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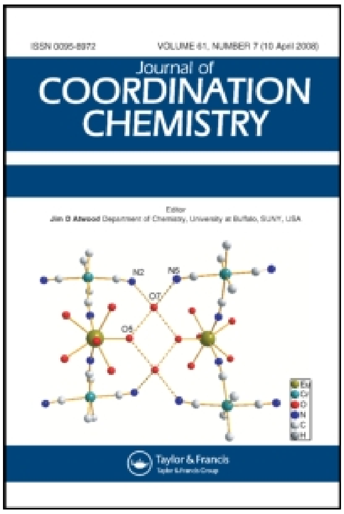

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Preparation and characterization of a metal-organic three-dimensional framework based on isonicotinate [Pb(INA)$_2$] (INA = isonicotinate, NC$_5$H$_4$-4-)

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Preparation and characterization of a metal-organic three-dimensional framework based on isonicotinate $[Pb(INA)_2]$ (INA = isonicotinate, NC_5H_4-4-CO_2^-)

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The coordination compound $[Pb(INA)_2]$ (INA = isonicotinate, NC_5H_4-4-CO_2^-) has been synthesized and characterized by elemental analysis, FT-IR spectra and thermogravimetric analysis. Its structure was confirmed by X-ray crystallography. The single-crystal X-ray data of this compound show a three-dimensional wave-like metal-organic framework as a result of INA ligand bridging. The lead atom has an unsymmetrical eight-coordinate geometry, coordinated by two nitrogen atoms and six oxygen atoms from the INA ligand. The arrangement of the INA ligands exhibits a coordination gap around the Pb atom occupied possibly by a stereoactive lone pair of electrons on lead(II), with the coordination around lead atoms being hemidirected. There are π-π stacking interactions between adjacent parallel INA ligands which act as a pillar that increases the gap in the coordination geometry around Pb(II). Photoluminescence properties of the compound have been examined in the solid state at room temperature. The compound has photoluminescence with maximum emission located in the UV region.

Keywords: Crystal structure; Metal-organic framework; Coordination gap; Photoluminescence

1. Introduction

Extensive studies have been carried out on the synthesis and design of functional coordination polymers because of their diverse structural properties and potential applications in catalysis, ion exchange, proton conductivity and materials chemistry [1–14]. Coordination chemistry of lead(II) with N and O donor ligands has been investigated with regard to the stereoactivity of the valence shell lone electron pair, besides examining the potential to extract harmful metals from the environment [15–20]. Since a lone pair is not directly detected but inferred on the basis of the spatial distribution of donor atoms surrounding the metal, it is not a straightforward process.

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Crystal packing may affect the size and extent of the lone-pair in the coordination sphere. Building new molecular species and modifying their architectures to control physical properties has been a topic for many research groups. A number of lead(II) carboxylate-bridged complexes with layered or three-dimensional network structures have been reported [21–25]. Three porous coordination polymers based on lead(II) and isonicotinic acid N-oxide, $[Pb(INO)_2] \cdot 7H_2O$ (**1**), $[Pb(INO)_2] \cdot nH_2O$ (**2**), and $[Pb_4(OH)_4(INO)_4] \cdot nH_2O$ (**3**) (HINO = isonicotinic acid *N*-oxide), have been reported. Compound **1** features a remarkable 3D framework with two distinct kinds of channels, while **2** possesses a 3D framework with 1D rectangular channels. Compound **3** consists of $[Pb_4(OH)_4]^{4+}$ cluster inorganic building blocks, which connect with μ_4-INO ligands to form rhombic channels [26]. The INA ligand is a suitable candidate for assembling complexes with novel structures and properties, but coordination polymers with INA ligand have not been extensively studied [27–29]. The reported complexes based on the INA ligand, $[Co(INA)_2] \cdot 0.5EtOH$, $[Mn(INA)_2] \cdot 0.5EtOH \cdot 0.5H_2O$ and $[Fe(INA)_2]$, have identical three-dimensional framework structures [28].

