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Full Length Research Paper

Synthesis, characterization, theoretical calculations and biological studies of potassium trifluorothiocyanoborate (III)

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Synthesis, characterization, spectral and theoretical calculations of potassium trifluorothiocya noborate (III) (PTFTCB) has been studied. Potassium trifluorothiocyanoborate (III) was synthesized and characterized by IR, UV/VIS, ^{11}B-NMR and mass spectrometer techniques. 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 anti-bacterial 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, Estreptococo* B and *Shigella.*

Key words: Potassium trifluorothiocyanoborate (III), new synthetic method, optimized, antitumor activity, K742 (human chronic myeloid leukemia) cells, anti bacterial activity.

INTRODUCTION

Boron compounds, when added as additives also improve the flame retardant properties of phenolic compounds. Non-flammable phenolic molding compounds have been prepared by adding boric acid and sodium borate. A number of patents have been issued which describe the formation of non-combustible phenolic resins. Most of the technology concerning the flame retardation of phenolic resins involves either the incorporation of substances known to exhibit flame retarding properties into the backbone structure of the organic polymers or the addition of various compounds or combinations of compounds into the resin system to impart flame resistant characteristics (Hussey, 1983).

There is an inverse proportionality between industrial importance and scientific interest in the case of boron compounds. It is a simple salt which dissociates in solution and whose properties have, with a few exceptions, been known for many years (Wasserscheid et al., 2000; Welton, 1999; Wilkes, 2002; Wasserscheid et al., 2002; Becke, 1993). Many efforts have been done on preparation of new borate compounds. In this paper, we report a new method of the synthesis of potassium trifluorothiocyanoborate (III). The compound was obtained by reaction of BF_3 and KSCN which was produced through a one-step reaction. Our procedure for producing the compound has some advantages. For example, there is no side product in preparing PTFTCB 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.

Synthesized $K^+[BF_3(SCN)]^-$ 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*, *Estreptococo* B and *Shigella*.

MATERIALS AND METHODS

Starting materials were obtained from Merck (Berlin, Germany)

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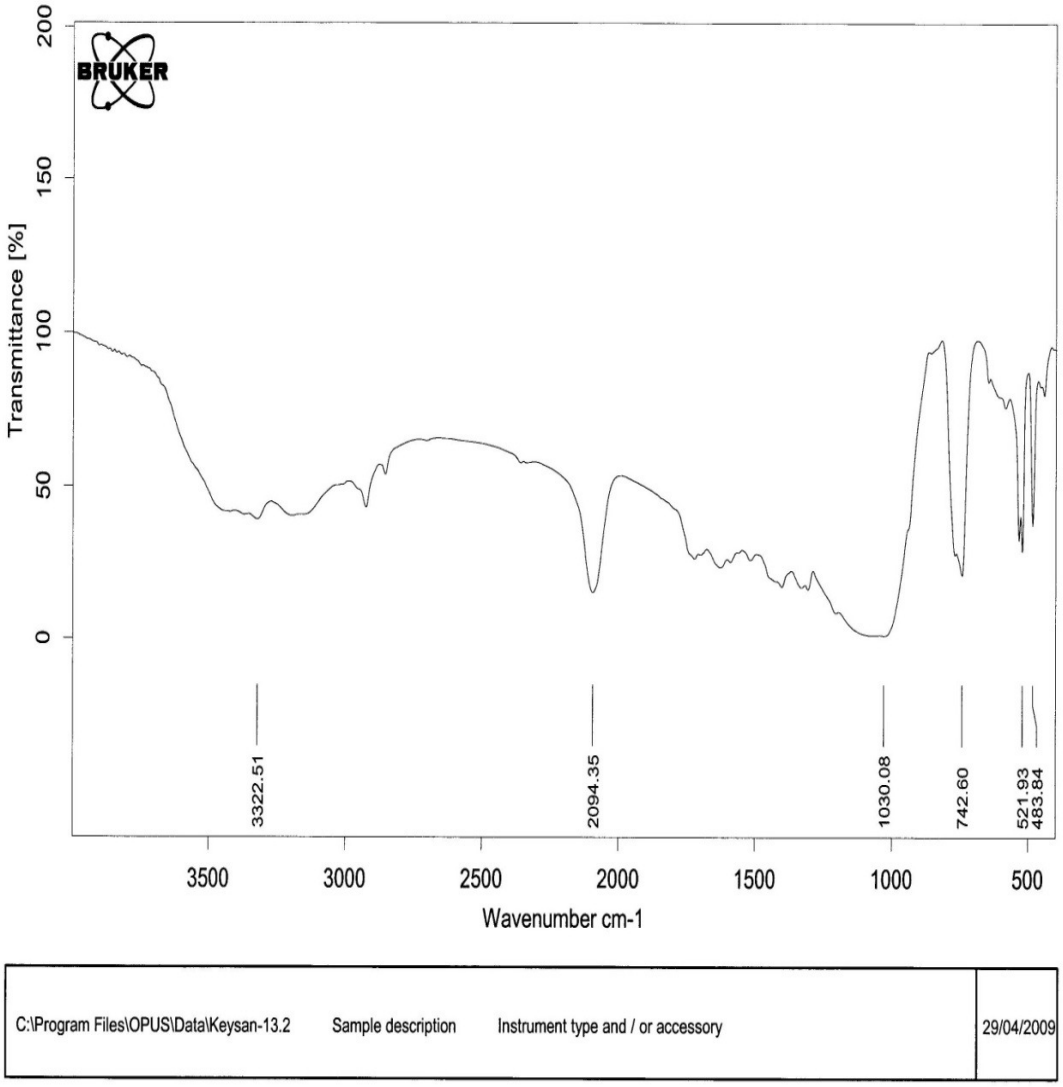

