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Synthesis, characterization, theoretical calculations and biological studies of nano Sodium tetrafluoroborate (III)

ABSTRACT

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Synthesis, characterization, spectral and theoretical calculations of sodium tetrafluoroborate (III) (STFB) has been studied in this research. Sodium tetrafluoroborate (III) was synthesized by a sonochemical method and characterized by IR, UV/VIS, ¹¹B-NMR and Mass spectrometer techniques. The nano compound was characterized by scanning electron microscopy (SEM), X-ray powder diffraction (XRD) and IR spectroscopy. The structure of synthesized compound was optimized at the B3LYP/LANL2DZ level of theory and theoretical parameters such as structural data, molecular specifications, and infrared spectra were extracted by using Gaussian 03 program. Theoretical data show good agreement with the experimental results. Biological properties of this compound such as antitumor and antibacterial properties studied. This new complex showed excellent antitumor activity against one kind of cancer cells that is K742 (human chronic myeloid leukemia) cells. Also the compound was tested against the bacterial species *Staphylococcus aureus*, *Escherichia coli*, *Staphylococcus Epidermidis*, *Streptococo B* and *Shigella*.

Keywords: Sodium tetrafluoroborate (III); Nano-particle preparation; Optimized; Antitumor activity; K742 (human chronic myeloid leukemia) cells; Antimicrobial activity.

INTRODUCTION

Room temperature ionic liquids have generated considerable excitement in recent years as a new type of solvent media that possesses minimal vapor pressure [1-4]. The tetrafluoroborate and other ionic liquids provide real practical advantages over earlier molten salt systems because of their relative insensitivity to air and water. Until recently, little was known about the fundamental physical chemistry of ionic liquids in general [5].

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Synthesized $\text{Na}^+[\text{BF}_4]^-$ showed antitumor activity against one kind of cancer cells that is K742 (human chronic myeloid leukemia) cells. Also the compound was tested against the bacterial species *Staphylococcus aureus*, *Escherichia coli*, *Staphylococcus Epidermidis*, *Streptococo B* and *Shigella*.

EXPERIMENTAL

Materials and Instruments

Starting materials were obtained from Merck (Berlin, Germany) and were used without further purification. Solvents were purified by standard methods. Fourier transform infrared (FT-IR) spectra were recorded on a Bruker spectrophotometer in KBr pellets. Surface morphology of product was characterized by using a LEO-1430.VP scanning electronic microscopy (SEM) with an accelerating voltage of 15 kV. X-ray powder diffraction (XRD) measurements were performed using a Philips diffractometer manufactured by X'pert with monochromatized Cu Ka radiation. Sizes of selected samples were estimated using the Scherer method. For identification a scanning electron microscope samples were gold coated.

Cell culture

The human chronic myeloid leukemia: K742 cell line, used for treatment with the drugs, was provided. K742 cells were grown at 37°C in an atmosphere containing 5% CO_2 , with RPMI-1640 MEDIUM HEPES Modification with L-glutamine and 25mM HEPES (SIGMA-ALDRICH CHEMIE GmbH) supplemented with 10% heat-inactivated fetal bovine serum (FBS) (Gibco), 2.7% sodium bicarbonate and 500 mg/L ampicillin.

Synthesis of sodium tetrafluoroborate (III) (STFB)

The compound was prepared by mixing (5ml) BF_3 with (0.4gr, 9.5 mmol) NaF at room temperature. The mixture was stirred for 7 h. White precipitate of desired product, $\text{Na}^+[\text{BF}_4]^-$, was dried and washed with hexane to remove all impurities and residues. The preparation reaction of compound is as follows:



Melting point of this compound is $372\text{--}374^\circ\text{C}$, and it is soluble in methanol, acetonitrile, DMSO, water and little soluble in ethanol and not soluble in ether, toluene, chloroform and hexane. Spectroscopic data of synthesized compound are reported below.

$\text{Na}^+[\text{BF}_4]^-$: IR (KBr): 485.55 (ν B-F), 732.9(ν B-F), 1129.58(ν B-F) cm^{-1} ; UV/Vis 280(43) [ϵ , $\text{M}^{-1}\text{cm}^{-1}$]; ^{11}B - NMR (DMSO): $\delta = -20.88$ ppm.

Synthesis of nano sodium tetrafluoroborate (III) (STFB)

Ultrasonic device was employed to improve the dispersibility of the STFB nanoparticles dispersed in aqueous solutions. To prepare the $\text{Na}^+[\text{BF}_4]^-$, solutions of NaF and BF_3 in MeOH was positioned in a high-density ultrasonic probe, operating at 20 kHz with a maximum power output of 600 W. The obtained precipitates were filtered off, washed with methanol and then dried in air. Spectroscopic data of synthesized compound are reported below.

