Growth, Structural, Thermal and Spectral Analysis of Inorganic Material Tetrabutylammonium Tetrabromo Zincate (II) $[N(C_4H_9)_4]_2ZnBr_4$

R. Umarani, M. A. Kandasamy, V. Mohanraj

Abstract— The growth of crystals containing two or more components plays an important role in several modern industrial applications. Single crystals of tetrabutylammonium tetrabromo zincate (II), was grown by slow evaporation method at room temperature. The grown crystals were characterized through elemental analysis, powder X-ray diffraction, thermogravimetric analysis, differential thermal analysis, low temperature differential scanning calorimetry techniques. The spectral studies of FTIR, ^{1}H and ^{13}C NMR spectra were obtained for the compound. Single crystal X-ray diffraction technique was solved and refined by full matrix least square method.

Index Terms— A1. Crystal growth, A2. Tetrabutylammonium tetrabromo zincate (II), B1.single crystal X-ray diffraction, B2. thermogravimetric analysis, B2 differential thermal analysis,

I. INTRODUCTION

The inorganic crystals of good quality, suitable size and perfection are required in technologically important fields like electronic industries, computer technology, fibre optic communications and ferroelectric materials [1]. Rapid advances in microelectronics, communication technologies and medical instrumentation, energy and space technologies are possible simply because of remarkable progress in the fabrication of large and rather perfect crystals. High-efficiency light emitting diodes for energy saving illumination and photovoltaic devices for transforming solar and other radiation into electric power with high yield depend on significant advances in crystal growth [2-6]. The large proportion of habit modifications recorded in literature has been associated with crystals grown at ordinary conditions, in particular with aqueous solutions and only occasionally with other solutions. The grown crystals, from the embryonic stage to fully grown stage are in the environments of mother liquor, thereby, any influence which causes an alteration in the rate of deposition on any surface of the crystal will influence the usual growth pattern of the crystal [7-12]. Here single crystals of tetrabutylammonium tetrabromo zincate (II), $[N(C_4H_9)_4]_2ZnBr_4$ [TBATBr-Zn] were grown by slow

evaporation method at room temperature The compound, $[N(C_4H_9)_4]_2ZnBr_4$, crystallized with hexagonal shaped habits were bright, transparent and colourless material. The TG thermogram of the compound shows a one stage weight loss when heated between room temperature and 700°C. A suitable decomposition pattern is formulated based on the weight losses observed in the TG thermogram. The DTG thermogram of the compound confirms to the TG weight loss pattern. The TG and DTG studies confirm the stoichiometric formula of the compound. The low temperature DSC indicates the occurrence of phase transition. The high temperature DSC indicates the decomposition temperature of the compound. The FTIR spectrum was used to assign properly the various vibrational frequencies due to different chemical bonds. The ^{1}H NMR and ^{13}C NMR spectrum of the compound confirm the presence of four types of protons and carbon. The sharp Bragg peaks obtained in the powder X-ray diffraction pattern confirm the crystalline nature of the compound. Single crystal X-ray diffraction technique was solved using SCHELXS – 97 and refined by full matrix least square method.

II. EXPERIMENTAL

A. Preparation and Crystal growth

Single crystals of tetrabutylammonium tetrabromo zincate (II), $[N(C_4H_9)_4]_2ZnBr_4$ (TBATBrZn(II)) were grown by slow evaporation method at room temperature scheme 1. Aqueous solutions of analar grade (E Merck) tetrabutylammonium bromide and zinc bromide were prepared separately in 2:1 molar ratio using triply distilled water. The two solutions were mixed thoroughly. In order to maintain acidic medium and to avoid hydrolysis 1 ml of HBr is added. The resulting solution was filtered using Whatmann paper 42. The filtrate collected in a beaker was covered by filter paper with minute pores and kept for growth of crystals care was taken to minimize temperature gradient and mechanical shock at the place of crystal growth. The crystals obtained were bright, colourless and transparent crystal fig.1.