Figure 1. The FT-IR spectra of compounds $K[BF_3(SCN)]$ (Disk KBr).

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. Vibrational spectra of compounds by IR instrument (BRUKER TENSOR) 420 model with the use of KBr tablet is taken. Electron spectra of all compounds using and Pablo wave has been recorded ^{11}B-NMR spectra using NMR 500 MHz spectrometer BRUKER AVANCE DRX 500 model, were recorded in dimethyl sulfoxide solvent. Mass spectra of the compounds synthesized by Agilent Technology Model 5973 were recorded.

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 25 mM 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 potassium trifluorothiocyanoborate (III)

The compound was prepared by mixing (3.3 ml) BF_3 with (0.6 g, 6.18 mmol) KSCN at room temperature. The mixture was stirred for 7 h. White precipitate of desired product $K^+[BF_3(SCN)]$, was dried and washed with hexane to remove all impurities and residues. The preparation reaction of compound is as follows:

$$BF_3 + KSCN \rightarrow K^+[BF_3(SCN)]^-$$

Material was analyzed after 240°C, and it is soluble in methanol, DMSO, water and little soluble in ethanol and acetonitrile, and not soluble in ether, toluene, chloroform and hexane.
Spectroscopic data of synthesized compound are reported as follows:

$K^+[BF_3(SCN)]^-$: IR (KBr): 1030 (v B-F), 742 (v B-S), 521(v S-C) cm^{-1}, 2094 (v C-N) cm^{-1}; UV/Vis: 242(1770) [ε, M^{-1} cm^{-1}], 283(900) [ε, M^{-1} cm^{-1}], 330 (170) [ε, M^{-1} cm^{-1}], ^{11}B-NMR (DMSO): δ = -20.88 ppm (Figures 1 to 4). For $K[BF_3(SCN)]$: C, 7.29; N, 8.50%. Found: C, 7.35; N, 9.1%.

