



Crystal growth and characterization studies of novel luminescent 2D coordination polymer of lead-benzilate possessing edge sharing PbO_6 polyhedra



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ABSTRACT

Single crystals of a new coordination polymer of lead-benzilate, $\text{C}_{28}\text{H}_{21}\text{O}_6\text{Pb}\cdot\text{C}_2\text{H}_5\text{OH}$ have been successfully grown by gel diffusion technique at room temperature. The colourless single crystals were obtained within a week. The crystal structure was elucidated using single crystal X-ray diffraction studies. The compound possesses a polymeric structure constructed from edge sharing PbO_6 polyhedra. Single crystal X-ray diffraction analysis showed that the compound crystallizes in triclinic space group $P\bar{1}$. The grown crystals were further characterized by elemental analysis, FT-IR, UV–Visible and thermogravimetric analysis. The photoluminescent properties of the complex and the ligand were also investigated.

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1. Introduction

The coordination polymers are constructed by the combination of metal ion centers with polytopic ligands. Coordination polymers exhibit intriguing network topologies and considerable applications in the field of molecular magnets, luminescence and optoelectronic devices [1–5]. The diverse structural features of coordination polymers possess wide range of applications in the field of gas storage, gas separation, catalysis, nanoparticle precursors and luminescence [6–8].

The aromatic polycarboxylic acids owing to their structural features and bridging abilities exhibit increasing interest in crystal engineering. The α -hydroxy carboxylates are widely used in iron and vanadium metabolism, pharmaceuticals and also serve as terminal chelators and bridging ligand in chemical reactions [9–12]. Benzilic acid or hydroxy diphenylacetic acid,

$[(\text{C}_6\text{H}_5)_2\text{C}(\text{OH})(\text{COOH})]$, is a very good complexing agent for the formulation of synergic corrosion inhibitors [13]. Lead is a heavy toxic metal and possesses unique coordination versatalities with ligands. It shows applications in the field of roofing, batteries and solder. Metal complexes of benzoic acid are extensively studied due to their importance in biological processes [14,15].

Herein we report a new coordination polymer of lead-benzilate system by gel diffusion technique. To the best of our knowledge this is the first report of the title compound. Single crystal X-ray diffraction studies reveal the crystal structure. The PbO_6 polyhedrons are connected by benzilate ligand to form the polymeric structure. The grown crystals were further characterized by elemental analysis, FT-IR, thermogravimetry and UV–Visible spectral studies. The luminescent property of the complex and the ligand were also discussed.

2. Experimental procedure

2.1. Growth procedure

Single gel diffusion technique was employed for the

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crystallization of the title compound [16]. AR grade sodium metasilicate obtained from CDH was used for gel preparation. Sodium metasilicate solution was prepared by using distilled water and the density of the solution was measured by using hydrometer. The crystals were grown in simple glass tubes of length 20 cm and 2.5 cm of diameter. The gel was prepared by dissolving the benzoic acid solution in ethanol of desired molarity (0.25–1 M) drop by drop to sodium metasilicate solution (1.03–1.05 g cm⁻³). The pH of the gel was adjusted by using glacial acetic acid in the pH range of 5–7.5. The gel solution was transferred to several test tubes for setting. After setting the gel, the lead acetate solution of desired molarity (0.25–1 M) was added as top solution carefully along the sides of the test tube without disturbing the gel surface. The test tubes are then covered with transparent plastic sheet to avoid contamination and evaporation of solution.

2.2. Characterization

The FTIR Spectra were recorded in a range 4000–400 cm⁻¹ using Thermo Nicolet, Avatar 370 Spectrometer in KBr pellets. The composition of carbon, hydrogen in the compound was determined by using Elementar Vario-EL 111 CHN analyzer. The UV–Visible spectral studies were carried out using Varian Cary 5000 UV–Vis-NIR spectrometer in the range 200–1200 nm. The thermogravimetric analysis of the grown crystals was carried out on a Perkin Elmer Diamond TG/DTG analyzer instrument with a heating rate of 10 °C/min in nitrogen atmosphere. The photoluminescence of the samples are recorded using Fluoromax-3 spectrofluorometer consisting of 150 W Xenon arc lamp, monochromator and a detector.

Single crystal X-ray diffraction studies of the complex were collected using Bruker AXS Kappa Apex2 CCD diffractometer, with graphite monochromated Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$). The unit cell dimensions and intensity data were recorded at 296 K. The structures were solved by direct methods using SIR92 and refinement were carried out by full-matrix least squares on F² using SHELXL-97 [17,18]. All the non-hydrogen atoms were refined anisotropically and the hydrogen atoms were refined isotropically. The structure was plotted by DIAMOND software version 3.1f [19].

