



Preparation and Characterization of bis (4-methoxyanilinium) tetrachlorozincate

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ABSTRACT

A new zinc complex of formula $[C_7H_{10}NO]_2ZnCl_4$ has been prepared and characterized by X-ray diffraction, IR and UV-Visible spectroscopies. The complex crystallizes in the monoclinic space group $P2_1/n$ with a minimal tetrahedral distortion of the $ZnCl_4^{2-}$ ion and with lattice parameters: $a = 12.054(2) \text{ \AA}$, $b = 7.129(3) \text{ \AA}$, $c = 23.480(2) \text{ \AA}$, $\beta = 100.67(2)^\circ$, $V = 1983.03(1) \text{ \AA}^3$ and $Z = 4$. The crystal structure was solved and refined to $R = 0.080$ and $R_w = 0.227$ with 9611 independent reflections. It can be described by organic layers of p-anisidinium cations held together by C-H...O hydrogen bonds parallel to (010) plane, linked to the inorganic groups of $ZnCl_4^{2-}$ anions through N-H...Cl hydrogen bonds, electrostatic and Van Der Waals interactions, to form a three-dimensional network.

Indexing terms/Keywords

Organic-inorganic hybrid, Crystal structure, IR Spectroscopy.



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1. INTRODUCTION

Organic-inorganic hybrid materials have gained enormous attention in recent years due to their interesting crystal structure and some special properties such as magnetic, optical, electrical and catalytic activity [1]. A recent advance in this field is to design the coordination frameworks of tetrahalometallates by the incorporation of various organic cations giving new structures with interesting applications [2]. Self-assembly process of such hybrid materials in solid state arises due to the variety of interactions including ionic interactions, hydrogen and halogen bondings and Van Der Waals interactions [3]. In the present investigation, we report the synthesis and crystal structure of a new organic-inorganic hybrid zinc complex, $[\text{C}_7\text{H}_{10}\text{NO}]_2\text{ZnCl}_4$. Characterization of this material by IR and UV-Visible spectroscopies is also reported.

2. EXPERIMENTAL

2.1 Material Preparation

The title compound was prepared in a Petri dish by slow evaporation of an ethanolic solution of 4-methoxyaniline (2 mmol), zinc chloride (1 mmol) and diluted hydrochloric acid (10 mL, 1M) at room temperature. The crystals remained stable under normal conditions of temperature and humidity. The chemical formula was determined by X-ray crystal structure analysis.

2.2 Physical measurement

The unit-cell dimensions were refined using X-ray diffraction data collected with a Mach 3 Enraf Nonius diffractometer using Ag $\text{K}\alpha$ radiation. Crystal data, parameters used for diffraction data collection and strategy used for the crystal structure determination and their results, are listed in Table 1. The atomic coordinates and equivalent isotropic displacements are shown in Table 2.

IR spectra were recorded using KBr pellets in the range of $4000\text{-}400\text{ cm}^{-1}$ on a Nicolet IR200 FT-IR Spectrometer at ambient temperature.

Electronic spectra absorptions were made on a Perkin-Elmer Lambda UV-Visible spectrophotometer for 2.10^{-3} M solution of $[\text{C}_7\text{H}_{10}\text{NO}]_2\text{ZnCl}_4$ in absolute ethanol solvent.

3. RESULTS AND DISCUSSION

3.1 X-ray diffraction analysis

The asymmetric unit of the title compound (Fig.1) contains two p-anisidinium cations and one tetrachlorozincate anion.

