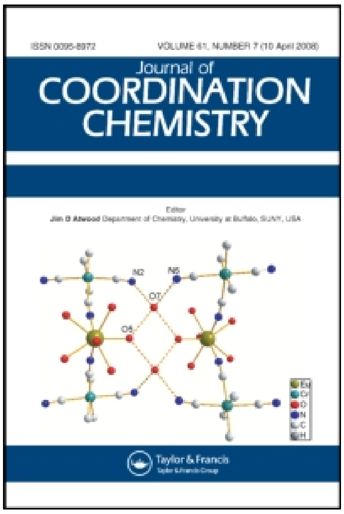

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Hydrothermal synthesis and structural characterization of a zigzag-chain polymer of {[<i>p</i>-MeBzlPh$_3$P][ZnCl$_2$(NA)]}$_{\text{<b><i>n</i>}}$ (NA = nicotinic acid)

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Hydrothermal synthesis and structural characterization of a zigzag-chain polymer of $\{[p\text{-MeBzlPh}_3\text{P}][\text{ZnCl}_2(\text{NA})]\}_n$ (NA = nicotinic acid)

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A metal-organic coordination polymer, $\{[p\text{-MeBzlPh}_3\text{P}][\text{ZnCl}_2(\text{NA})]\}_n$ (**1**) (NA = nicotinic acid), has been hydrothermally synthesized and characterized by IR, UV-Vis, TG analysis, elemental analysis, fluorescence analysis and single crystal X-ray diffraction. Compound **1** crystallizes in the monoclinic system, space group $P2_1/c$, $a = 10.1049(3)$ Å, $b = 25.3888(6)$ Å, $c = 14.7244(3)$ Å, $\beta = 129.2740(10)°$, $V = 2924.31(13)$ Å^3, $Z = 4$, $R_1 = 0.0639$, $wR_2 = 0.1695$ and $S = 1.133$. The structure of **1** has a one-dimensional structure with $[p\text{-MeBzlPh}_3\text{P}]^+$ counter-cations alternately residing on both sides of the one-dimensional anionic chains of the zigzag-chain polymer. Compound **1** exhibits strong fluorescence in solid state at room temperature.

Keywords: Zinc(II) complexes; Nicotinic acid; One-dimensional structure; Zigzag-chain polymer; Fluorescent property

1. Introduction

Design and synthesis of supramolecular architectures based on metal-organic frameworks continues to receive attention because of aesthetically pleasing structures and spin-crossover behavior, magnetic, optical, dielectric, and anticorrosive properties [1–5]. Supramolecular compounds with interesting structures have been synthesized and characterized, such as the 1-D chains (heliced, zigzag, etc.) [6], 2-D layers (honeycomb, square, etc.) [7], and 3-D open frameworks [8]. However, it is difficult to predict the occurrence of structures, since a variety of factors can influence the self-assembly process. Additionally, H-bonding, π–π stacking, and van der Waals interactions play important roles in formation of noncovalent supramolecular frameworks. Attempts to obtain products with desired dimensionality have been focused on judicious selection of multidentate ligands, correct templates and metal ions with the appropriate ligands.

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Organic phosphonium salts have been used as templates for generating novel coordination compounds. Newcomb *et al.* [9] prepared $[Ph_3BzlP][Sn_2Cl_2(C_8H_{16})_3 \cdot Cl]$ with a cavity; M. P. García *et al.* [10] synthesized a series of the rhodium complexes with $[Ph_3BzlP]^+$ and Dai *et al.* [11] obtained a ribbon-candy-like supramolecular polymer $\{[Ph_3PCH_2Ph][Cd(tp)Cl]2H_2O\}_n$. We have attempted to employ 4-methylbenzyltriphenylphosphonium chloride, $[p\text{-MeBzlPh}_3P]Cl$, as a template to construct metal-organic frameworks. Herein, we report the synthesis and solid state crystal structure of $\{[p\text{-MeBzlPh}_3P][ZnCl_2(NA)]\}_n$ (**1**), which resulted from the template reaction of $[p\text{-MeBzlPh}_3P]Cl$ with $Zn(CH_3CO_2)_2 \cdot 2H_2O$ and nicotinic acid. Compound **1** features a one-dimensional polymeric structure and the $[p\text{-MeBzlPh}_3P]^+$ counter-cations alternately reside on both sides of the one-dimensional anionic coordination polymeric chains to yield a zigzag-chain polymer.

