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NEW TETRAPROPYLAMMONIUM TETRABROMOZINCATE COMPLEX $[(C_3H_7)_4N]_2ZnBr_4$(II) - SYNTHESIS, SPECTRAL, THERMAL CHARACTERIZATION AND ANTIOXIDANT ACTIVITY

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ABSTRACT. The importance of the A_2BX_4 complex (A = bivalent ion, NH_4^+ and its alkyl radical derivatives; B = bivalent transition metal ion and X = halogen) has increased in recent years due to fascinating physical properties such as ferro elastic, ferroelectric, and corresponding – unequal phases at low temperatures. In modern technologies the use of transistors, ferromagneticgarnets, sensor systems, softener templates, and ultraviolet light, as well as IR solid-state lasers, efficient crystalline materials are expected. A slow evaporation approach at room temperature was used to grow the TPAPBr-Zn $[(CH_3CH_2CH_2)_4N]_2ZnBr_4$(II) challenging kind A_2BX_4. Elemental analysis, powder diffraction, differential thermal analysis, FT-IR, proton and carbon-13 NMR spectroscopic techniques are used to characterize the synthesized compound. The presence of chemical groups and methylene radical groups in the compound are confirmed by the FT-IR spectra. The presence of an N-propyl group in the molecule is indicated by the nuclear magnetic resonance spectra. Thermogram of the compound reveals two-stage decomposition showing endo followed by exothermic decomposition resulting zinc oxide as an end product. As synthesised compound shown significant inhibitory activity towards free radical.

KEY WORDS: Synthesis, Elemental analysis, Spectroscopic studies, TG analysis, Antioxidant, Tetrapropylammonium tetrabromozincate(II)

INTRODUCTION

Tetraalkylammonium bromide (TAAB) is used as a catalyst, which are recyclable and have reproducible results without any loss of its biological activity. As antioxidants inhibit and scavenge radicals, they play an important role in protecting humans from infections and degenerative diseases [1]. Neelamegan Haridharan reported a very economical, inexpensive amide-based compound capable of exhibiting a high property for Hg^{2+} with TAAB [2].

A new metallopolymer device containing quaternary ammonia salts by oxidation of a compound unit is synthesized by using tetrapropyl ammonium bromide [3]. Among many quaternary ammonia salts, characid group ammonia Bromide (TPABr) could be an absorptive white-coloured soluble salt that's utilized as a tool for venomous metals. Currently, the large quantity of economic solid waste from scientific discipline and burning plants, attracts world attention on metals [4] as a result; it is hazardous to the environment and can result in major health problems [5]. Heterogeneous catalysts have earned a lot of attention as adequate methodology in polymer-based metal catalysts [6]. Tetra propyl ammonium bromide (TPABr) is used in various

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for biological application [7] because of their wise combination of the advantages [8]. The impact of tetra propyl ammonium bromide as a structure directive agent (SDA) on chemical science properties [9]. At sonochemical conditions, TPAB competing for the role of structural template to adjust the dimensions, shape, and curvature of vesicles [10].

Tetra alkylammonium thiometallates $(R_4N)_2MS_4$ (where R = propyl, octyl and M = Mo, W) are often produced, implying that ammonium thiometallates (ATM and ATT) can be easily combined with tetraalkylammonium bromides in ammonium ion and thiometallates are supportive compounds for modelling biological system and catalysts precursors [11]. An efficient stabilization of ink corrosion is achieved by peroxide decomposer tetrabutylammonium bromide [12]. New complexes of $[(CH_3CH_2CH_2)_4N]_2CoCl_4$ and $[(CH_3CH_2CH_2)_4N]_2MnCl_4$ were characterised by suggests that of single-crystal X-ray's diffraction, FT-IR, Raman vibrational study, NMR of ^{13}C, electrical properties, and thermal analysis [13]. The new organic–inorganic compound tetrapropylammonium tetrabromozincate $[N(C_3H_7)_4]_2ZnBr_4$ has been synthesized and characterized by single-crystalX-ray diffraction, differential scanning calorimetry, IR, Raman and impedance measurements [14]. In order to analyse the phase transition of this compound, bis-tetrapropylammonium tetrabromozincate with a monoclinic system (C_2/C space group) was synthesized and investigated as a function of temperature and frequency using Raman spectra and electrical characteristics [15]. Using three hydrogen bond donors at various salts: molar ratios in HBD, a new set of tetrapropylammonium bromide (TPAB)-based deep eutectic solvents (DESs) was synthesized [16]. TPABr is used as a solid catalyst and removes impurities [17].