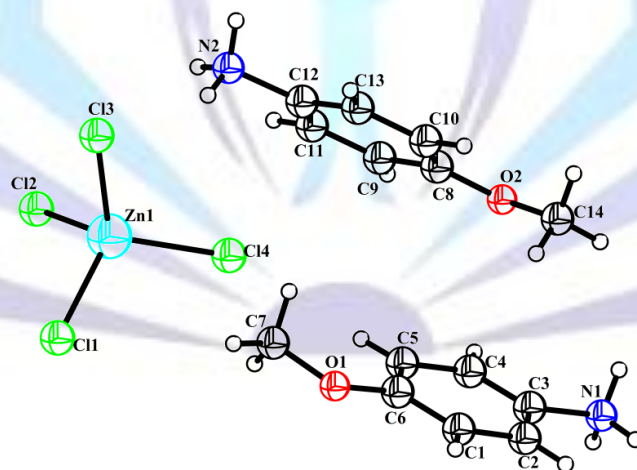


Figure 1. ORTEP view of $[\text{C}_7\text{H}_{10}\text{NO}]_2\text{ZnCl}_4$, showing 50% probability ellipsoids

The crystal structure consists of organic layers of p-anisidinium cations, parallel to the (b,c) plane, held together by C-H...O hydrogen bonds. These layers are attached to the inorganic groups of ZnCl_4^{2-} anions through N-H...Cl hydrogen bonds, electrostatic and Van Der Waals interactions, to form a three-dimensional infinite network (Fig.2).

Table 1. Crystal data and structure refinement

Chemical formula	C ₁₄ H ₂₀ Cl ₄ N ₂ O ₂ Zn ₁
Formula weight (g.mol ⁻¹)	364.4
Crystal system	Monoclinic
Space group	P2 ₁ /n
a (Å)	12.054 (2)
b (Å)	7.129 (3)
c (Å)	23.480 (2)
β (°)	100.67 (2)
V (Å ³)	1983.03 (1)
Z	4
D (mg.m ⁻³)	1.53
μ (Ag K α) (mm ⁻¹)	0.930
F (000)	927.9
Crystal size (mm)	0,50x0,40x0,20
Reflections collected	13844
Independent reflections parameters	9611
Goodness-of-fit on F ²	1.1
T (K)	293
R	8.07%
W _R	22.73%

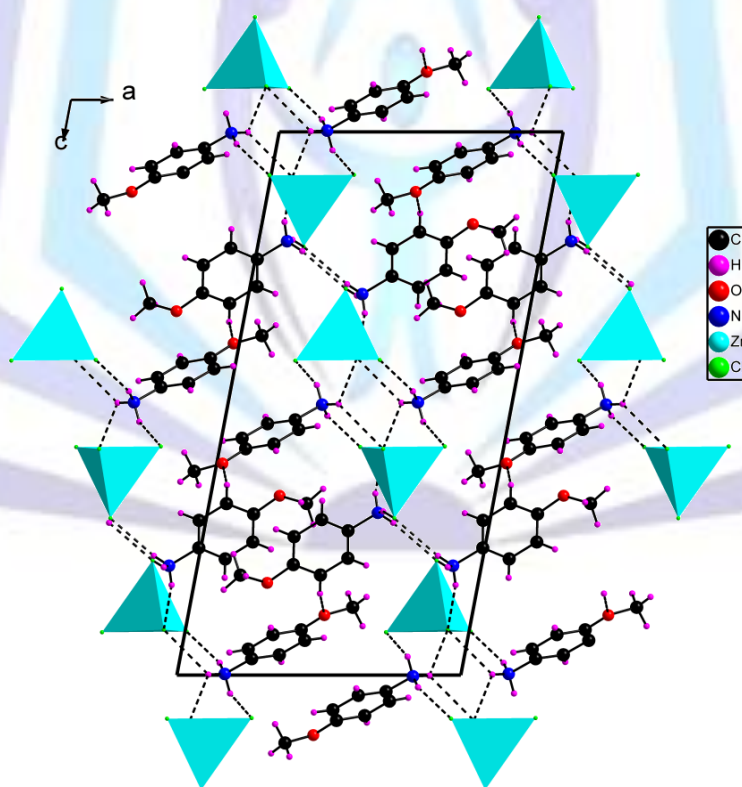

 Figure 2. Projection of the structure of [C₇H₁₀NO]₂ ZnCl₄ along the b axis

Table 2. Fractional atomic coordinates and equivalent isotropic displacements for [C₇H₁₀NO]₂ ZnCl₄