3. Results and discussion

3.1. Crystal growth

Single crystals of the title complex were grown by gel diffusion technique. The crystals were appeared at the gel interface within 1 week. The optimum condition for crystal growth are, density of sodium metasilicate solution = 1.04 g cm⁻³, pH = 5.5, concentration of benzoic acid = 0.5 M, concentration of lead acetate = 0.5 M. The crystals were separated and washed and dried. The photograph of



Fig. 1. Photograph of crystalline lead-benzilate.

the grown crystals is shown in Fig. 1.

3.2. FT-IR spectral studies

The FT-IR spectrum of the title complex is shown in Fig. S1 (supply. data). The changes in molecular vibrations of the complex are due to the coordination of metal with the ligand. The assignment of FT-IR spectral bands of the complex is based on the previous reports of metal benzilates [20–23]. The band observed at 3608 cm⁻¹ is assigned to the free $\nu(\text{O-H})$ of the ligand. The sharp peak at 3060 cm⁻¹ corresponding to the $\nu(\text{O-H})$ of the ligand, which implies the coordination of hydroxyl oxygen to the central lead ion. The carbonyl absorption, observed at 1719 cm⁻¹ in the FT-IR spectrum of ligand is absent in the complex indicating that the ligand coordinates to the metal ion through the carboxylate group after deprotonation. The compound exhibits two strong asymmetric C=O vibrations at 1616 and 1554 cm⁻¹ whereas two symmetric vibrations are found at 1384 and 1312 cm⁻¹ respectively, supports this observation. The separation $\Delta\nu = [\nu_{\text{asym}}(\text{COO}^-) - \nu_{\text{sym}}(\text{COO}^-)]$ values, 304 cm⁻¹, 170 cm⁻¹, 242 cm⁻¹ and 232 cm⁻¹ may be due to monodentate, bidentate bridging and tridentate chelating bridging modes of carboxylate oxygen atoms respectively. The large difference in $\Delta\nu$ value also indicates that the anti-anti coordination mode [24–26]. Pb–O stretching is identified the band at 607 cm⁻¹.

3.3. Elemental analysis

The fine powdered compound was subjected for elemental analysis. The carbon and hydrogen present in the compound were theoretically calculated using the formula $[\text{Pb}(\text{C}_{14}\text{H}_{11}\text{O}_3)_2]\text{C}_2\text{H}_5\text{O}$ and compared with experimentally found values. Anal. Calc. (%): C, 50.94; H, 3.82. Found: C, 50.90; H, 3.25. The elemental analysis data obtained corresponds to the formula assumed.

Table 1
Crystal data and structure refinement parameters of lead benzilate.

Parameters	$[\text{Pb}(\text{C}_{14}\text{H}_{11}\text{O}_3)_2]\text{C}_2\text{H}_5\text{O}$
Empirical formula	C ₃₀ H ₂₇ O ₇ Pb
Formula weight	706.70
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions	a = 8.5659(5) Å, $\alpha = 81.609(4)^\circ$ b = 11.1121(7) Å, $\beta = 75.058(4)^\circ$ c = 14.8062(10) Å, $\gamma = 85.013(4)^\circ$
Volume	1345.31(15) Å ³
Z	2
Density (calculated)	1.745 Mg/m ³
Absorption coefficient	6.317 mm ⁻¹
F(000)	690
Crystal size	0.200 × 0.200 × 0.150 mm ³
Theta range for data collection	2.195–24.999°
Index ranges	–10 ≤ h ≤ 10, –13 ≤ k ≤ 13, –17 ≤ l ≤ 17
Reflections collected	25553
Independent reflections	4732 [R(int) = 0.0769]
Completeness to theta = 24.999°	100.0%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.478 and 0.358
Refinement method	Full-matrix least-squares on F ²
Data/restraints/parameters	4732/111/346
Goodness-of-fit on F ²	1.111
Final R indices [I > 2σ(I)]	R ₁ = 0.0456, wR ₂ = 0.1108
R indices (all data)	R ₁ = 0.0681, wR ₂ = 0.1307
Extinction coefficient	n/a
Largest diff. peak and hole	3.476 and –1.843 e.Å ⁻³

$$R1 = \sum ||F_o| - |F_c|| / \sum |F_o|, wR2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}.$$

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