In the present article, we report the synthesis, characterization and crystal structure of a new metal-organic three-dimensional wave-like framework $[Pb(INA)_2]$, in which the lead atom is eight-coordinate and hemidirected. To the best of our knowledge, the title complex is the first three-dimensional wave-like framework constructed from the INA ligand, in which the carboxylate group of INA ligand exhibits chelating/bridging bidentate mode instead of the usual bidentate and monodentate modes [27–29]. Photoluminescence properties of the compound have been examined in the solid state at room temperature.

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2. Experimental

2.1. *Materials and characterization*

All reagents were used as purchased. The volume ratio of the mixed solvent is $CH_3OH : H_2O : DMF = 1 : 1 : 1$. Elemental analyses (C, H and N) were carried out on a 240 C Elemental analyzer. Infrared spectrum (400–4000 cm^{-1}) was recorded from KBr pellet on a Magna 750 FT-IR spectrophotometer. The solid state emission spectrum was recorded using a 48000DSCF fluorescence spectrometer.

2.2. *Synthesis*

To a solution of nicotinamide (0.073 g, 0.6 mmol) in $CH_3OH : H_2O : DMF$ (4.0 mL) was added a solution of $Pb(NO_3)_2$ (0.199 g, 0.6 mmol) in $CH_3OH : H_2O : DMF$ (6.0 mL) and stirred. A solution of NaOH ($1.0 \, mol \cdot L^{-1}$, 1.2 mL) was added to a solution of isonicotinate (0.148 g, 1.2 mmol) in $CH_3OH : H_2O : DMF$ (8.0 mL); after the reaction mixture was stirred continuously for several minutes, the former reaction mixture was added. The mixture was filtered. The filtrate was kept for several days at ambient temperature and white crystals formed. The pH before and after the synthesis is about 5.5 and 6.5, respectively. The crystals were collected by filtration, washed thoroughly with a minimum amount of water and dried under vacuum (yield: 21.7% based on isonicotinate ligand). Anal. Calcd for $C_{12}H_8N_2O_4Pb$: C, 31.91; H, 1.53; N, 6.21. Found: C, 31.73; H, 1.58; N, 5.98%.

2.3. *X-ray crystallography*

A colorless crystal having approximate dimensions 0.58 × 0.28 × 0.06 mm was used for data collection. Diffraction data were collected at 293(2) K with a Siemens SMART CCD diffractometer using graphite-monochromated (Mo-Kα) radiation ($\lambda = 0.71073$ Å), ψ and ω scan mode. There were 11661 reflections collected and cell constants were determined from the full-matrix least-squares fit of 7761 reflections with θ in the range 2.37 and 25.02°. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 to $R_1 = 0.0450$ ($wR_2 = 0.1112$) for 2152 reflections $[I > 2\sigma()]$ collected in the range $2.37° \le \theta \le 25.02°$. Intensity data were corrected for Lorenz and polarization effects and an empirical absorption correction was performed. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were added geometrically and allowed to ride on their respective parent atoms. The contribution of these hydrogen atoms was included in the structure factor calculations. In the final difference map, the residual maxima and minima were 1.803 and -2.218 eÅ^{-3}, respectively. The goodness of fit on F^2 is 1.235. All calculations were carried out on a PC computer using SHELXL-97 [30]. Details of crystal data, collection and refinement are listed in table 1.

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Table 1. Crystallographic data and structure refinement for the title complex.