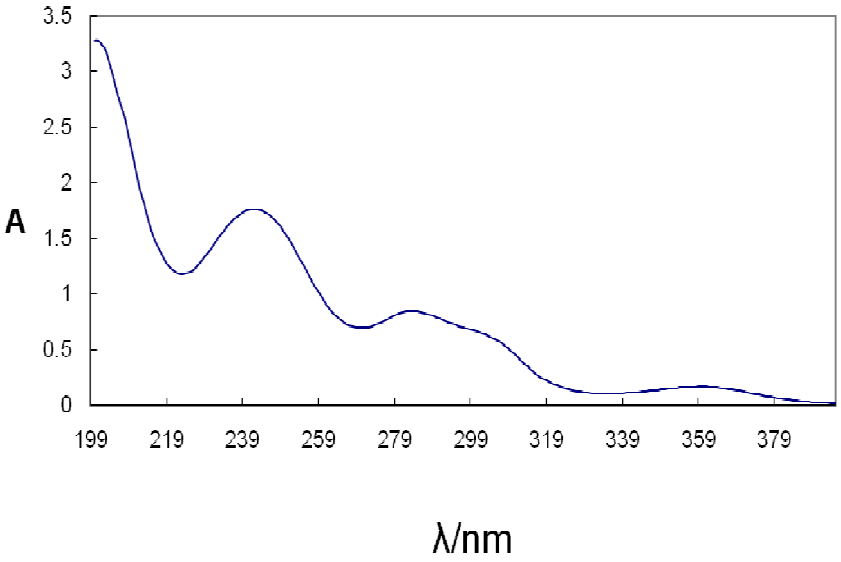

Figure 2. The electronic spectrum of $K[BF_3(SCN)]$ in acetonitrile solvent concentration C = 10-3 M.

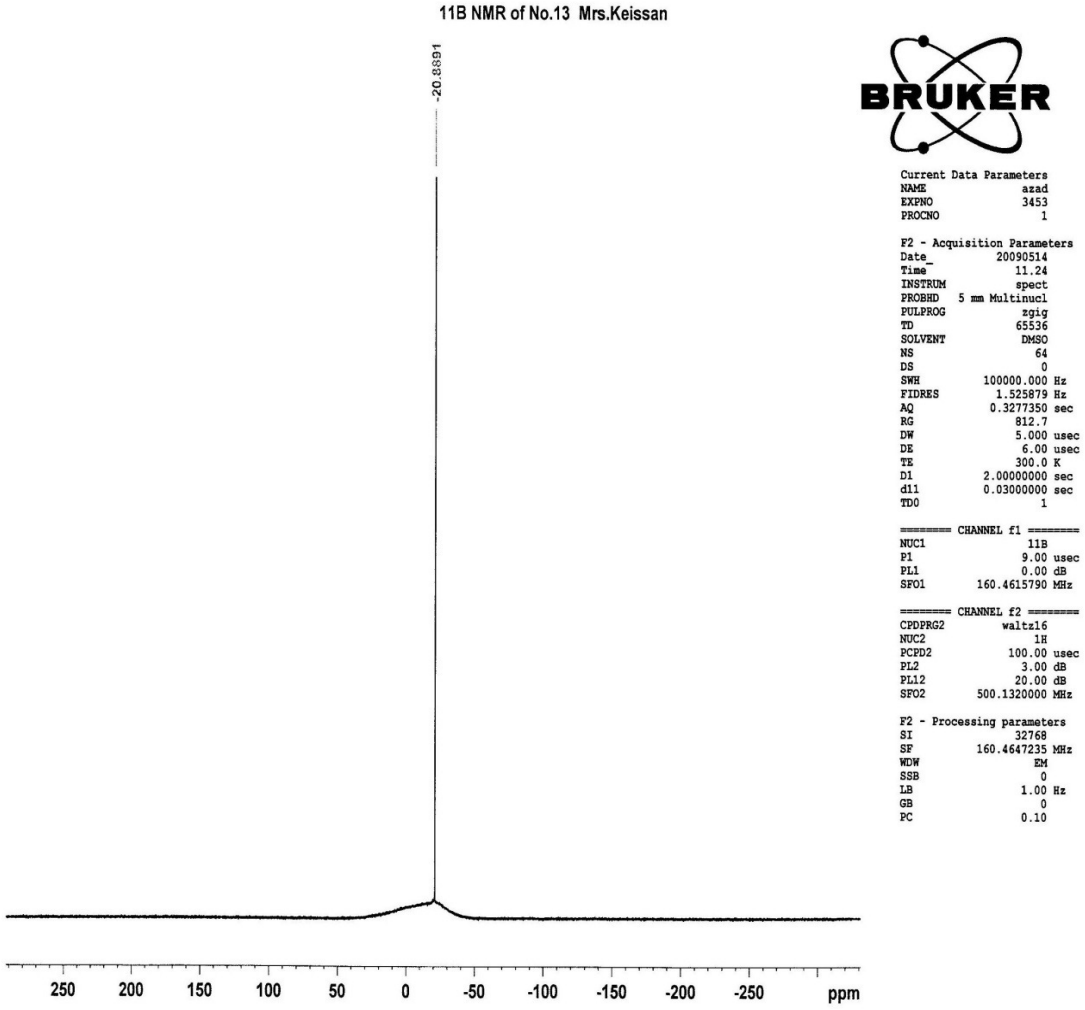

Figure 3. The ^{11}B-NMR spectrum of $K[BF_3(SCN)]$ in the DMSO solvent.

