TWO-DIMENSIONAL COORDINATION POLYMER OF Pb(II) COMPLEX WITH M-SULFANILIC ACID: SYNTHESIS AND STRUCTURAL ANALYSIS.

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Abstract This study reports the synthesis, structure, and characterization of a novel two-dimensional coordination polymer (CP) composed of Pb(II) ions and *m*-sulfanilic acid. The polymer was synthesized via a hydrothermal method using resorcinol as a surfactant. Single-crystal X-ray diffraction revealed that each Pb(II) ion is coordinated by two nitrogen and six oxygen atoms from the amino and sulfonate groups of the ligand, forming a distorted square antiprismatic geometry. The presence of a stereochemically active lone pair on Pb(II) causes a hemidirected coordination environment. The resulting polymeric network is stabilized by hydrogen bonding, leading to high lattice stability and unique structural properties.

Keywords: coordination polymer, Pb(II) complex, m-sulfanilic acid, crystal structure, hydrothermal synthesis, hydrogen bonding, stereochemical activity.

Annotatsiya. Ushbu maqolada Pb(II) ioni va *m*-sulfanil kislotadan tashkil topgan yangi ikki o‘lchovli koordinatsion polimerning sintezi, tuzilishi va xossalari bayon etilgan. Polimer gidrotermik usulda rezorsinol ishtirokida sintez qilindi. Rentgenostruktur tahlil natijasida har bir Pb(II) ioni amin va sulfonat guruhlarining azot va kislorod atomlari bilan koordinatsiyalanganligi, natijada deformatsiyalangan kvadrat antiprizmatik geometriya hosil bo‘lishi aniqlangan. Pb(II) ionining faol erkin jufti tufayli gemidireksion koordinatsion muhit hosil bo‘ladi. Polimer tuzilmasi vodorod bog‘lari bilan mustahkamlangan.

Kalit so‘zlar: koordinatsion polimer, qo‘rg‘oshin kompleksi, m-sulfanil kislota, kristall tuzilma, gidrotermik sintez, vodorod bog‘i, stereokimyoviy faoliyat.

Аннотация. В данной статье представлены результаты синтеза, структурной характеристики и анализа нового двумерного координационного полимера, состоящего из ионов Pb(II) и *m*-сульфаниловой кислоты. Полимер был получен гидротермальным методом с использованием резорцина в качестве поверхностно-активного вещества. Рентгеноструктурный анализ показал,

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что каждый ион Pb(II) координируется с двумя атомами азота и шестью атомами кислорода, формируя искаженную квадратную антипризматическую геометрию. Наличие стереохимически активной неподелённой пары электронов у Pb(II) приводит к гемидиректной координационной среде. Полученная структура стабилизируется водородными связями, обеспечивая прочность решётки.

Ключевые слова: координационный полимер, комплекс свинца, m-сульфаниловая кислота, кристаллическая структура, гидротермальный синтез, водородные связи, стереохимическая активность.

Introduction

In recent years, there has been increasing interest in the intentional synthesis of novel coordination polymers (CPs) [1]. Porous coordination polymers (PCPs), commonly known as metal–organic frameworks (MOFs), have drawn considerable interest owing to their diverse structures and wide range of potential applications [2]. In coordination polymers, supramolecular isomerism occurs when different network superstructures are formed from the same building blocks. This phenomenon is due to the inherent uncertainties in the self-assembly process [3]. However, it also presents a valuable opportunity to investigate the mechanisms of self-assembly and crystal growth, as well as to explore the structure–property relationships in these intriguing materials [4]. Coordination polymers (CPs) are compounds made of metal-ligand coordination bonds that create extended structures in one-dimensional (1D) chains, two-dimensional (2D) sheets, or three-dimensional (3D) frameworks [5]. These applications include gas storage, adsorption and separation, heterogeneous catalysis, drug delivery, magnetic properties, molecular recognition, and selective luminescent probes, among others [6-7]. Several metal complexes with sulfanilic acid or metanilic acid have been documented. Lead(II) ions, in particular, often display unique coordination chemistry compared to other divalent transition metal ions. Consequently, examining the crystal structures of lead(II) sulfonates is of significant interest. Large and polarizable, heavier Pb(II) is particularly interested in forming tetrel bonds among these group IV elements. Pb(II) can arise thanks to a Hemi-directed coordination environment and a stereochemically active lone pair 6s2, leading to a significant coordination gap.