2. Experimental section

2.1. *Physical measurements*

All chemicals purchased were of reagent grade and used without further purification. Elemental analysis (C, H and N) was performed using a Perkin-Elmer 2400 CHNS/O analyzer. The infrared spectrum in KBr pellets in the range 4000–400 cm^{-1} was recorded using a Shimadzu FTIR-8900 spectrophotometer. UV-Vis analysis was performed using a Perkin-Elmer Lambda35 analyzer. The fluorescent analysis was performed using a Hitachi F4500 analyzer. The combined measurement on thermogravimetric and differential thermal analysis (TG/DTA) was carried out in the range 25–800°C on powdered samples in nitrogen stream using a Perkin-Elmer TGS-2 analyzer with a heating rate of 20°C min^{-1}.

2.2. *Synthesis*

2.2.1. Preparation of phosphonium salt [*p*-MeBzlPh₃P]Cl. The phosphonium salt was prepared according to the reported method [12]. The 4-methylbenzylchloride (0.01 mol) and triphenylphosphine (0.01 mol) were added to dry chloroform (30 mL). The resulting mixture was stirred under reflux for 4 h. After the mixture cooled, diethyl ether (20 mL) was added and the precipitates were collected by filtration, washed with ether, and dried *in vacuo*. The product was used for the next reaction without recrystallization. Yield: 86.3%. IR (KBr, pellet, cm^{-1}): 3039(m), 2884(s), 1514(m), 1438(s), 1110(s), 824(s), 738(s), 718(s), 499(s). ^1H NMR ($CDCl_3$, δ, ppm): 2.53 (s, 3H, $-CH_3$), 5.40 (s, 2H, $-CH_2-$), 6.92∼6.95 (m, 4H, Ar), 7.63∼7.77 (m, 15H, three Ph).

2.2.2. Preparation of 1. A mixture of $Zn(CH_3CO_2)_2 \cdot 2H_2O$ (0.1100 g, 5.0 mmol), nicotinic acid (0.0620 g, 5.0 mmol), $[p\text{-MeBzlPh}_3P]Cl$ (0.2040 g, 5.0 mmol) and water (12 mL) was added to a 20 mL Teflon reactor and kept at 160°C for 72 h under autogenous pressure, then cooled to room temperature at a rate of 10°C h^{-1}; colorless crystals were obtained in yield of 45.7% based on the initial zinc salt. Anal. Calcd for $C_{32}H_{28}Cl_2NO_2PZn$ (**1**) (%): C, 61.34; H, 4.47; N, 2.24; Found: C, 61.32; H, 4.42; N, 2.21.

2.3. *X-ray crystallography*

A colorless single crystal of **1** with dimensions $0.520 \times 0.280 \times 0.180\,\mathrm{mm}^3$ was glued on a glass fiber. Data were collected on a Bruker Smart Apex II CCD diffractometer at 298(2) K using graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). Absorption corrections were applied using the SADABS program [13]. The structure was solved using SHELXL-97 [14, 15] by weight atoms methods and refined by full-matrix least-squares on F^2. Hydrogen atoms were included in calculated positions and refined in the riding mode. Anisotropic thermal parameters were used to refine all non-hydrogen atoms. Further details of the X-ray structural analysis are given in table 1. Selected bond lengths and angles are listed in table 2. Crystal data are available in supplementary crystallographic data.

3. Results and discussion

3.1. *Crystal structure of 1*

Compound **1** consists of $[p\text{-MeBzlPh}_3\text{P}]^+$ cation complexes and $[\text{ZnCl}_2(\text{NA})]^-$ polymeric anion chains. The P atom in $[p\text{-MeBzlPh}_3\text{P}]^+$ bonds to four C atoms (C7, C13, C19 and C25), whose P–C bond lengths are in the range 1.789(4)–1.815(4) Å, with average length 1.798(5) Å, longer than that of complex $[(\text{C}_2\text{B}_9\text{H}_{11})\text{In}(\text{SCH}_2\text{CH}_2\text{S})]_2 \cdot (\text{PPh}_3\text{-}p\text{-xylyl-PPh}_3)$ $(4 \cdot (\text{PPh}_3\text{-}p\text{-xylyl-PPh}_3))$ [16] and slightly shorter than that of complex $[\text{C}_7\text{H}_7(\text{C}_6\text{H}_5)_3\text{P}]_2 \cdot [(\text{S}_2\text{CC}(\text{COOC}_2\text{H}_5)_2)_3\text{Fe}]$ [17]. The phosphorus is a