III. CHARACTRERIZATION

Single crystals of tetrabutylammonium tetrabromo zincate (II) (TBATBr-Zn)(II), was grown by slow evaporation method at room temperature. The grown crystals were characterized through elemental analysis, powder X-ray diffraction, thermogravimetric analysis, differential thermal analysis, low temperature differential scanning calorimetry techniques. The spectral studies of FTIR, ^{1}H and ^{13}C NMR spectra were obtained for these compounds. Single crystal

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X-ray diffraction technique was solved using SCHELXS – 97 and refined by full matrix least square method

A. Structure analysis of tetrabutylammonium tetrabromo zincate(II)

The Structure of the compounds was determined by single crystal X-ray diffraction technique. The X-ray data for the compounds were collected at 293K using the M_oK_α radiation (λ =0.71073A°). For X-ray data collection, a crystal of approximately 0.45 x 0.39 x 0.35mm was used. The unit cell parameters of the crystals were determined by least square method using several reflections. The structure was solved using SCHELXS - 97 and refined by full matrix least square method. The intensity data were collected for h = -21 to 19, k = -19 to 19, l = -34 to 35. From the molecular formula and from the structure we confirmed the presence of Tetrabutlylammonium tribromo monoaquo zincate (II) in the synthesized sample and Tetrabutylammonium tetrabromo zincate (II). The ORTEP plot of the molecule with 50% probability and the packing of the molecule down the a, b and c axes are given in fig 2. The crystal structure data are presented in Table 1.

Table -1 the crystal structure data of TBATBr - Zn(II).

Emprical Formula	$C_{48}H_{110}Zn_2Br_7N_3O$
Formula Weight	1435.50
Temperature	293K
Wave Length	0.71073 A°
Crystal System	MONOCLINIC
Space Group	$P2_1/n$
Cell Dimensions	a=16.6262(19) A°
	b=15.3949(18) A°
	c=26.769(13) A°
	$\alpha= \gamma= 90°; \beta = 101.011°$
Volume	6725.6 (13) Å
Z, Number of molecules per unit cell	4
Density	1.418 Mg m^{-3}
Crystal Size	$0.45 \times 0.39 \times 0.35$ mm
Theta Range For Data Collection	2.5–27.0°
Index Range	$h = -21\rightarrow19$
	$l = -34\rightarrow35$
	$k = -19\rightarrow19$

B. Powder X-ray diffraction pattern

The sharp Bragg peaks obtained in the powder X-ray diffraction pattern confirm the crystallinity of the compound fig 3. The crystals obtained were bright, colourless and transparent crystal. The elemental analysis of the compound confirms its formation in the stiochiometric ratio. The structure of the compound was determined as monoclinic with space group C2/C. The unit cell dimensions are a = 13.0740, b = 10.2226 and c =15.9933 with Z = 4.

C. Fourier transform infrared spectroscopic (FTIR) studies

The FTIR spectra of TBATBr-Zn(11) is shown in fig. 4. The various absorption frequencies and their assignments are presented in table-2. Since no peak is observed above 3000 cm^{-1}, the absence of water molecule in the sample is confirmed. The peak at 2960 cm^{-1} is due to γ Csp^3-H asymmetric stretching vibration of methyl and methylene groups. C-H symmetric stretching of methyl and methylene groups is observed as a peak at 2872 cm^{-1}. C-H in-plane asymmetric bending vibration due to methyl and methylene group is seen at 1476 cm^{-1}. Sharp peak at 1380 cm^{-1} is due to C-H inplane symmetrical bending vibration of only methyl group and not methylene group. The peak also indicates the absence of isopropyl and tertiary butyl group. The C-C-C stretching vibrations are all weak and unstable due to strong coupling with the remainder of the molecule. Methyl and methylene twisting modes is seen as a strong peak at 1150 cm^{-1}. CH_3 rocking mode is seen at 1106 cm^{-1}. Peak at 1057 cm^{-1} is due to methylene rocking mode. γ asymmetric C-C-N vibration is observed at 1027 cm^{-1}. γ asymmetric C-C-C vibration is seen at 883 cm^{-1}. Strong bands at 740 cm^{-1} is due to in-plane bending vibration of methylene group and it is also due to C-N-C and C-C-N deformation modes.Therefore, IR spectral analysis of TBATBr-Zn(II) confirms the presence of various chemical bonds in the compound.