Experimental.

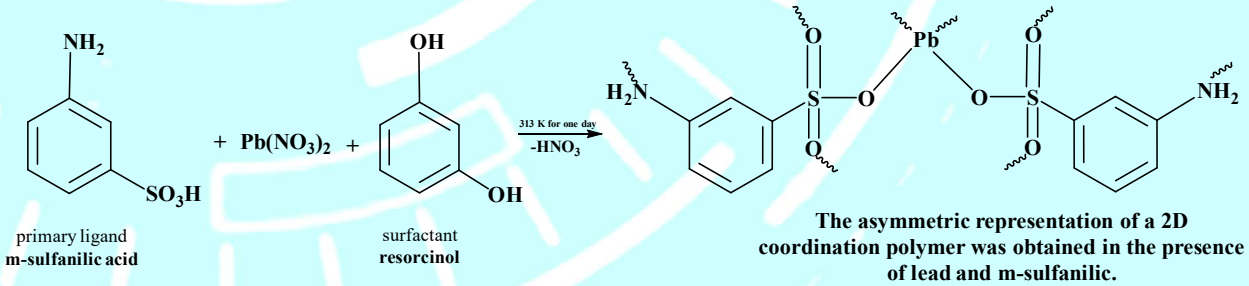
All chemicals used in this study were sourced from Sigma-Aldrich and employed in their original form

Materials: All chemicals were utilized in their as-received state. Lead (II) acetate decahydrate (99%, $Pb(CH_3COO)_2 \cdot 10H_2O$), m-sulfanilic acid (99.5%, $C_6H_7NO_3S$), resorcinol (99.5%, $C_6H_6O_2$), and distilled water.

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Synthesis Method: A hydrothermal approach was employed to synthesize a 2D coordination polymer. The primary ligand, m-sulfanilic acid ($C_6H_7NO_3S$), (20 mg, 0.116 mmol), was dissolved in 0.3 mol of distilled water. A secondary ligand, resorcinol ($C_6H_6O_2$), (20 mg, 0.182 mmol), was dissolved in 0.3 mol of distilled water and served as a surfactant. Subsequently, the lead (II) acetate decahydrate ($Pb(CH_3COO)_2 \cdot 10H_2O$), (20 mg, 0.04 mmol) was also dissolved in water.

The salt solution was gradually introduced into the m-sulfanilic acid solution, and the resulting solution was supplemented with the resorcinol solution. The combined solution underwent hydrothermal treatment in a heating furnace at 313 K for one day to enhance the reaction yield. Subsequently, the solution was transferred to a thermostat and maintained at a temperature of 303 K for 7 days to facilitate crystal growth. Following the complete evaporation of the solution, needle-like yellow crystals were formed. Yield: 61 % (based on Pb): Anal. calcd. for CP: $C_{12}H_{12}N_2O_6PbS_2$: C, 26.134 %; H, 2.2 %; O, 17.4 %; N, 5 %; Found: C, 25.8 %; H, 2.1%; O, 17.1%; N, 4.8 %.



Scheme: Synthesis of CP.

Single crystal X–ray structure analysis

Crystal data collection and structure refinement parameters are provided in Table 1. The **CP** crystallizes in the orthorhombic crystal system, specifically within the space group $Pna2_1$, indicating a non-centrosymmetric crystal structure. This non-centrosymmetric nature may influence the material's physical properties, such as optical behavior or piezoelectric response.

As shown in Fig. 1(a), the asymmetric unit of the catena-(bis(μ3-3-aminobenzenesulfonato) lead(II)) (**CP**) reveals the coordination environment around the lead(II) ion. The lead(II) ions are coordinated by two nitrogen atoms and six oxygen atoms from the amino and sulfonate groups of the 3-aminobenzenesulfonate ligands. A notable feature of this coordination is the presence of a stereochemically active lone pair on the Pb(II) atoms. This lone pair leads to a hemidirected configuration, characterized by an asymmetrical distribution of ligands around the lead ion. The bond angles around the lead(II) center, represented by X–Pb–X (where X = N, O), vary significantly, ranging from 72.2(2)° to 91.08(18)°. This wide range of angles indicates a substantial distortion in the PbO_6N_2 coordination environment, which can be described as a distorted

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square antiprismatic geometry. The distortion is evident from the deviation of bond angles from the ideal 90° expected in a perfect square antiprism. Illustrates this distorted square antiprismatic coordination, highlighting the irregular arrangement of the ligands around the lead ion.

