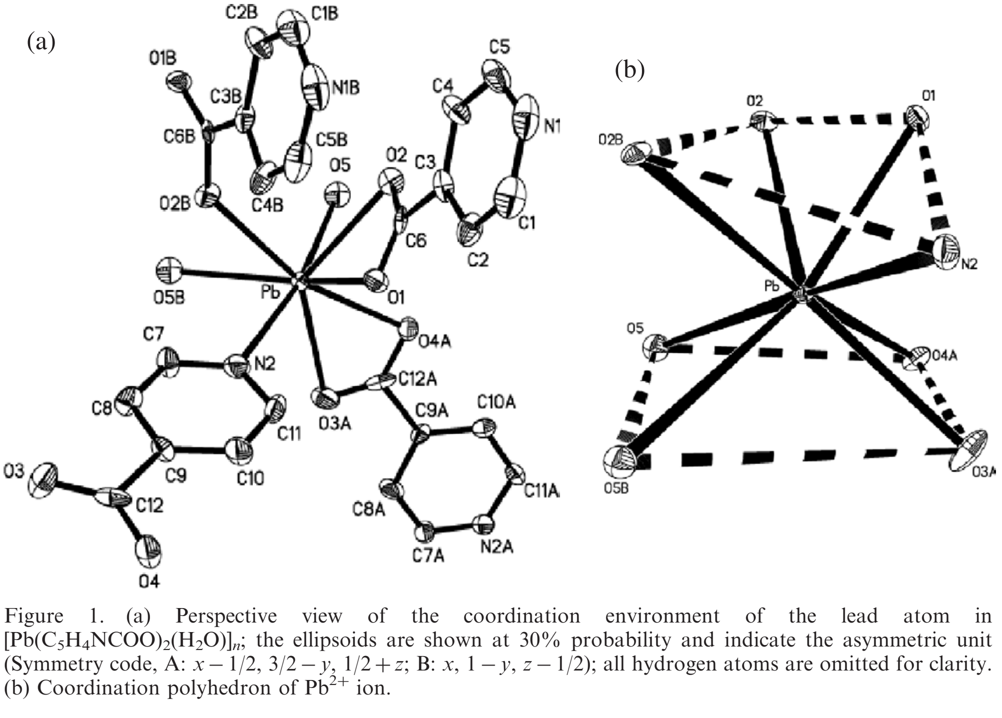

Figure 1. (a) Perspective view of the coordination environment of the lead atom in [Pb(C$_5$H$_4$NCOO)$_2$(H$_2$O)]$_n$; the ellipsoids are shown at 30% probability and indicate the asymmetric unit (Symmetry code, A: $x-1/2$, $3/2-y$, $1/2+z$; B: x, $1-y$, $z-1/2$); all hydrogen atoms are omitted for clarity. (b) Coordination polyhedron of Pb^{2+} ion.

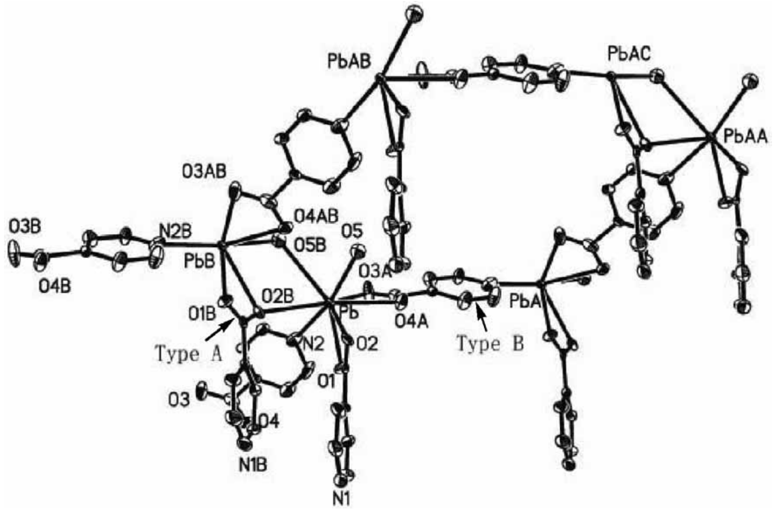

Figure 2. A view of the hexanuclear macrometallacyclic unit showing the coordination modes of ligand in $[Pb(C_5H_4NCOO)_2(H_2O)]_n$ (Symmetry code, A: $x-1/2$, $3/2-y$, $1/2+z$; B: x, $1-y$, $z-1/2$; C: x, $1-y$, $1/2+z$).

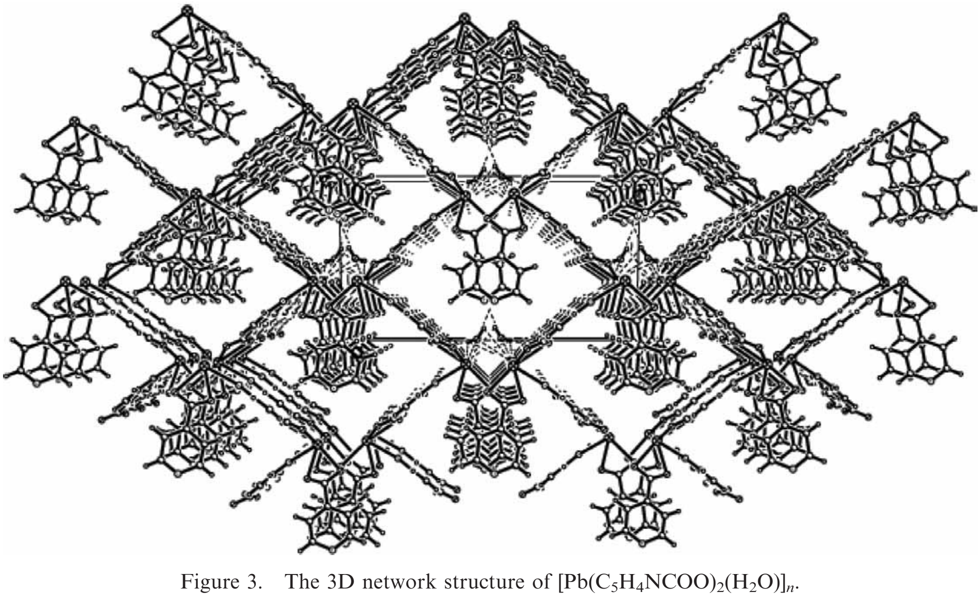

Figure 3. The 3D network structure of $[Pb(C_5H_4NCOO)_2(H_2O)]_n$.

on the *ab* plane (figure 3). While isonicotinate ligand (type A) and water molecule join the adjacent layers creating the 3D architecture, which is further stabilized by hydrogen bonding between the coordinated water molecule and atom O4 of an adjacent carboxylate group [O5–H5A···O4^{i}; O···O 2.756(18) Å; O–H···O 162(16)°; Symmetry code A: $x-1/2$, $3/2-y$, $1/2+z$; *i*: $-1/2+x$, $-1/2+y$, z], and between the coordinated water molecule and atom N1 of an adjacent uncoordinated pyridine group

[O5–H5B $\cdots$ N1^{ii}; N $\cdots$ O 2.84(2) Å; O–H $\cdots$ N 168(17)°; Symmetry code B: x, $1-y$, $z-1/2$; ii: x, y, $-1+z$].

Supplementary material

Crystallographic data for the structure of $[Pb(C_5H_4NCOO)_2(H_2O)]_n$ has been deposited with the Cambridge Crystallographic Data Centre as supplementary publications CCDC 281556. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax:+44-1223-336033; E-mail: deposit@ccdc.cam.ac.uk).

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