Atoms	X	Y	Z	U _{eq} /U _{iso}
Cl1	0.0762(1)	0.5663(2)	0.0837(5)	0.0517(3)
Cl2	-0.0056(1)	1.0619(2)	0.0801(5)	0.0443(3)
Cl3	0.1617(1)	0.8648(2)	0.2112(5)	0.0568(3)
Cl4	0.2918(1)	0.9449(2)	0.0790(5)	0.0573(3)
N1	0.8322(3)	0.7334(6)	0.0022(2)	0.0479(1)
C1	0.6884(4)	0.3684(8)	0.0746(3)	0.0595(1)
C3	0.7475(4)	0.6378(6)	0.0302(2)	0.0411(1)
C4	0.6525(4)	0.7314(7)	0.0373(2)	0.0476(1)
C2	0.7659(4)	0.4548(7)	0.0478(2)	0.0540(1)
C5	0.5726(4)	0.6429(7)	0.0640(2)	0.0502(1)
C6	0.5921(4)	0.4608(7)	0.0834(2)	0.0517(1)
O1	0.5203(4)	0.3626(6)	0.1104(2)	0.0769(1)
C9	0.5609(4)	0.9609(7)	0.1843(2)	0.0462(1)
C7	0.4258	0.4544(1)	0.1248(3)	0.0830(2)
C8	0.6632(4)	0.8724(6)	0.2034(2)	0.0394(1)
O2	0.7430(3)	0.8929(5)	0.1698(1)	0.0504(8)
N2	0.3998(3)	0.8294(6)	0.2987(2)	0.0468(9)
C10	0.6791(4)	0.7730(7)	0.2549(2)	0.0509(1)
C13	0.5932(4)	0.7612(7)	0.2861(2)	0.0513(1)
C11	0.4753(4)	0.9479(7)	0.2151(2)	0.0462(1)
C14	0.8427(4)	0.7823(9)	0.1841(3)	0.0708(2)
C12	0.4928(3)	0.8466(6)	0.2657(2)	0.0381(9)
Zn1	0.1374(4)	0.8585(7)	0.1122(2)	0.0397(2)
H1A	0.8897	0.6561	0.0010	
H1B	0.8573	0.8354	0.0224	
H1A	0.8897	0.6561	0.0010	
H1	0.7006	0.2452	0.0873	
H2	0.8289	0.3910	0.0416	
H2A	0.3398	0.8921	0.2804	
H2B	0.4218	0.8767	0.3341	
H2C	0.3820	0.7090	0.3014	
H4	0.6409	0.8543	0.0243	
H5	0.5071	0.7054	0.0686	
H7A	0.3839	0.3678	0.1440	
H7B	0.3785	0.5001	0.0902	
H7C	0.4506	0.5578	0.1502	
H9	0.5502	1.0299	0.1501	
H10	0.7477	0.7140	0.2684	
H11	0.4064	1.0067	0.2020	
H13	0.6038	0.6952	0.3208	

H14A	0.8917	0.8083	0.1571
H14B	0.8228	0.6518	0.1821
H14C	0.8808	0.8123	0.2226

As shown in Fig.3, in the crystal structure of the title complex, ZnCl_4^{2-} groups are connected by hydrogen bonds N-H...Cl. The organic and inorganic species interact by mean of seven N-H...Cl hydrogen bonds (Table 3), giving rise to a porous layer. The corresponding N...Cl distances vary between 3.173(4) and 3.413(4) Å, which can be considered relatively weak [4]. In the organic layer, there are no π - π interactions between the 4-methoxyanilinium cations, between which there is a face-to-face distance of 4Å which is longer than values observed in similar compounds [5].