Empirical formula	$C_{12}H_8N_2O_4Pb$
Formula weight	451.39
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Orthorhombic
Space group	*Pbcn*
a (Å)	16.6078(2)
b (Å)	10.0415(2)
c (Å)	14.6671(3)
α (°)	90
β (°)	90
γ (°)	90
V (Å^3)	2445.99(8)
Z	8
Calculated density Mg m^{-3}	2.452
$F(000)$	1664
Theta range for data collection (°)	2.37 to 25.02
Limiting indices	$-19 \le h \le 13$, $-11 \le k \le 11$, $-17 \le l \le 17$
Reflections collected/unique	11661/2152 [R(int) = 0.0877]
Completeness to $\theta = 25.02°$	100%
Absorption correction	Empirical
Max. and min. transmission	1.0000 and 0.3893
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	2152/0/172
Goodness-of-fit on F^2	1.235
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0450$, $wR_2 = 0.1074$
R indices (all data)	$R_1 = 0.0511$, $wR_2 = 0.1112$
Largest diff. peak and hole (e Å^{-3})	1.803 and -2.218

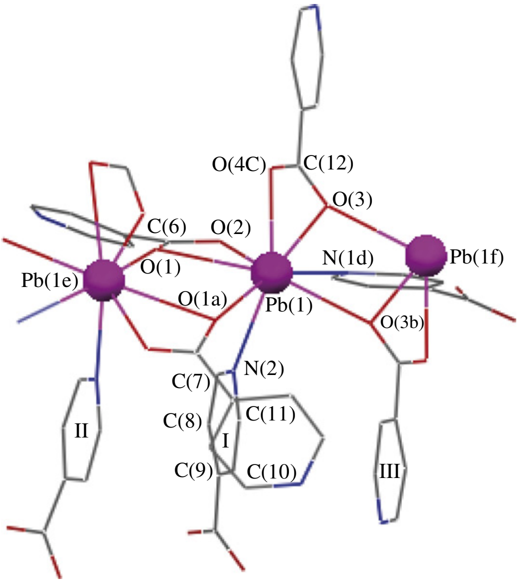

Figure 1. View of the environment of the lead atom, showing the π-π stacking interaction between the adjacent parallel N(2)C(7)C(8)C(9)C(10)C(11) ring planes (I, II, III) and two different Pb2O2 rings. (Only part of the polymer was shown for clarity.) Symmetry code of a: $1-x$, y, $1/2-z$; b: $1-x$, $1-y$, $1-z$; c: x, $y-1$, z; d: $-x$, y, $1/2-z$; e: x, $-y$, $1/2+z$; f: $1/2-x$, $1/2+y$, z). (Scheme: Pb, purple; O, red; C, grey; N, blue.)

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3. Results and discussion

3.1. *Preparation*

The reaction between stoichiometric amounts of isonicotinate acid and mixture of lead(II) nitrate with the appropriate *N*-donor nicotiamide in the presence of NaOH provided a colorless metal-organic framework analyzed as [Pb(INA)$_2$]. Single crystals suitable for X-ray analysis were grown from concentrated solutions by slow solvent evaporation. The complex is stable in air. Nicotiamide is important for the quality of the crystals. Although it does not appear in the complex, omission leads to formation of polycrystals instead of single crystals.

3.2. *Structural description*

The single-crystal X-ray analysis reveals that the lead is coordinated by six oxygen atoms and two nitrogen atoms of INA ligands and exhibits eight-coordinate geometry, as shown in figure 1. Selected bond distances and angles are listed in table 2. The carboxylate group in the INA ligand is chelating/bridging bidentate while it exhibits bidentate coordination in reported complexes containing INA [27, 28]. The complex consists of two kinds of Pb2O2 rings. The dihedral angle between the two Pb2O2 rings is 81.1(1)°. The Pb(1)Pb(1e)O(1)O(1a) ring which shares an edge with Pb(1)O(1)O(2)C(6) quadrilateral is not the same as the Pb(1)Pb(1f)O(3)O(3b) ring