IR (KBr): 485 (ν B-F), 732 (ν B-F), 1129 (ν B-F) cm^{-1} .

Characterization of nanoparticles

X-ray diffraction (XRD) technique was used to determine the ingredients of the sample. The morphology of nanoparticles was observed using a scanning electronic microscopy (SEM). The obtained samples were characterized and compared via FT-IR analysis with bulk (non-nano) forms. FT-IR spectrometer at room temperature in the range from 400 to 4000cm^{-1} . (Figure 1).

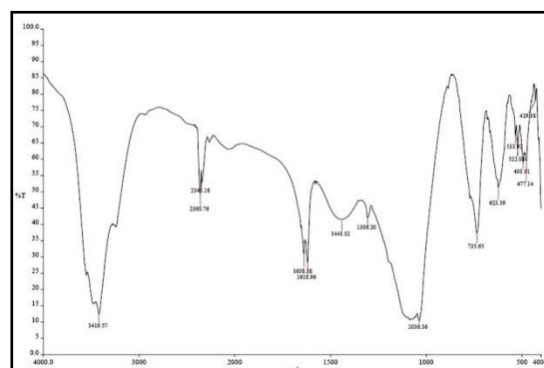


Fig. 4. FT-IR spectra of NaBF_4 nanoparticles.

Computational Method

The DFT method was applied to optimize and calculate molecular data of synthesized compound. The calculation was done by using the Gaussian 03 programs [6]. For DFT, Becke's three-parameter exchange functional [7] was used in combination with the Lee–Yang–Parr correlation functional (B3LYP) [8] with LANL2DZ basis set [9]. After the optimization procedures, frequency calculations were done to extract vibrational mode and test the correctness of true minima. The vibrational frequencies and intensities (spectra) and the eigenvectors for the normal modes were corrected with the appropriate factor [10] and displayed on a computer screen to identify the dominating motions. The calculated and experimental vibrational spectra are in good agreement.

Antimicrobial activity

The compound was tested against the bacterial species, *Staphylococcus Epidermidis*, *Streptococo B* and *Shigella*. These studies were carried out using *Amikacin* as standard antibacterial agent by Kirby Bauer disc diffusion method [11]. The test solutions were prepared in DMSO. Diffusion method [12, 13] was used to evaluate the antimicrobial activities of the tested compounds as follows: 0.5 ml spore suspension (10^6 to 10^7 spore ml^{-1}) of each of the investigated organisms was added to a sterile agar medium just before the solidification, then poured into sterile Petri dishes (9 cm in diameter) and left to solidify. Using sterile cork borer (6mm in diameter), wells were made in each dish, then 0.1 ml of the tested compounds dissolved in DMSO were poured into three wells and the dishes were incubated at 37 °C for 24 h, where clear or inhibition zones were detected around each well.

In Vitro anti-cancer Activities

The compound was assayed for cytotoxicity in vitro against K742 (human chronic myeloid leukemia) cells. The cell lines were provided by the Pastour Institute Laboratory of natural and Biomimetic in Iran. The procedure for cytotoxicity studies was similar to that of reported earlier [13]. Briefly, in order to calculate the concentration of each drug which produces a 50% inhibition of cell growth (IC_{50}), 190 mL of cell suspension (5×10^4 cell/mL) were exposed to

various concentrations of compound dissolved in sterile DMSO. The final concentration of DMSO in the growth medium was 2% (v/v) or lower, concentrations without effect on cell replication [14, 15]. After incubation periods 72 h for all cell lines, the cell concentrations were determined both in control and in drug-treated cultures. All experiments were carried out in six times.

RESULTS AND DISCUSSION

In this paper, we report the synthesis of sodium tetrafluoroborate (III) and its nano compound. The compound was obtained by reaction of BF_3 and NaF and was synthesized through a one-step reaction. Nano-particle of this compound was prepared by ultrasonication of the methanolic solution. Our procedure for producing compound has some advantages. For example, there is no side product in preparing (STFB) in our method, the reaction is quite fast and does not require any severe conditions such as high pressure or high temperature, and it is not sensitive to air. After preparing compound, it was characterized by IR, NMR, and mass spectrometric. The theoretical calculations have been used for this compound. Therefore, we applied the Gaussian program and the molecule was optimized by the DFT method using B3LYP/LANL2DZ basis set. The infrared spectrum of the (STFB) was studied using the same method and basis set. Table 1 consists of calculated (theoretical) IR frequencies in $1\text{--}4000 \text{ cm}^{-1}$ of (STFB) after applying correction by an appropriate scaling factor.