Table 3. Hydrogen-bond parameters (Å, °) for $[\text{C}_7\text{H}_{10}\text{NO}]_2\text{ZnCl}_4$

D-H...A	D-H (Å)	H...A (Å)	D...A (Å)	D-H...A (°)
N(1)-H(1A)...Cl(1)	0.89	2.76	3.413 (4)	131
N(1)-H(1A)...Cl(1)	0.89	2.63	3.268 (4)	129
N(1)-H(1B)...Cl(2)	0.89	2.52	3.366 (4)	159
N(1)-H(1C)...Cl(4)	0.89	2.48	3.173 (4)	135
N(2)-H(2A)...Cl(3)	0.89	2.45	3.215 (4)	145
N(2)-H(2B)...Cl(1)	0.89	2.35	3.205 (4)	160
N(2)-H(2C)...Cl(3)	0.89	2.52	3.393 (4)	169
C(9)-H(9)...O(1)	0.93	2.55	3.337 (6)	143

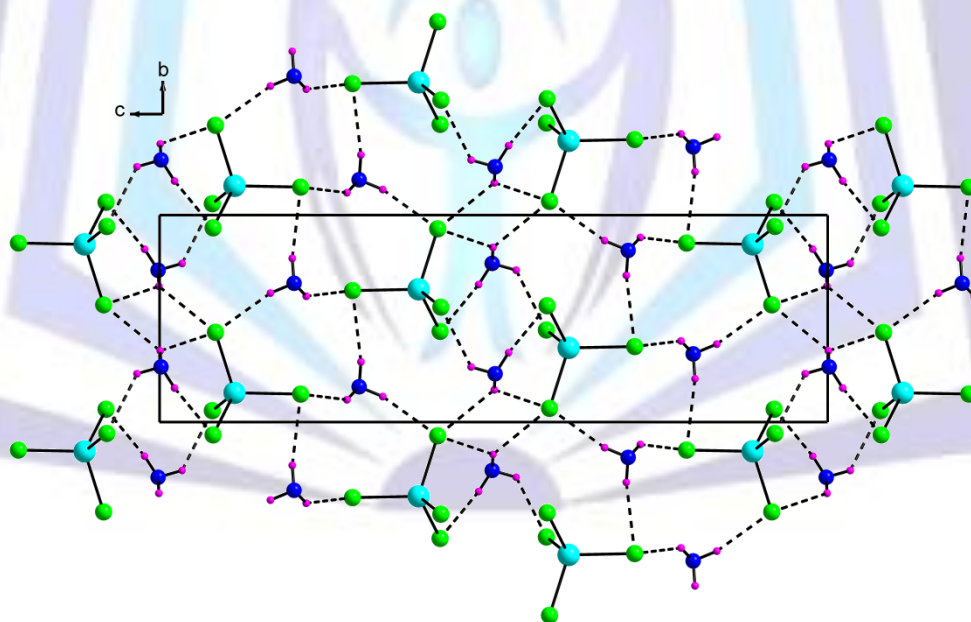


Figure 3. Projection of a layer of the structure of $[\text{C}_7\text{H}_{10}\text{NO}]_2\text{ZnCl}_4$ along the a direction

The zinc atom is tetrahedrally coordinated by chlorine atoms, with Zn-Cl distances ranging from 2.234(1) to 2.288(1)Å and Cl-Zn-Cl angles varying from 105.76(5) to 113.32 (5)° (Table 4). These values show a slight distortion of the ZnCl_4^{2-} tetrahedra, which can be explained by the involving of the chlorine ions in the hydrogen bonding. These results are in agreement with those found in anilinium tetrachlorozincate [6]. The organic molecule exhibits a regular spatial configuration with normal distances C-C, C-N and angles C-C-C, C-C-N (Table 5). The mean value of the C-C length of the C_6 -ring is 1.4038Å, which is between single and double bonds and agrees with that observed in the C_6 -ring of benzene derivatives [7]. All the carbon atoms of the C_6 -ring are coplanar and they form conjugated planes with average deviation of ± 0.042 Å and ± 0.079 Å, and they form between them a dihedral angle of 7.45°.