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

Empirical formula	$\text{C}_{32}\text{H}_{28}\text{Cl}_2\text{NO}_2\text{PZn}$
Formula weight	625.79
Temperature (K)	298(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2_1/c$
a (Å, °)	10.1049(3)
b (Å, °)	25.3888(6)
c (Å, °)	14.7244(3)
α (Å, °)	90.00
β (Å, °)	129.2740(10)
γ (Å, °)	90.00
V (Å^3)	2924.31(13)
Z	4
D_{Calcd} (mg m^{-3})	1.421
Absorption coefficient (mm^{-1})	1.107
F(000)	1288
Crystal size (mm^3)	$0.520 \times 0.280 \times 0.180$
θ range (°)	1.96–27.92
Limiting indices	$-13 \le h \le 13$, $-27 \le k \le 33$, $-19 \le l \le 18$
Reflections collected	6884
Independent reflections	5266
Max. and min. transmission	0.823, 0.694
Data/restraints/parameters	6884/0/352
Goodness-of-fit on F^2	1.133
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0639$, $wR_2 = 0.1695$
R indices (all data)	$R_1 = 0.0814$, $wR_2 = 0.1775$
Largest diff. peak and hole (e Å^{-3})	1.003 and -0.588

Table 2. Selected bond lengths (Å) and angles (°) for **1**.

Zn(1)–O(1)	1.989(3)	Zn(1)–N(1)	2.098(4)
Zn(1)–Cl(2)	2.2447(14)	Zn(1)–Cl(1)	2.2521(16)
P(1)–C(7)	1.789(4)	P(1)–C(19)	1.790(5)
P(1)–C(13)	1.796(5)	P(1)–C(25)	1.815(4)
O(1)–Zn(1)–N(1)	101.85(15)	O(1)–Zn(1)–Cl(2)	115.79(14)
N(1)–Zn(1)–Cl(2)	100.96(12)	O(1)–Zn(1)–Cl(1)	117.94(15)
N(1)–Zn(1)–Cl(1)	101.77(13)	Cl(2)–Zn(1)–Cl(1)	114.59(6)
C(7)–P(1)–C(19)	109.4(2)	C(7)–P(1)–C(13)	109.3(2)
C(19)–P(1)–C(13)	108.9(2)	C(7)–P(1)–C(25)	109.1(2)
C(19)–P(1)–C(25)	109.2(2)	C(13)–P(1)–C(25)	110.9(2)
C(27)–C(26)–C(25)	119.5(4)	C(31)–C(26)–C(25)	121.8(4)
C(28)–C(29)–C(32)	120.8(5)	C(30)–C(29)–C(32)	121.3(5)

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

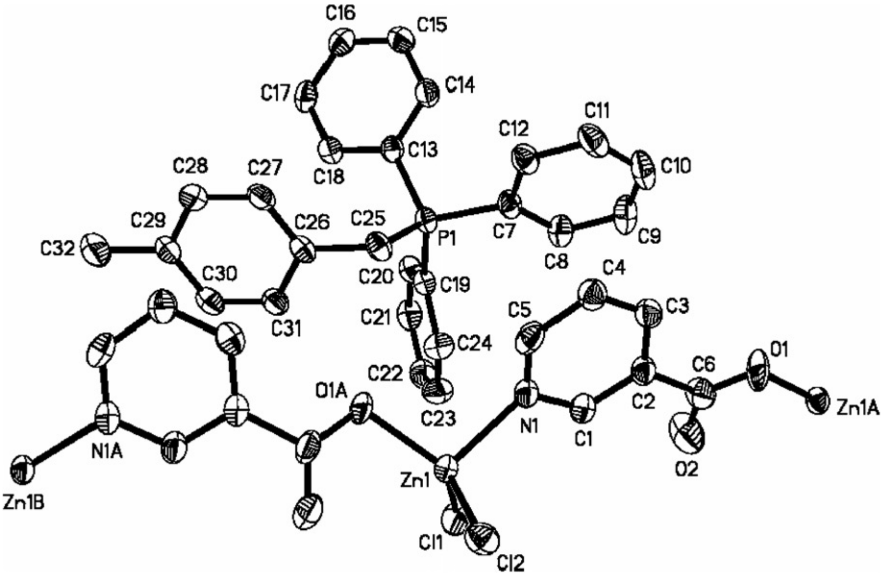

Figure 1. Perspective view of the coordination environment of zinc in **1**. Displacement ellipsoids are drawn at the 30% probability level; hydrogen atoms are omitted for clarity.

slightly distorted tetrahedral geometry, in which the ∠C–P–C bond angles range from 108.9(2) to 110.9(2)°; other parameters in the cation are as expected [18, 19].