Table-2 Infrared absorption frequencies of TBATBr - Zn(II).

Wavenumber(cm^{-1})	Assignment
2960	C-H asymmetric stretching of methyl and methylene groups.
2872	C-H symmetric stretching due to methyl and methylene groups.
1476	C-H in-plane asymmetric bending due to methyl and methylene groups.
1380	C-H in plane symmetric bending due to methyl group.
1150	CH_2 and CH_3 twisting modes.
1106	CH_3 rocking mode.
1057	CH_2 rocking mode.
1027	γ asymmetric C-C-N
883	γ asymmetric C-C-C stretching vibration
740	Methylene inplane bending vibration, C-N-C and C-C-N deformation modes.

D. ^1H NMR spectroscopy

The normal proton NMR spectrum and the expanded spectrum of TBATBr-Zn (II) are shown in fig 5. In the spectra four signals are observed at different δ values for the methyl and methylene groups present in the n-butyl group of the compound. The expected δ values for methylene and methyl protons are 1.2 to 1.4 ppm and 0.7 to 1.1 ppm respectively. The observed higher δ value is due to the deshielding effect which confirms the presence of positive charge on the nitrogen of tetrabutylammonium group. The signal at 1.1δ is due to the presence of methyl protons (I) in the compound. Signal observed at 1.75 δ is due to methylene protons (III). The signal

for the methylene protons (IV) is observed as a triplet at 3.361 δ, 3.34 δ, 3.318 δ. The higher δ value is due to strong deshielding effect experienced by the protons. There are altogether eight butyl groups in the compound. All the butyl groups are in the same magnetic and chemical environment. Thus, the splitting of the NMR peak confirms the presence of four different kinds of protons characteristic of methyl and three different kinds of methylene protons present in n-butyl groups.

E. . ^{13}C - NMR spectroscopy

The ^{13}C-NMR spectrum of the compound TBATBr-Zn(II) is shown in fig 6. Hence, the methylene carbon nearer to the nitrogen atom has a higher δ value of 57. For the second methylene carbon atom from the nitrogen atom the δ value is 23. For the third methylene carbon atom from the nitrogen atom the δ value decreases further leading to a value of 19. Since the methyl group carbon atom is far away from the positively charged nitrogen atom the deshielding effect is very minimum leading to a δ value of 13. Though there are eight n-butyl groups in the tetrabutylammonium groups only four signals are observed confirming that all the eight n-butyl groups are identical.
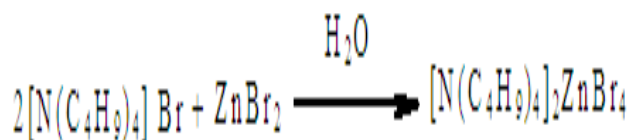
F. 3.5 Thermal analysis

The TG-DTG thermogram of the compound (TBATBr-Zn(II)) is shown in fig 7. The TG-DTG curve shows a one stage weight loss when heated between the room temperature and 700ºC i.e., the decomposition starts at 225ºC and ends at 480ºC. There is a weight loss of 92% which can be substantiated through the following decomposition reaction for the compound. This loss of 92% weight of the original compound can be accounted for by formulating the above decomposition reaction in which both tetrabutylammonium bromide and bromine vapours are simultaneously evolved. Zinc remains as a residue at these temperatures which accounts for   7.5 % residue. The observed value is 8 % for the residue. Zinc does not melt and vapourize at this temperature. For the zinc compound, three peaks are observed in the differential thermogram at 256.6, 385.4 and 470.5 suggesting absence of moisture in the compound. The compound melts at 256.6º C. The first stage of decomposition occurs between 256.6ºC and 385.4ºC whereas the second stage occurs between 385.4ºC and 470.5ºC. Though the TG curve indicates one stage decomposition, the DTG curve certainly confirms the two stage decomposition. Hence the one stage decomposition observed in the TGA can be split into two stages according to DTG observations. By comparing the TG and DTG analysis curves it is clear that the observed percentage loss by weight for the first stage is 72 which is very close to the theoretical value of 74. Low temperature DSC curves recorded for the sample (TBATBr-Zn(II)) between room temperature and -100ºC is shown in fig.8. It is found that the DSC thermogram contains one endothermic peak at -0.6ºC and another exothermic peak at 19.4ºC. The area of the first peak corresponds to -0.3678kj/mol and for the second peak 1.1375 kj/mol. The first peak corresponds to a phase transition at -0.6ºC while the second peak corresponding to 19.4ºC may be due to another phase transition involving liberation of heat. In the high temperature DSC thermogram of the zinc compound there is only one peak observed at 265.3ºC ignoring the other very small peaks observed at 73ºC, 94.1ºC and 112.2ºC fig 9. From the DTG and DSC curves we can