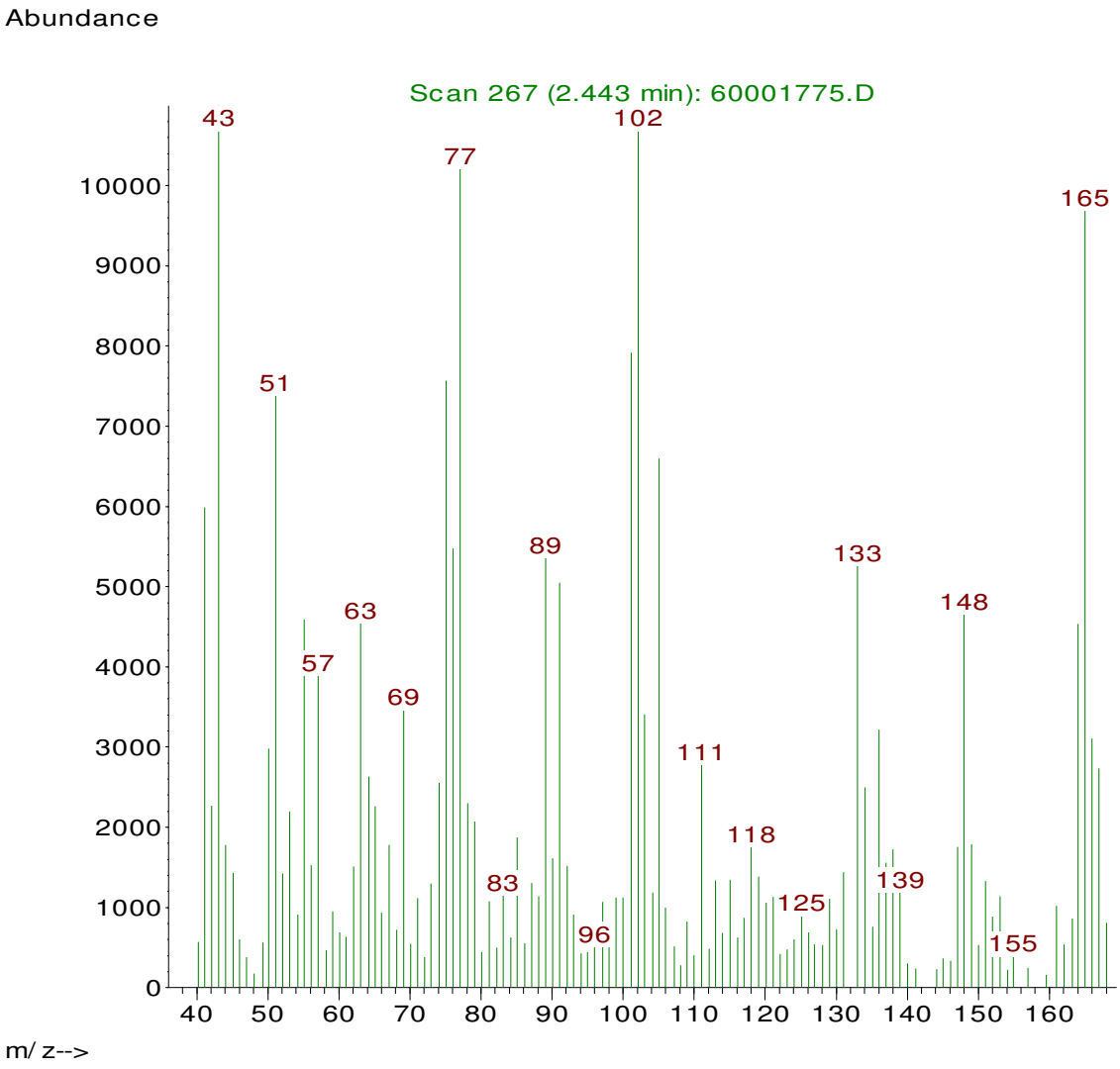

Figure 4. The mass spectrum of $K[BF_3(SCN)]$.