**Table 4. Main interatomic distances (Å) and bond angles (deg) for $ZnCl_4^{2-}$**

Zn	Cl1	Cl2	Cl3	Cl4
Cl1	2.269 (1)	3.665 (1)	3.662 (1)	3.762 (1)
Cl2	107.63 (5)	2.272 (1)	3.636 (1)	3.685 (1)
Cl3	106.96 (5)	105.76 (5)	2.288 (1)	3.772 (1)
Cl4	113.33 (5)	109.72 (5)	113.04 (5)	2.234 (1)

Table 5. Main interatomic distances (Å) and bond angles (°) for organic groups**4-(OCH₃)C₆H₄N(1)H₃⁺**

N1-C3	1.48 (6)	C3-C2-C1	118.7 (5)	C4-C3-N1	119.6 (4)
C2-C3	1.374 (7)	C2-C3-C4	121.4 (4)		
C1-C2	1.367 (7)	C1-C6-C5	119.7 (5)		
C1-C6	1.382 (7)	C3-C4-C5	120 (4)		
C5-C6	1.382 (7)	C4-C5-C6	118.9 (4)		
C4-C5	1.393 (6)	C6-C1-C2	121.2 (5)		
C4-C3	1.362 (7)	C2-C3-N1	119.6 (4)		
C6-O1	1.358 (6)	O1-C6-C1	116.65 (5)		
O1-C7	1.409 (8)	O1-C6-C5	123.64 (4)		

4-(OCH₃)C₆H₄N(2)H₃⁺

N2-C12	1.48 (6)	C8-C10-C13	120 (4)	C13-C12-N2	119.3 (4)
C10-C8	1.383 (6)	C11-C9-C8	120.8 (4)		
C10-C13	1.376 (7)	C9-C8-C10	119.2 (4)		
C9-C11	1.369 (6)	C10-C13-C12	119.6 (4)		
C9-C8	1.385 (6)	C9-C11-C12	118.9 (4)		
C11-C12	1.373 (6)	C11-C12-C13	121.6 (4)		
C13-C12	1.36 (6)	C11-C12-N2	119.1 (4)		
C8-O2	1.360 (5)	C9-C8-O2	116.52 (4)		
O2-C14	1.424 (6)	C10-C8-O2	124.29 (4)		

Furthermore, the distances of C(7)-O(1), C(14)-O(2), C(3)-N(1) and C(12)-N(2) [1.409 (7) Å, 1.424 (6) Å, 1.480(6) Å, 1.481 Å] indicate two single bonds in each cation.

However, the C(6)-O(1) and C(8)-O(2) distances [1.358(3) Å and 1.360(1) Å] are shorter which is probably due to the mesomeric effect of the methoxy groups [8].

The coplanar methoxy groups are characterized by the torsion angles C(1)-C(6)-O(1)-C(7) and C(9)-C(8)-O(2)-C(14) being 174.6° and -171.3° respectively.

The O(1)-C(6)-C(5) and O(2)-C(8)-C(10) angles [123.64 and 124.29°] are larger than the O(1)-C(6)-C(1) and O(2)-C(8)-C(9) angles [116.65° and 116.52°]. This can be attributed to the establishment of weak C-H...O intramolecular hydrogen bonds [8].

3.2 Infrared Spectroscopy

The IR vibrational frequencies of the free 4-methoxyaniline have been taken for band assignments and to verify the shift in their frequencies with the present compound [9-10].