confirm the decomposition of the compound around 265.6ºC with an enthalpy of 94.982kj/mol.

IV. CONCLUSIONS

Single crystals of tetrabutylammonium tetrabromo zincate (II) (TBATBr-Zn), was grown by slow evaporation method at room temperature. The grown crystal was characterized through the elemental analysis of the compounds provides a useful method of confirming the stoichiometry of the compound. The powder X-ray pattern can be identified crystalline nature of the compound. In TG the mass or mass change of a system is measured as a function of temperature. In derivative thermogravimetry (DTG) rate of change of mass with time dw/dt is studied as a function of temperature and low temperature differential scanning calorimetry, techniques can be discussed. The spectral studies of FTIR, ^1H and ^{13}C NMR spectra were obtained for these compounds. Single crystal X-ray diffraction technique was solved using SCHELXS – 97 and refined by full matrix least square method Single crystal XRD method is a versatile method of determining the structure of crystalline compounds.

$$2[N(C_4H_9)_4] \, Br + ZnBr_2 \xrightarrow{\ H_2O\ } [N(C_4H_9)_4]_2 ZnBr_4$$

Scheme - 1   [N (C_4H_9)_4]_2ZnBr_4 crystal   TBATBr-Zn(II)]
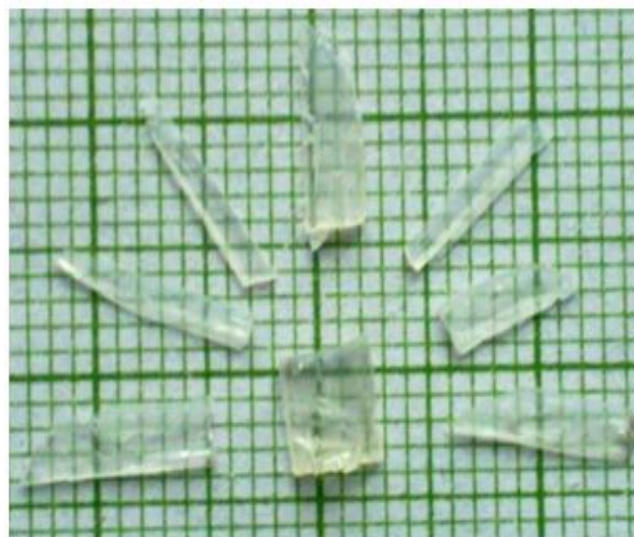
Fig 1   Structure of [N(C_4H_9)_4]_2ZnBr_4 crystal   TBATBr-Zn(II)
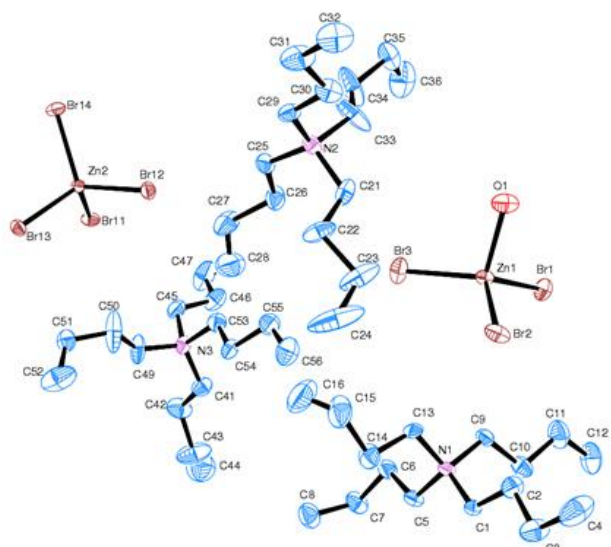
Fig 2   Single crystal structure X-ray diffraction of TBATBr-Zn(II)
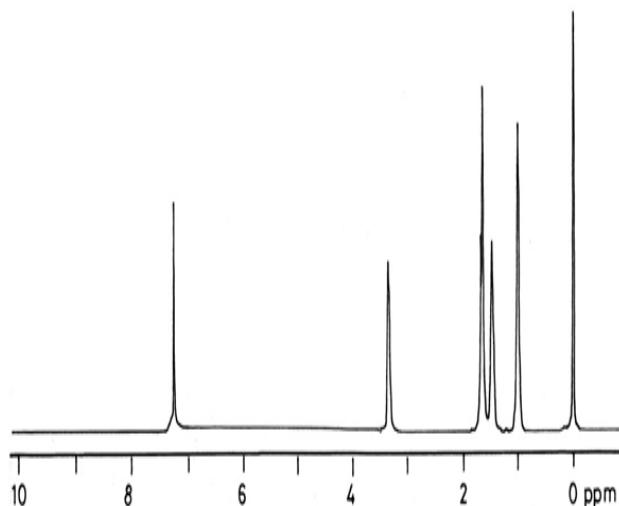