Table 1. Comparison of the experimental and calculated data of frequencies for $[\text{BF}_4]^-$

Bond	Experimental	Calculated
B-F	485.55	493.51
B-F	732.9	733.24
B-F	1129.58	1140.45

The same conclusion can be drawn by comparing other experimental frequencies with the related calculated frequencies. Moreover, calculated frequencies are helpful in prediction of the structure–property relationship of (STFB) and

the infrared spectra of this salt spotted the structure of compound. This geometrical structure can be obtained from the optimized structure of the compound; **Figure 2** shows the final optimized structure of (STFB) which is obtained following the calculations. From the optimized structure of the title compound, molecular parameters can be deduced. Molecular parameters can depict molecular structure. Therefore, we computed bond lengths and bond angles of (STFB) and these are listed in **Table 2**.

Figure 3 shows the XRD pattern of compound prepared by the sonochemical process. Estimated from the Sherrer formula for the calculation of particle sizes from the broadening of the XRD peaks ($D = 0.891\lambda/\beta\cos\theta$, where D is the average grain size, λ is the X-ray wavelength (0.15405 nm), and θ and β are the diffraction angle

and full width at half maximum of an observed peak, respectively). The average size of the particles was found to be around 45 nm, which is in agreement with the value obtained from the SEM images (**Figure 4**).

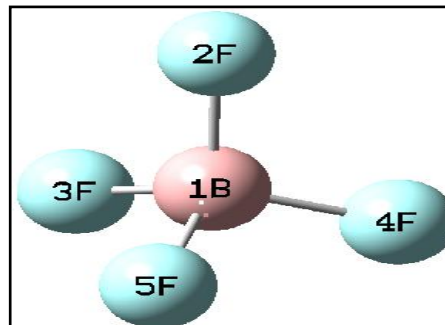


Fig. 2. Optimized structure of $[\text{BF}_4]^-$

Table 2. The Calculated Bond lengths [\AA] and Bond angles [$^\circ$] of $[\text{BF}_4]^-$

Bond	Bond lengths [\AA]	Angles	Bond angles [$^\circ$]
R(B1,F2)	1.4361	A(F2,B1,F4)	109.4712
R(B1,F3)	1.4361	A(F2,B1,F5)	109.4712
R(B1,F4)	1.4361	A(F3,B1,F4)	109.4712
R(B1,F5)	1.4361	A(F3,B1,F5)	109.4712
		A(F4,B1,F5)	109.4712

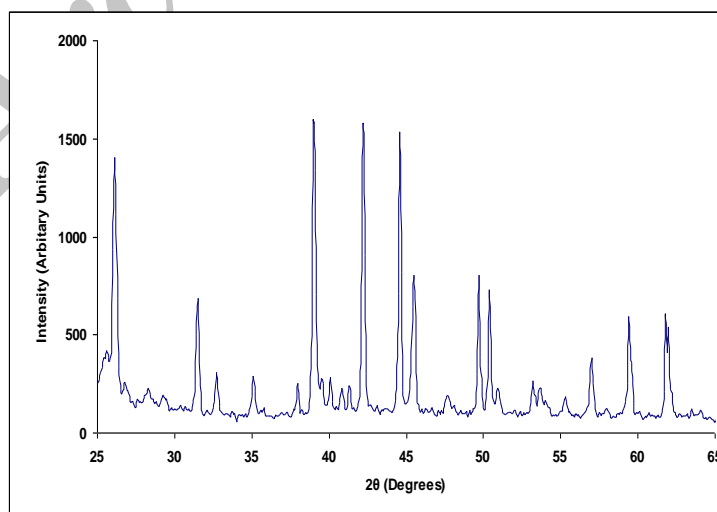


Fig. 3. The XRD pattern of NaBF_4 nanoparticles.