Each Zn^{2+} is tetrahedrally coordinated by two Cl^-, a nitrogen from one NA ligand and an oxygen atom from another NA ligand. That is, end of the nitrogen atom of NA connects with one Zn^{2+} and the end of the oxygen atom of NA connects with another Zn^{2+}. Therefore the tetrahedrally coordinated Zn^{2+} atoms are linked by the bidentate bridged NA into one-dimensional chains along the [100] direction. The Zn(1)–Cl(1) bond distance (2.2521(16) Å) is slightly longer than the Zn(1)–Cl(2) bond distance (2.2447(14) Å), and the average ZnCl bond length (2.2484(15) Å) is longer than that in $[ZnC1_2(4\text{-CN-py})_2]$ [20] and shorter than that in $[ZnCl_2(bppz)(dmf)]$ [21]. The Zn–N (2.098(4) Å) and Zn–O(9) (1.989(3) Å) bond lengths are comparable to those in a corresponding complex [22]. The bond angles (table 2) for zinc are in the range

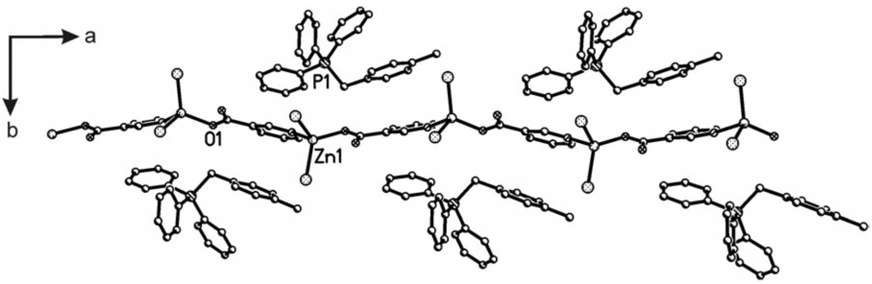

Figure 2. View of the one-dimensional layer of **1**.

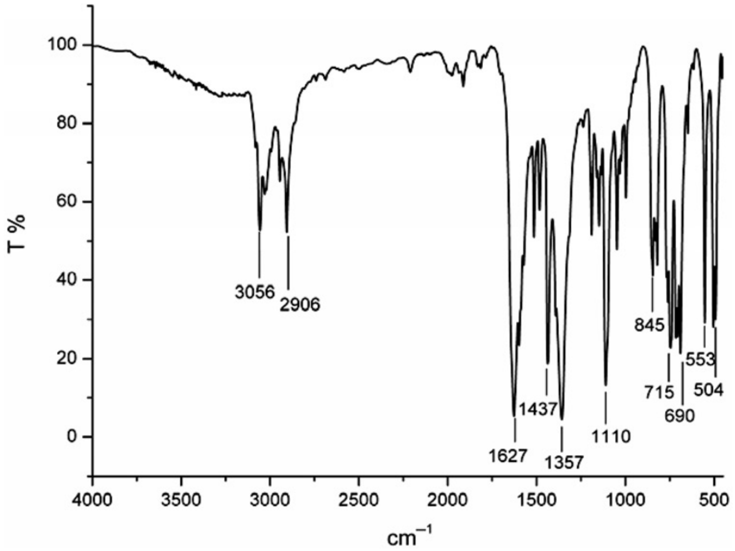

Figure 3. The IR spectrum of **1** at room temperature.

100.96(12)–117.94(15)°, which are within the allowable range [23] for distorted tetrahedron conformations. The $[p\text{-MeBzlPh}_3\text{P}]^+$ counter-cations alternately reside on both sides of the one-dimensional anionic chains to yield the zigzag-chain polymer (figure 2).