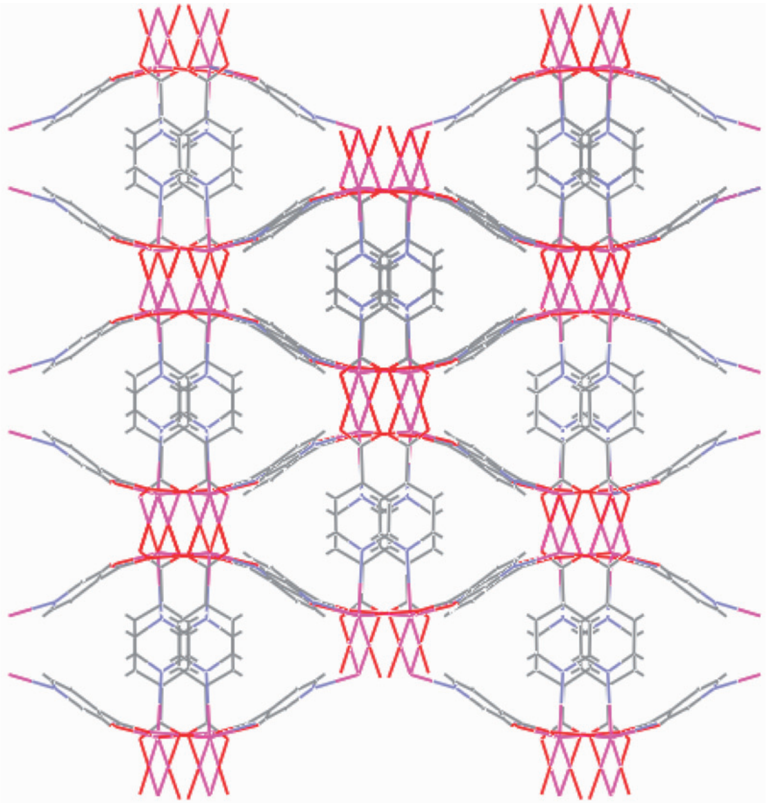

Figure 2. View of the three-dimensional wave-like framework along the *c* direction.

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which shares an edge with the Pb(1)O(3)O(4c)C(12) quadrilateral. The long edge of the Pb(1)Pb(1e)O(1)O(1a) ring [2.826(4) Å] is considerably shorter than that in the Pb(1)Pb(1f)O(3)O(3b) ring [2.847(6) Å]. Furthermore, the Pb(1)...Pb(1e) distance is 4.478(4) Å, shorter than the Pb(1)...Pb(1f) distance [4.684(2) Å].

The three-dimensional metal-organic wave-like framework was formed as a result of INA ligand bridging, as shown in figure 2. In this framework INA ligands [N(2)C(7)C(8)C(9)C(10)C(11) ring] parallel with each other and act as a pillar, while the other INA ligand is the wave edge. The centroid-centroid distance and the dihedral angle are 3.818(4) Å and 7.6(1)°, respectively, for the adjacent pyridyl rings (I) and (II), while those for the adjacent pyridyl rings (I) and (III) is 4.429(2) Å and 0°, respectively, as shown in figure 1. So, there are π-π stacking interactions between the adjacent parallel N(2)C(7)C(8)C(9)C(10)C(11) rings, but not between the adjacent parallel N(1)C(1)C(2)C(3)C(4)C(5) rings (the centroid-centroid distance: 10.041(4) Å), as shown in figure 3. The arrangement of the ligands suggest a gap or hole in the coordination geometry around the metal ion [O(4c)–Pb(1)–N(2): 155.1(3)°], occupied possibly by a stereoactive lone pair of electrons on lead(II). The observed shortening of the Pb(1)–O(2) [2.447(6) Å] bonds on the side of the Pb(II) ion opposite to the putative lone pair compared with those adjacent to the lone pair supports the presence of this feature [31].