Fig 5 ^{1}H NMR spectrum of TBATB- Zn(II)
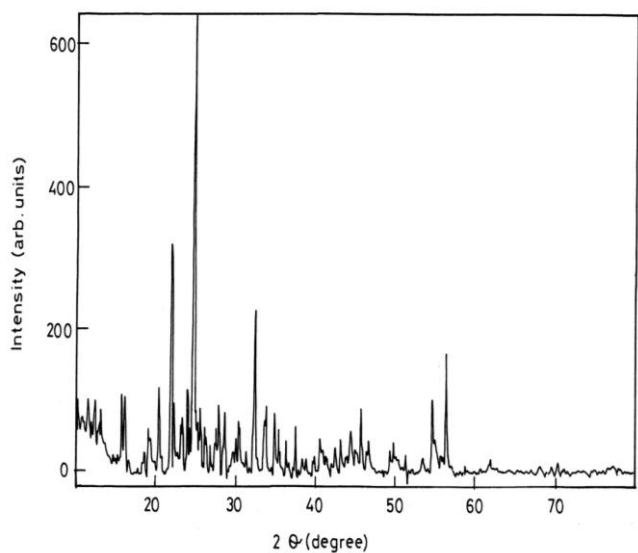

Fig 3   X-ray powder diffraction pattern of TBATBr-Zn(II)
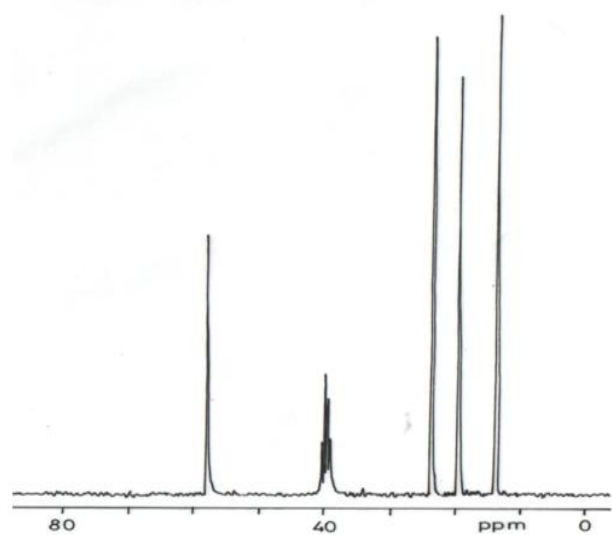