Based on the findings, we decided to investigate new eutectic solvents based on tetra propylammonium bromide (TPABr) as a quaternary ammonium salt in combination with a metal salt for the synthesis of tetra propyl ammonium tetrabromide zincate(II). The research focuses on the synthesis and characterisation of novel metal complexes, as well as their potential applications in biological activities such as antioxidants.

EXPERIMENTAL

TPABr and zinc(II) bromide were sourced from Sigma Aldrich, and the chemicals and reagents were Analgar grade and utilised without purification in this present work. The solvent used in the experiments was double distilled water.

Synthesis of [TPATBr-Zn] complex

A warm aqueous solution containing tetra propyl group ammonium ion bromide was added with and zinc(II) bromide in a 1:1 molar proportion and kept for stirring for an hour. The resulting solution was filtered through Whatman-40 filter paper and set aside at room temperature for gradual evaporation after stirring. A white-colored substance was extracted and recrystallized after fifteen days. The complex is around $0.5\times0.5\times0.5$ cm^3 in size. The compound was separated and properly washed with water prior to getting air dried.

Characterization techniques

Physiochemical techniques are used to precisely characterise the as-synthesised complex. Using the same techniques utilised to get the FTIR, a Bruker IFS 66V spectrometer was used between the frequency bands of 4000 and 500 cm-1. At CECRI, Karaikudi, the X-ray diffraction pattern was recorded using Bruker AXS D8 Advance Model X-ray diffraction melts at a scanning speed of 50 per min, with X-ray reflections obtained between 100 and 800 degrees Celsius. A nitrogen atmosphere DTA thermal analyser was used to gather TG-DTG thermograms. The sample was heated from room temperature to roughly 820 °C at a rate of 10 °C per min. To carry out this

analysis, an advanced – II300 MHz spectrometer wasused. For the synthesized complex ^1H NMR and ^{13}C NMR spectrum was recorded using an advanced–II 300 MHz spectrometer. A JASCO V-630 UV-Visible spectrophotometer was used to measure the free radical scavenging activity. The radical scavenging activities of antioxidants was tested using the DPPH radical and the result was compared to that of normal vitamin C (ascorbic acid). The following formula was used to calculate the percentage of activity

$$\% \text{ of the capacity for scavenging} = (A_0\text{-}A_C)/A_0 \times 100. \quad (I)$$

RESULTS AND DISCUSSION

In aqueous medium, tetrapropyl group ammonium ion bromide reacts with zinc(II) bromide to form a complex.

$$2[(C_3H_7)_4N]\,Br + ZnBr_2 \rightarrow [(C_3H_7)_4N]_2ZnBr_4 \quad (II)$$

The elemental analysis of the complex (TPAPBr-Zn) is displayed in Table 1. The experimental data correlates with the theoretical data, confirming the synthesised complex's stoichiometry.

Table 1. Elemental analysis of the complex (TPAPBr-Zn).

Compound	C %		H %		N %		Zn %	
TPAPBr- Zn	Exp.	Theo.	Exp.	Theo.	Exp.	Theo.	Exp.	Theo.
	33.9	34	7.4	7.45	3.68	3.7	8.75	8.63