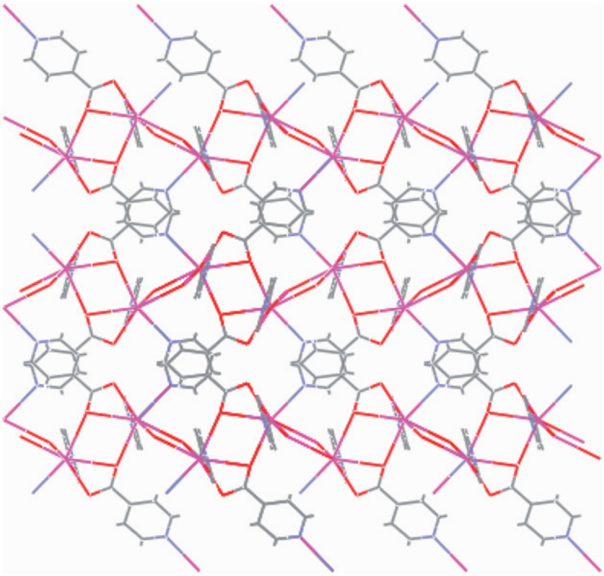

Figure 3. View of the three-dimensional network along the *b* direction, showing the N(1)C(1)C(2)C(3)C(4)C(5) rings parallel with each other.

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3.3. *FT-IR spectra*

The value of $\Delta\nu(\mathrm{COO}) = \nu_{as}(\mathrm{COO})–\nu_s(\mathrm{COO})$, which is commonly used in determining the coordination mode of carboxylate group, usually follows the order $\Delta\nu_{\mathrm{monodentate}} > \Delta\nu_{\mathrm{ionic}} > \Delta\nu_{\mathrm{chelate}}$ [32]. The FT-IR spectra (*Supplementary* Figure) of the title compound show characteristic bands of carboxylate groups as a chelating/bridging bidentate ligand at 1580 cm^{-1} for the asymmetric stretch and at 1386 cm^{-1} for the symmetric stretch [33]. The band at 3066 cm^{-1} may be attributed to stretching vibrations of C–H in the pyridyl rings.

3.4. *Thermogravimetric analysis*

Thermal behavior of the title coordination compound has been deduced from the TG curve in N_2 (figure 4). The thermogravimetric analyses of the title complex indicated a sharp weight loss followed by a long tail with a total weight loss of 48.69% in the temperature range 92–800°C, which is in agreement with the weight loss calculated for the loss of INA ligands leading to the formation of Pb_2O_3 as final residuals above 800°C (Calcd: 48.78%).

3.5. *Photoluminescence properties*

The solid-state photoluminescence spectra of the free H_2INA acid and the title complex upon excitation at 228 nm have been measured at room temperature. The maximum emission occurs at 345 nm for H_2INA. The maximum emission for the title complex

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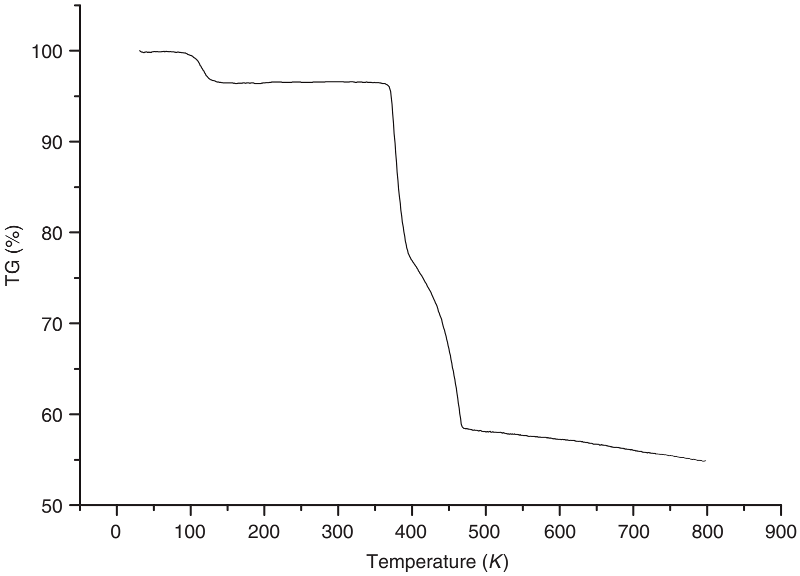

Figure 4. TG curve of the title complex.