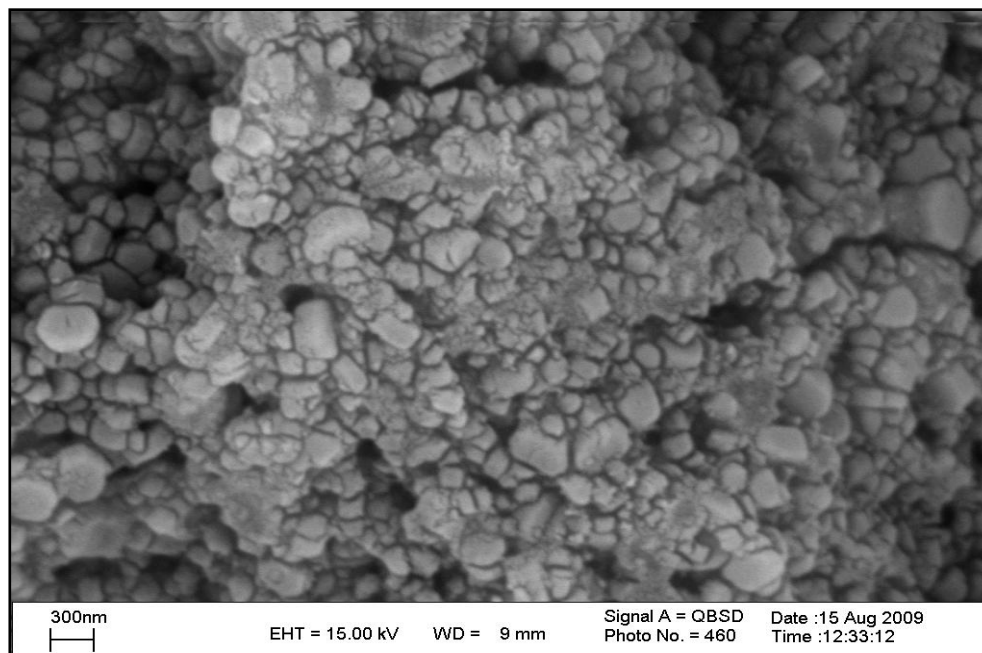


Fig. 4. SEM photographs of the sample NaBF_4 nanoparticles.

Antimicrobial activity

The antibacterial activity of the (STFB) is given in Table 3. The activity increases with the increase in concentration of test solution containing the complexes [12].

Table 3. In vitro antibacterial studies of the NaBF_4 .

Compound	STFB
<i>Escherichia coli</i>	-
<i>Streptococo B</i>	2mm
<i>Staphylococcus Epidermidis</i>	-
<i>Staphylococcus aureus</i>	1mm
<i>Shigella</i>	-

Cytotoxicity studies

(STFB) and nano-(STFB) compounds have been tested against one human cancer cell lines: K742. The general method used for testing on anti-tumor properties of these compounds is the standard testing method that has been previously described in greater detail in some papers [16] and abbreviated in following:

After preincubation lasting 24h at 37°C in a 5% CO_2 atmosphere and 100% humidity, the

tested compounds in the concentration rang 0.1-28 μM for (STFB), 0.1-20 μM for nano-(STFB) were added. The incubation lasted 72 h and at the end of this period IC_{90} and IC_{50} of the dead cells and live cells was measured by Trypan blue. IC_{90} and IC_{50} values which are the compounds concentrations lethal for 90% and 50% of the tumor cells were determined both in control and in compounds concentrations. The compounds were first dissolved in DMSO and then filtrated. The corresponding 50% and 90% inhibitory dose (IC_{50} and IC_{90}) values are shown in Table 4. After the incubation periods 72 hours for all cell lines, the cell concentrations were determined both in control and in drug-treated cultures. All experiments were done for six times (Figure 5).



Fig. 5. Tumor cell after 72h with $\text{Na}[\text{BF}_4]$ compound

Table 4. 72 h IC₅₀ and IC₉₀ values (m) obtained for Na[BF₄] nanoparticles.

compound	IC ₅₀ for cell line	IC ₉₀ for cell line
Na[BF ₄] nanoparticles	>0.1 mM	>0.01 M

CONCLUSION

In this research the detail studied the synthesis, characterization, biological properties and theoretical data of Sodium Tetrafluoroborate (III) and Nano Sodium Tetrafluoroborate (III). In summary, the molecular structure of Nano particles is confirmed by the presence of functional groups in FTIR spectra. Also theoretical data show good agreement with the experimental result. In addition, the values of crystallite size in nano scale are demonstrated by X-ray diffraction method for Nano Sodium Tetrafluoroborate (III) powders. Based on the results of biological tests Nano Sodium Tetrafluoroborate (III) showed antitumor activity against one kind of cancer cells that is human cancer cell lines: K742. Also the nanoparticles were tested against the bacterial species *Staphylococcus Epidermidis*, *Estreptococo B* and *Shigella*.

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