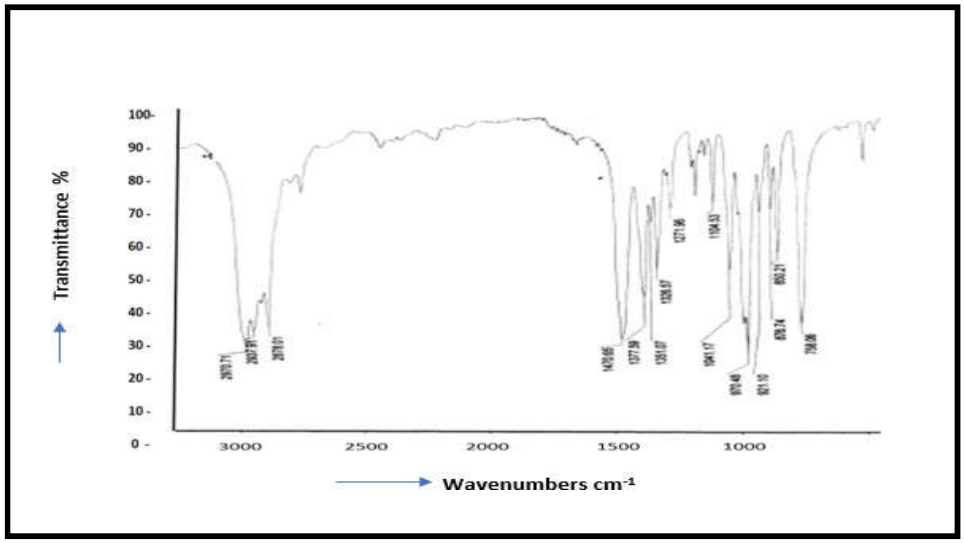

Figure 1. FT-IR spectra for TPAPBr-Zn(II) complex.

FTIR spectroscopy

Figure 1 shows the FT-IR spectrum of the synthesised complex, and Table 1 shows the absorption frequencies assigned to the complex. The peak at 2937 cm^{-1} is due to the CH_2 group's symmetric

C-H stretching vibration, whereas the peak at 2878 cm^{-1} is due to the CH_3 group's symmetric C-H stretching vibration [18]. The CH_3 and CH_2 groups have bending deformation modes at 1470 and 1377 cm^{-1}, respectively. The C–N stretching modes present in the tetrapropylammonium group are represented by a prominent band at 1041 cm^{-1}. The presence of asymmetric C-C and C-H vibrations causes the set of peaks at 876.74 and 850.21 cm^{-1}. At 758.06 cm^{-1}, the rocking modes of C-C-N and C-N-C deformation vibrations are found.

Thermal analysis

The thermal stability and reactivity of the complex may be studied by using TG-DTG analysis. Figure 2 shows the TPAPBr-Zn (II) TG-DTG thermogram. The compound is heated uniformly at 10 °C/min in a nitrogen environment to 840 °C. A sharp endothermic peak at 125.38 ºC without weight loss refers the melting point of the grown crystals. Subsequent endothermic followed by exothermic decomposition observed at 252.38 and 436.61 ºC relates to the two-stage decomposition resulting zinc oxide as an end product (obsd. 10%; calcd. 10.7%).

$$[N(C_3H_7)_4]_2ZnBr_4 \rightarrow N_2\uparrow + ZnO + 2Br_2\uparrow + \text{Hydrocarbons}\uparrow \quad \text{(III)}$$

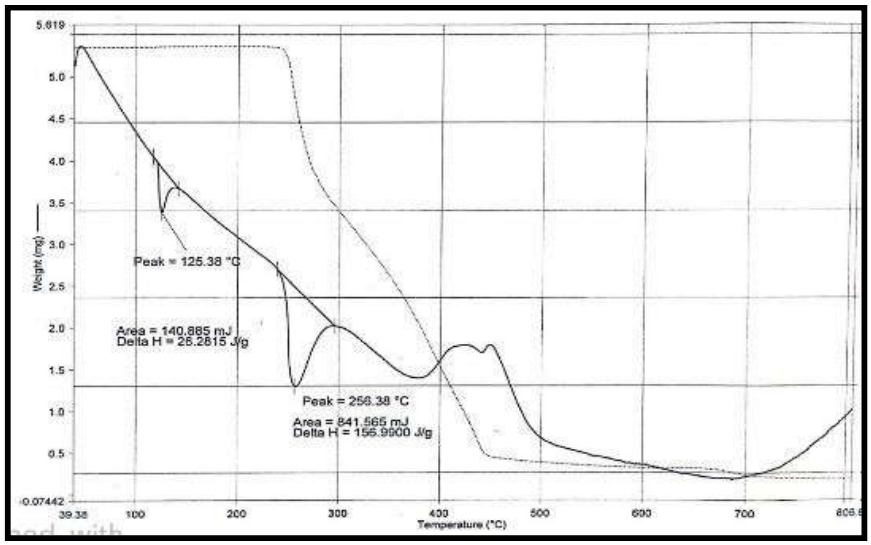

Figure 2. TG -DTG thermogram of TPAPBr-Zn(II) complex.