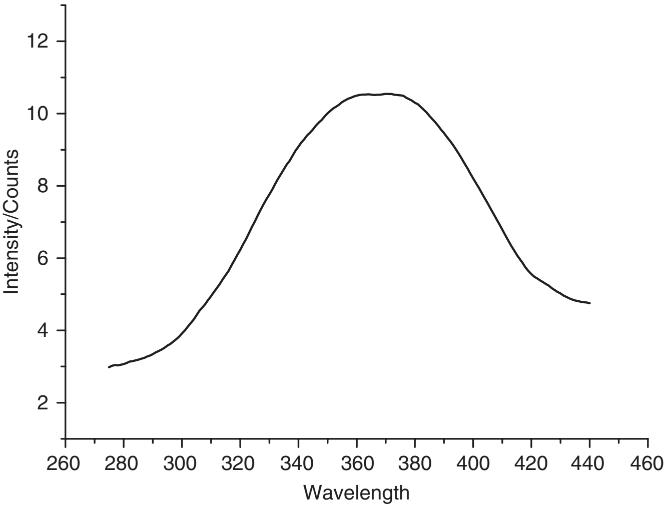

Figure 5. The emission spectra of the title complex in the solid state at room temperature. The corresponding excitation wavelength (λ_{ex}) is 228 nm.

is at 357 nm corresponding to the $S_0 \rightarrow S_1$ absorption, which is red-shifted about 12 nm compared to free H_2INA (figure 5). Apparently, this strong fluorescence emission arises from the Pb^{2+} lone pair to ligand charge transfer [34], and the red-shift may be due to the coordination or an excited state of a metal-perturbing intraligand transition [35].

Table 2. Selected bond distances (Å) and angles (°) for the title complex.

Pb(1)–O(2)	2.447(6)
Pb(1)–O(4c)	2.536(7)
Pb(1)–N(2)	2.737(9)
Pb(1)–N(1d)	2.710(8)
Pb(1)–O(1a)	2.791(6)
Pb(1)–O(3b)	2.798(7)
Pb(1)–O(3)	2.847(7)
Pb(1)–O(1)	2.826(7)
O(2)–Pb(1)–O(4c)	80.7(2)
O(1a)–Pb(1)–O(3b)	87.7(2)
O(2)–Pb(1)–N(1d)	74.7(2)
O(4c)–Pb(1)–N(2)	155.1(3)
O(4c)–Pb(1)–N(1d)	97.9(3)
O(4c)–Pb(1)–O(1a)	104.6(3)
O(2)–Pb(1)–N(2)	76.4(3)
N(1d)–Pb(1)–O(1a)	154.3(2)
N(2)–Pb(1)–O(1a)	79.6(3)
O(2)–Pb(1)–O(3b)	146.0(2)
N(1d)–Pb(1)–N(2)	85.3(3)
O(4c)–Pb(1)–O(3b)	111.5(2)
N(1d)–Pb(1)–O(3b)	72.3(2)
O(2)–Pb(1)–O(1a)	120.89(19)
N(2)–Pb(1)–O(3b)	93.0(8)

Symmetry transformations used to generate equivalent atoms:
a: $-x+1$, y, $-z+1/2$; b: $-x+1$, $-y+1$, $-z+1$; c: x, $y-1$, z; d: $-x+1/2$, $-y+1/2$, $z+1/2$.

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Supplementary data

Complete listings of bond distances and angles, hydrogen atom coordinates and isotropic displacement parameters, anisotropic displacement parameters and least-squares plans are available either quoting the deposition number CCDC – 280428 (12 Union Road, Cambridge, CB2 1EZ, UK) or from the authors on request.

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