Fig 6 ^{13}C-NMR spectrum of TBATBr- Zn(II)
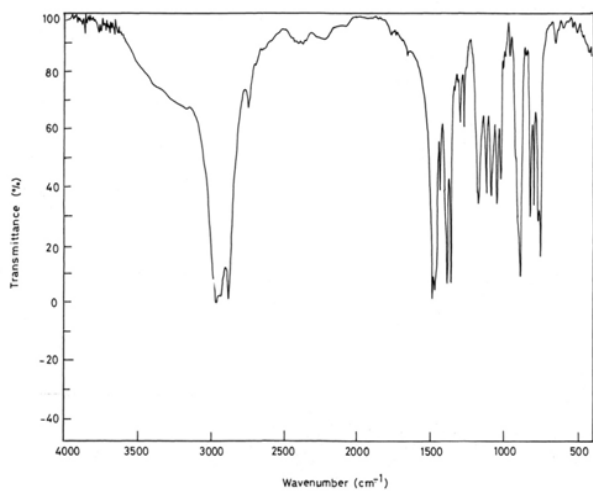

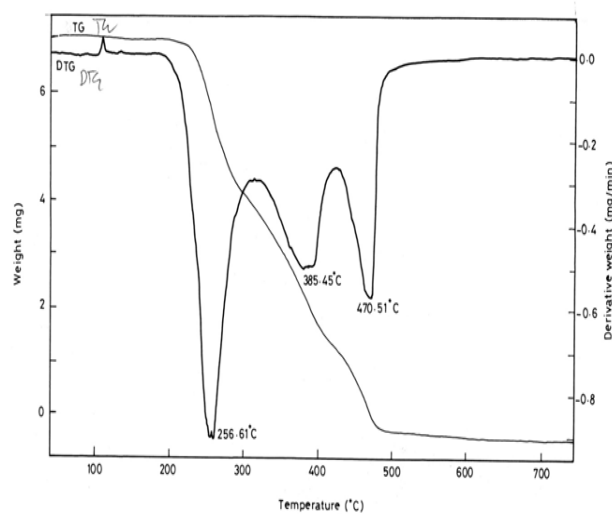**Fig 4**   FT-IR spectrum of TBATBr-Zn(II)

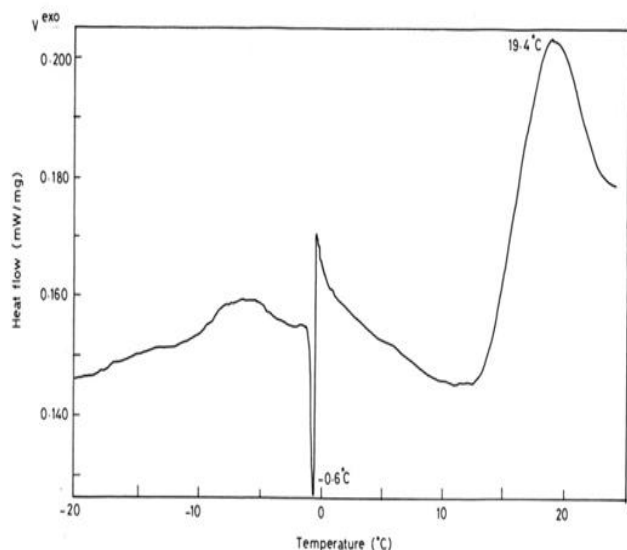**Fig 7**   the TG -DTG Thermogram of   TBATBr–Zn (II)
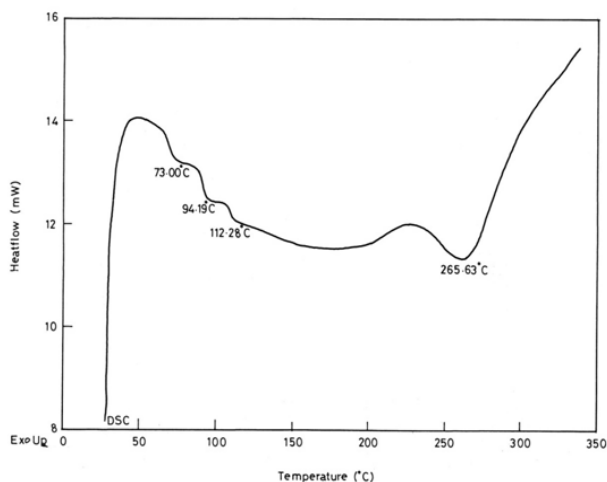
Fig 8 Low temperature DSC of TBATBr–Zn(II)

Fig 9 High temperature DSC of TBATBr-Zn (II)

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