^{1}H NMR spectroscopy

The proton nuclear magnetic resonance spectrum of the zinc complex was shown in Figure 3 and in Table 2. The spectra revealed four signals for the methyl and methylene groups within the compound's n-propyl group. For the methylene radical and methyl protons, a multiplet wasseen in the range of 1.5 to 1.7 ppm and 0.8 to 1.0 ppm, respectively. Deshielding caused by thepresence of positive charge on nitrogen in the tetrapropylammonium group accounts for the higher δ value. The signal of the methylene group (III) is observed as a multiplet with values of 3.169 δ, 3.137 δ and 3.118 δ. The higher δ value is due to the protons' strong weakening effect. There are eight different protons in the synthesized molecule. The presence of four different kinds of methyl

group protons and three different kinds of methylene group protons in N-propyl groups is confirmed by the nuclear magnetic resonance peak.

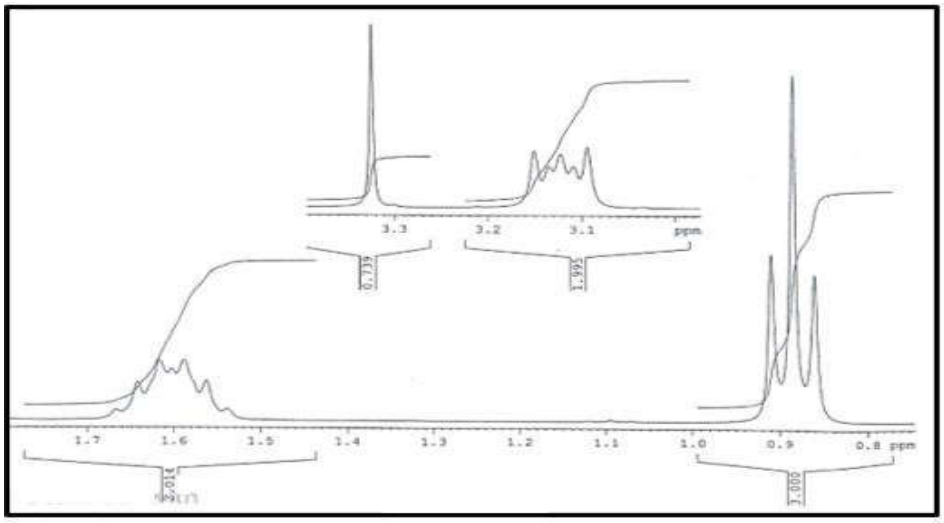

Figure 3. ^{1}H NMR spectrum of TPAPBr-Zn(II).

Table 2. ^{1}H NMR spectrum values of TPAPBr-Zn(II).

Protons	TPATBr-Zn (δ ppm)
Methyl(III)	0.8861
Methylene(II)	1.6031
Methylene(I)	3.1350