The IR spectrum (Fig. 4) of $[C_7H_{10}NO]_2ZnCl_4$ shows absorption bands in the region 3500-2800 cm^{-1} due to the N-H and C-H antisymmetric and symmetric stretching modes respectively of $-NH_3^+$ and $-CH_3$ groups. These bands are shifted to lower wave number in the spectrum of $[C_7H_{10}NO]_2ZnCl_4$ which is due to the formation of hydrogen bonds N-H...Cl.

Bending vibrations of $-NH_3^+$ and $-CH_3$ groups appear in the region 1650-1400 cm^{-1} . The vibrations observed in the domain 1400-1000 cm^{-1} can be assigned to aromatic C-N stretches. The bands situated between 1000-650 cm^{-1} are due to aromatic C-H, C-C and C-N out of plane deformations.

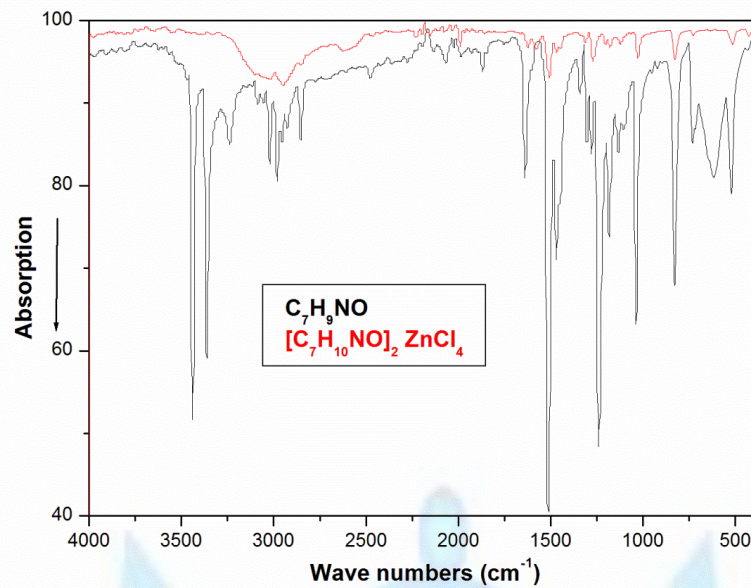


Figure 4. IR absorption spectrum of $[\text{C}_7\text{H}_{10}\text{NO}]_2\text{ZnCl}_4$

3.3 UV Absorption and Diffuse Reflectance

The optical absorption spectrum of $[\text{C}_7\text{H}_{10}\text{NO}]_2\text{ZnCl}_4$ was measured in the range 200-800 nm and the spectrum is shown in Fig.5.

In figure 5, we observe two strong absorption bands at 276 and 282 nm due to the $\pi \rightarrow \pi^*$ transitions. The spectrum shows also a broad weak band around 306 nm which can be attributed to the $n \rightarrow \pi^*$ transition.

As the direct band gap $[\text{C}_7\text{H}_{10}\text{NO}]_2\text{ZnCl}_4$ has an absorption coefficient (α) obeying the relation for high photon energies ($h\nu$):

$$\alpha = \frac{A(h\nu - E_g)^{1/2}}{h\nu} \quad (11)$$

where E_g is the band gap energy of the crystal and A is a constant.

The plot of variation of $(\alpha h\nu)^2$ vs. $h\nu$ is shown in Fig.6. The band gap energy is found to be 4.26 eV. This value suggests that the studied compound could be used for optical applications in far UV region [12] as well as for dielectric properties [13].