The self-assembled polymeric network of the **CP** is depicted in Fig. 1(b), illustrating the extended structure formed through μ3-bridging by the 3-aminobenzenesulfonate ligands. Each lead ion is surrounded by six 3-aminobenzenesulfonate ligands, forming a network that highlights the **CP**'s structural organization and coordination geometry. The Pb–O bond lengths range from 2.560(7) to 2.781(7) Å, and the average N–Pb bond length is 2.694(8) Å, suggesting a coordination number of eight around the Pb(II) atoms. The non-bonded Pb–Pb distance along the chain is 5.2991(4) Å. The crystal structure is further stabilized by intermolecular hydrogen bonds, predominantly classic N–H•••O hydrogen bonds. These occur specifically between the N(1)–H(1A) and O(5) atoms, as well as the N(2)–H(2A) and O(3) atoms, with donor-acceptor distances (D•••A) of 3.08(1) Å and 3.11(1) Å, respectively. These hydrogen bonds are crucial for maintaining the integrity of the polymeric network, enhancing the overall stability of the **CP**. They play a significant role in bridging adjacent chains or molecules, contributing to the robustness of the crystal lattice and potentially influencing the material's mechanical properties.

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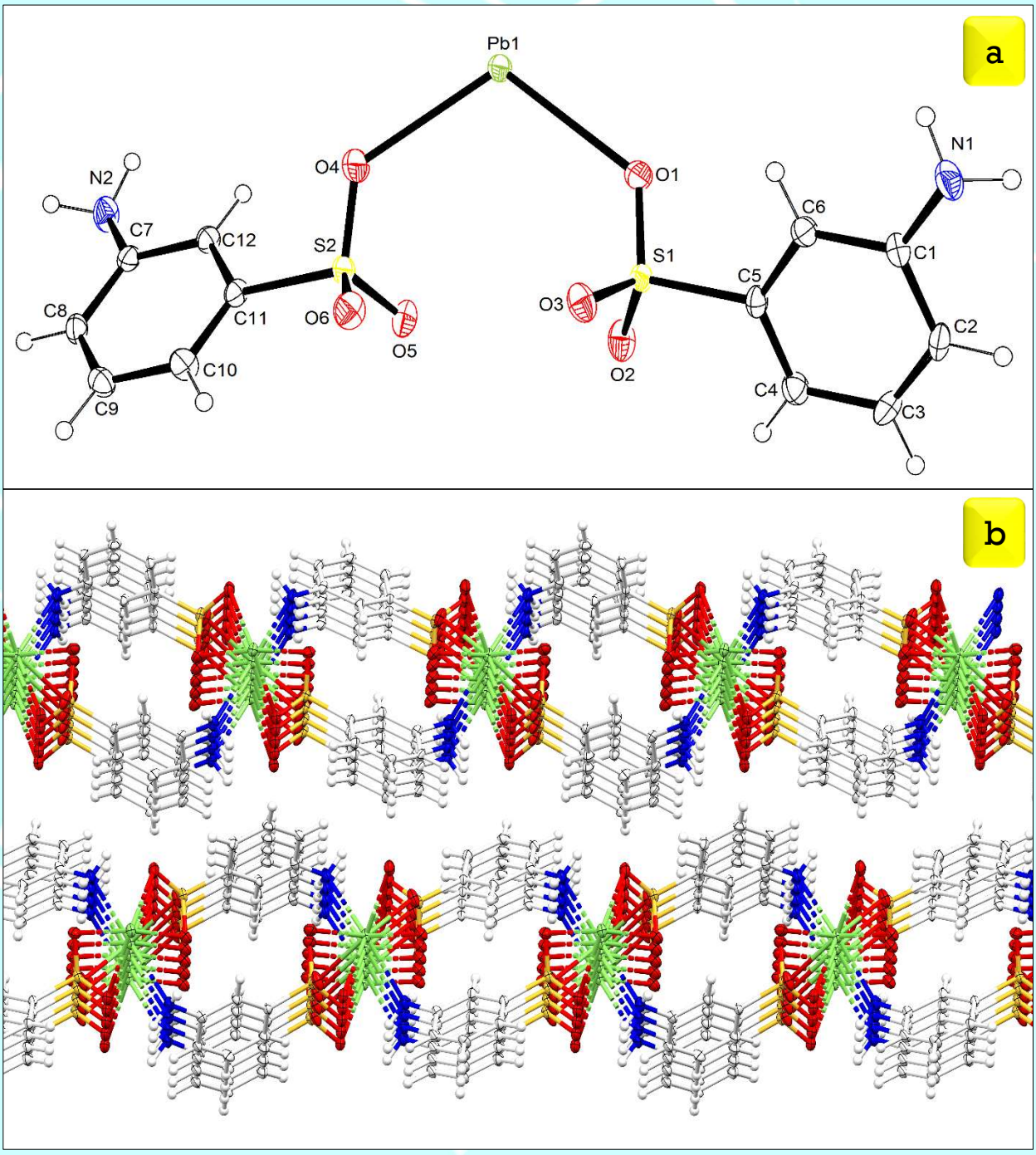