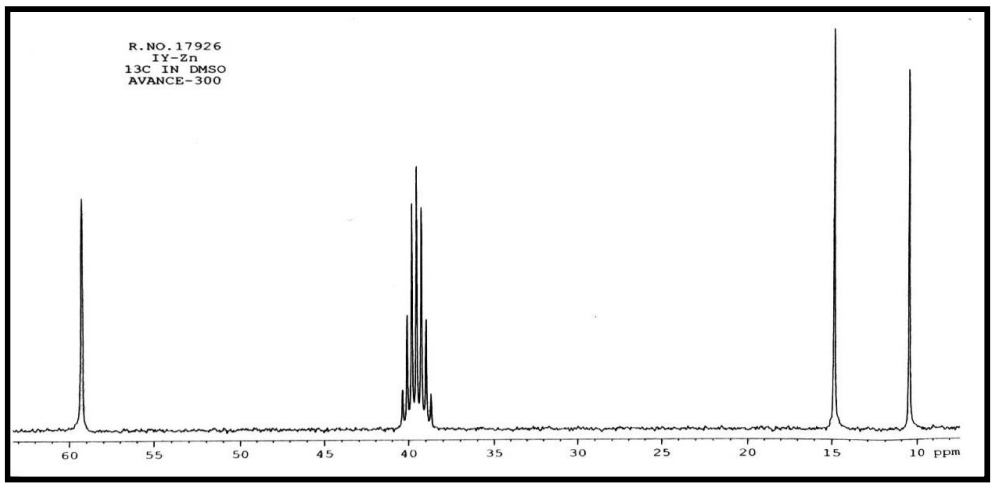

Figure 4. ^{13}C NMR spectrum of TPAPBr-Zn(II).

^{13}C - NMR spectroscopy

Figure 4 shows the ^{13}C-NMR spectra of the TPATBr-Zn(II) molecule. As a result, the methylene carbon, which is directly attached to the nitrogen atom, has a higher δ - value of 59. A signal at δ - value 14 can be seen on the neighbouring methylene carbon. The value of the carbon atom methyl(III), which ends up with a value of δ-10. Although the alkyl's carbon atomis distanced from the nitrogen atom, the resulting shielding effect is negligible, and it has the δ-13 [19]. The presence of three signals indicating that the four n-propyl group in the similar environment.

PXRD

Powder X-ray diffraction measurements were also used to characterise the compound.The d-spacing and diffraction angle values of the PXRD peaks are represented in Table 3, and the powder pattern is shown in Figure 5. Sharp peaks were obtained at specific 2θ angles which reveal the crystalline nature and homogeneity of the synthesized complexes.

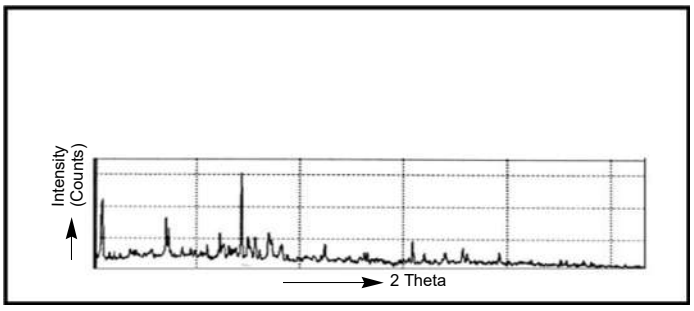

Figure 5. X-ray powder diffraction pattern of TPAPBr-Zn(II).

Table 3. PXRD data of complex.

d	2 Theta	I
8.24615	10.72	55
5.22468	16.9566	40
5.14464	17.2224	29
4.22087	21.0306	15
3.9909	22.2575	24
3.6461	24.3932	100
3.29753	27.0181	26
3.15662	28.2487	15
2.7583	32.4328	17
2.45846	36.5196	12
2.20355	40.9223	29
2.14595	42.072	13
2.05433	44.0441	13
1.98121	45.76	17
1.84871	49.2489	15
1.79857	50.7175	3
2.12056	42.6002	5
1.9678	46.0898	3
1.93507	46.9156	8
1.82078	50.0559	7

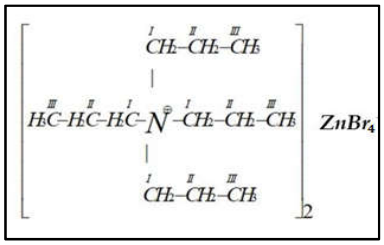

Figure 6. Structure of TPAPBr-Zn.