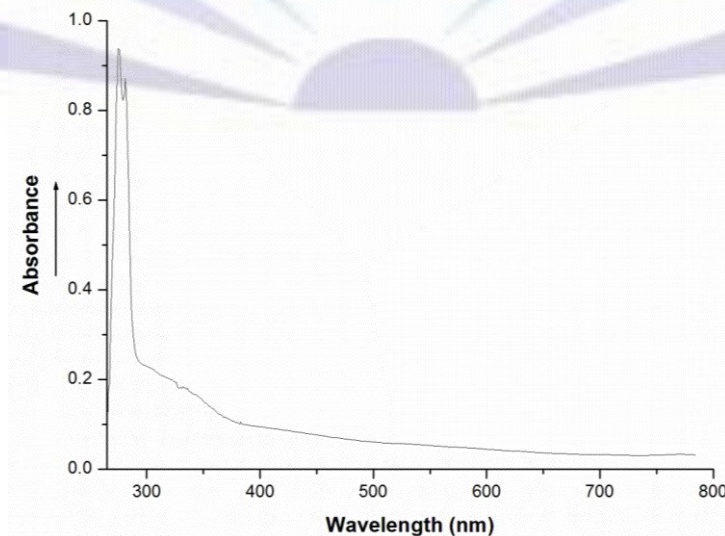


Figure 5. UV Absorption spectrum of $[\text{C}_7\text{H}_{10}\text{NO}]_2\text{ZnCl}_4$

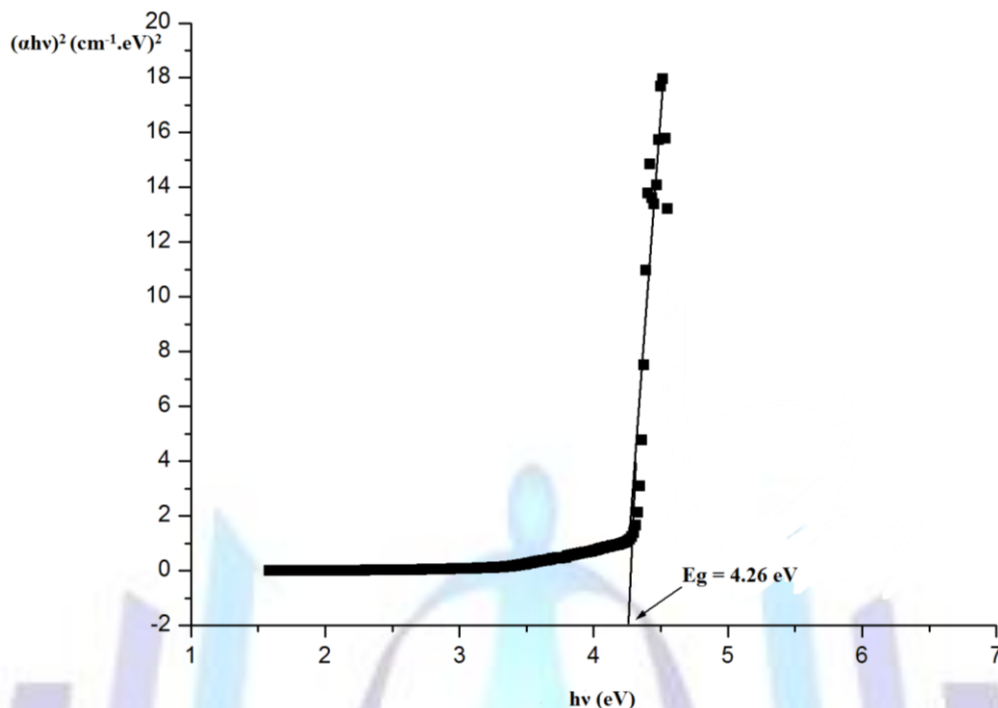


Figure 6. Plot of $(\alpha hv)^2$ vs. hv

3.4 Conclusion

A new hybrid material, $[C_7H_{10}NO]_2 ZnCl_4$, has been prepared. Its atomic arrangement is described by organic layers of 4-methoxyanilinium cations attached to the inorganic groups of $ZnCl_4^{2-}$ anions through N-H...Cl hydrogen bonds as to form a three-dimensional network. The UV-Vis spectral analyses reveal that the crystal can be used as dielectric with a band gap energy of 4.26 eV.

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