Fig. 1 (a) Asymmetric unit showing the atom numbering scheme and displacement ellipsoids drawn at the 35% probability level. (b) Polymeric network of catena-(bis(μ3-3-aminobenzenesulfonato) lead(II)).

Table 1.

Crystal data and structure refinement of the catena-(bis(μ3-3-aminobenzenesulfonato)-lead(II))

CCDC	**2383711**
Empirical formula	$C_{12}H_{12}N_2O_6PbS_2$
Formula weight	551.55

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Temperature (K)	293(2)
Radiation type	CuKα (1.54184 Å)
Crystal system	Orthorhombic
Space group	$Pna2_1$
a, b, c (Å)	16.31877(13), 5.29905(4), 16.95526(17)
α, β, γ (°)	90, 90, 90
Volume ($Å^3$)	1466.19(2)
Z	4
Density (calculated) (Mg/μ3)	2.499
Absorption coefficient (mm^{-1})	25.371
F(000)	1040
Crystal size (mm^3)	0.18 x 0.14 x 0.14
Theta range for data collection	2.5920 to 71.3490°
Index ranges	-19≤h≤17, -6≤k≤6, -20≤l≤19
Reflections collected	10779
Independent reflections	2765 [R(int) = 0.0451]
Data/restraints/parameters	2765/1/210
Goodness-of-fit on F^2	1.076
Absorption correction	multi-scan
Max. and min. transmission	0.197 and 1.000
Refinement method	Full-matrix least-squares on F^2
Final R indices [I>2sigma(I)]	R1 = 0.0270, wR2 = 0.0274
R indices (all data)	R1 = 0.0674, wR2 = 0.0676
Extinction coefficient	0.00048(5)

Table 2.

Geometric details of hydrogen bonding [Å and °] in catena-(bis(μ3-3-aminobenzenesulfonato)-lead(II))

D-H•••A	d(D-H)	d(H•••A)	d(D•••A)	<(DHA)
N(2)-H(2A)•••O(3)	0.89	2.29	3.08(1)	146.5
N(1)-H(1A)•••O(5)	0.89	2.34	3.11(1)	144.3

Symmetry transformations used to generate equivalent atoms:

Conclusion

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A novel two-dimensional Pb(II) coordination polymer based on *m*-sulfanilic acid was successfully synthesized using a hydrothermal method. Structural analysis confirmed the hemidirected square antiprismatic geometry around the Pb(II) centers and the stabilizing role of intermolecular hydrogen bonds. The findings demonstrate how ligand design and synthesis parameters govern dimensionality and geometry in Pb(II) frameworks. Future studies will focus on the electrical and sorption behavior of this polymer to explore its potential in adsorption and sensor applications.

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