Antioxidant activity

The antioxidant activity of Zn complex was investigated using ascorbic acid as astandard against DPPH. Free radicals play an important function in causing biological damage. In vitro, radical scavenging studies were carried out in triplicate, with an absorbance varianceof less than 10% of the mean. Within the experiments, ascorbic acid (AA) was used as a positive control. The 1,1-diphenyl-2-picrylhydrazyl (DPPH) radical is temperature stable and widely used to verify the scavenging activity of organic and inorganic compounds [20]. The spectrophotometric approach was used to measure the DPPH atom scavenging activity [21]. DPPH is a firm free radical that can receive an electron or hydrogen radical to form a stable diamagnetic molecule. Because DPPH has an odd electron, it absorbs strongly at 517 nm. Theabsorbance reduces stoichiometrically in relation to the quantity of electrons or hydrogen atomstaken up when this electron becomes paired off. The ability of numerous compounds to behaveas free radical scavengers has been thoroughly tested using this reaction's change in absorbance. As a result, the compound's antioxidant effect is stronger the faster the absorbancedecreases. Blois' technique was used to examine the zinc complex's free radical scavenging effects using the DPPH radical [22] under the same condition. Various concentrations of the test compound (20, 40, 60, 80, and 100 µg/mL) in 1 mL DMF were added to a 4 mL 0.004 percent (w/v) methanol solution of DPPH. The absorbance was measured against a blank at 517 nm after a 30-min incubation period at room temperature. The bleaching of the purple-colored methanol solution of DPPH was used to determine the compound's hydrogen atom or electron donation capacity. The results of all tests and analyses were averaged after three repetitions were completed.

All of the assays in the above mentioned were performed in triplicate, and the proportion of activity was calculated using the formula zip, where A_0 and A_C are the absorbance's in the absence and presence of the tested compounds, respectively, scavenging capacity = $[(A_0–A_C)/A_0] \times 100$. The percentage of activity can be used to calculate the 50% activity (IC_{50}). According to the results, the complex has an IC_{50} value of 25.20±0.50 mg/mL, which is comparableto the standard ascorbic acid (19.45±1.02 mg/mL), and shown an active inhibition above 60 µg/mL concentration. According to the results, the synthesized complex has the ability to scavenge free radicals and will operate as a potent free radical inhibitor or scavenger, as expected.

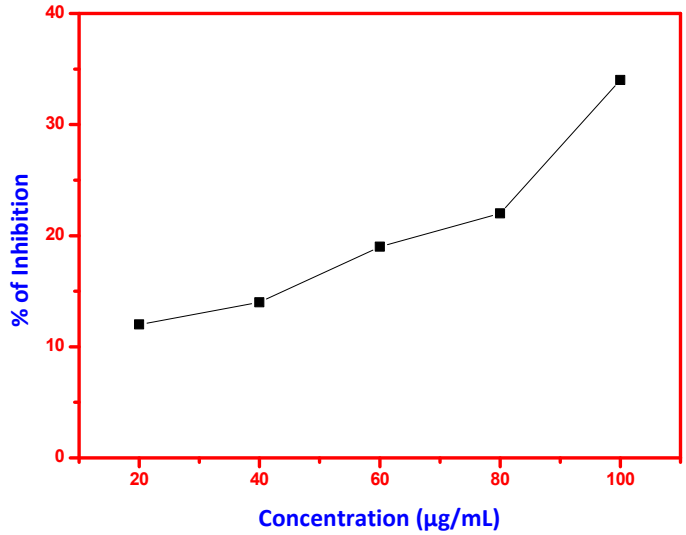

Figure 7. DPPH scavenging assay, percentage inhibition of zinc complex at different concentration varying from 20. 40, 60, 80 and 100 µg/mL.

CONCLUSIONS

The newly synthesized tetrapropylammonium tetra bromo zincate(II) (TPAPBr-Zn) chemical was found to be crystalline in nature. Elemental analysis, powder X-ray diffraction (PXRD), Fourier transform infrared (FT-IR), proton and carbon-13 nuclear magnetic resonance chemical analyses were used to characterize the prepared compound. Elemental analysis confirmed the compound's molecular formula: $[(CH_3CH_2CH_2)_4N]_2ZnBr_4$(II). The compound's powder XRD pattern reveals the expected sharp peaks that characterize a crystal. The crystalline nature of the solution-prepared compound is evidenced by well-defined peaks at completely different 2 θ values. The presence of methyl, methylene, C-C and C-N bonds is confirmed by the FT-IR spectrum. The anti-oxidant activity of the compound as synthesized suggests that it has the flexibility to scavenge free radicals and will behave as a potent free radical inhibitor or scavenger, as expected. These studies reveal that the prepared zinc complexcould have potential biological applications.

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