3.2. *IR spectroscopy of 1*

Figure 3 shows the IR spectrum of **1**. The absorption peak at $1626\,\text{cm}^{-1}$ should be assigned to $\nu_{\text{as}}(\text{CO}_2^-)$ of carboxylate groups of NA ligands and the absorption peaks centered at $1357\,\text{cm}^{-1}$ should be assigned to $\nu_{\text{s}}(\text{CO}_2^-)$. Comparison to the bands of free nicotinic acid molecules, both the significant red-shift of $\nu_{\text{as}}(\text{CO}_2^-)$ of **1** may be attributed to coordination. The unsaturated $\nu_{=\text{C–H}}$ and saturated $\nu_{-\text{C–H}}$ stretching vibration peaks reside at 3054 and $2905\,\text{cm}^{-1}$, respectively. The characteristic peaks of P–C are at $745{\sim}689\,\text{cm}^{-1}$ [24].

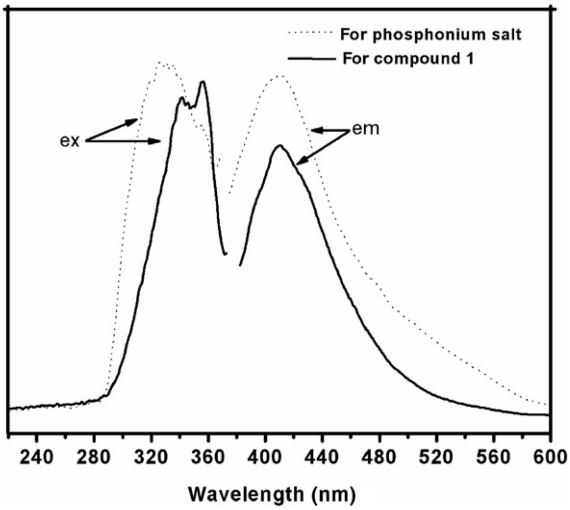

Figure 4. Fluorescent spectra of **1** in solid state at room temperature.

3.3. *UV-Vis spectroscopy and fluorescence spectrum of 1*

The peak centered at 270 nm can be attributed to the benzene ring and the pyridine ring $\pi \rightarrow \pi^*$ transitions. A $2.05 \times 10^{-4}\,\mathrm{mol\,L^{-1}}$ aqueous solution has $\varepsilon^{270} = 3.00 \times 10^3\,\mathrm{M^{-1}\,cm^{-1}}$.

The solid-state fluorescence spectra of [*p*-MeBzlPh$_3$P]Cl and **1** in solid state at room temperature are depicted in figure 4. Comparing the intensity of **1** and organic phosphonium salt, it is obvious that the intensity of fluorescent emission in **1** is weaker than in the organic phosphonium salt. Because there are many excited states [25] from which the electron comes back to ground state, it perhaps produces nonradiative transitions for the energy decay. The organic phosphonium salt and **1** display strong fluorescent emission peaks at ca 388 and 389 nm upon excitation at 324 and 341 nm, respectively. In contrast, $[\mathrm{Zn(NA)_2(H_2O)_4}]_n$ displays two strong fluorescent emission peaks at 382 and 400 nm when excited at 340 nm [25]. Therefore, the fluorescence peak shape of **1** may result from the large cation [*p*-MeBzlPh$_3$P]$^+$ which has a strong impact on the morphology of the crystal [11].

3.4. *Thermal analysis*

The TGA curve of **1** exhibits only one well-separated weight loss in the temperature range 364–595°C (87.6%), corresponding to the release of ligands, NA, Cl$^-$ anions and [*p*-MeBzlPh$_3$P]$^+$ groups (Calcd 87.0%). The remaining weight of 12.4% corresponds to the percentage (Calcd 13.0%) of Zn and O components, indicating that the final product is ZnO.

4. Conclusions

In summary, we have synthesized and characterized a zinc(II) polymer by template reaction of the [*p*-MeBzlPh$_3$P]Cl salt with the mixture of $\mathrm{Zn(CH_3CO_2)_2 \cdot 2H_2O}$

and nicotinic acid. Compound **1** has a one-dimensional structure and the $[p\text{-MeBzlPh}_3\text{P}]^+$ counter-cations reside alternately on both sides of the one-dimensional anionic chains of the zigzag-chain polymer. This work shows that structure-directing effects of the template reagent may affect assembly architecture.

Supplementary material

Crystallographic data for structural analysis have been deposited with the Cambridge Crystallographic Data Center with the deposited numbers CCDC 628557. Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; Email: deposit@ccdc.cam. ac.uk).

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