Computational method

The Density functional theory (DFT) method was applied to optimize and calculate molecular data of synthesized compound. The calculation was done by using the Gaussian 03 programs. For DFT, Becke's three-parameter exchange functional (Lee et al., 1988), was used in combination with the Lee–Yang–Parr correlation functional (B3LYP) with LANL2DZ basis set (Bauer et al., 1996). 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 (Ferrari et al., 1999), 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, *S. epidermidis, Estreptococo* B and *Shigella.* These studies were carried out using *Amikacin* as standard antibacterial agent by Kirby Bauer disc diffusion method (Wahab et al., 2004). The test solutions were prepared in DMSO. Diffusion method (Zhao et al., 1998) was used to evaluate the antimicrobial activities of the tested compounds as follows: 0.5 ml spore suspension (106 to 107 spore ml^{-1}) of each of the investigated organisms was added to a sterile agar medium just before solidification, then poured into sterile Petri dishes (9 cm in diameter) and left to solidify. Using sterile cork borer (6 mm 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 Instutiute Laboratory of Natural and Biomimetic in Iran. The procedure for cytotoxicity studies was similar to that reported earlier. Briefly, in order to calculate the

Table 1. Combined mass spectra profile of $K[BF_3(SCN)]$.

As expected	The species	m/e	Intensity
Na $[F_4]$	B	98	10000
$Na[BF_3]$	F	49	610
$[BF_4]$	Na	95	8000
Na $[F_3]$	BF	85	10000
Na [F]	BF_3	105	4800
$[F_3{}^{12}C^{14}N]$	K[B]	83	12000

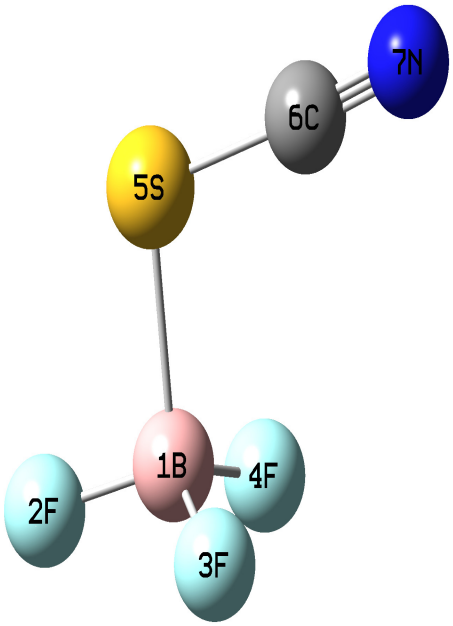

Figure 5. Optimized structure of $[BF_3(SCN)]^-$.

concentration of each drug that 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. After incubation periods of 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 and series.

RESULTS

In this paper, we report a new method of the synthesis of potassium trifluorothiocyanoborate (III) and its compound. The compound was obtained by reaction of BF_3 and KSCN and was synthesized through a one-step reaction. Our procedure for producing compound has some advantages. For example, there is no side product in preparing PTFTCB 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.

$$BF_3 + KSCN \rightarrow K^+[BF_3(SCN)]^-$$

After preparing, compound was characterized by IR, NMR, and mass spectrometry. Details of mass parts are shown in Table 1. The theoretical calculations have been used for this compound. Therefore, we applied the Gaussian program and molecule was optimized by the DFT method using B3LYP/LANL2DZ basis set. The infrared spectrum of the PTFTCB was studied using the same method and basis set consists of calculated (theoretical) IR frequencies in 1 to 4000 cm^{-1} of PTFTCB after applying correction by an appropriate scaling factor (Figures 5 and 6; Tables 2 to 4).

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 PTFTCB and the infrared spectra of this salt tell about the structure of compound. This geometrical structure can be obtained from the optimized structure of the compound. Figure 6 shows the final optimized structure of PTFTCB that is obtained after 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 PTFTCB and these are listed in Table 3.

Antimicrobial activity

The antibacterial activity of the PTFTCB is given in Table 5. The activity increases with increase in concentration of test solution containing the complexes (Wahab et al., 2004).

Cytotoxicity studies

STFTCB compound have been tested against one human cancer cell lines: K742. The general method used for testing on anti-tumor properties of this compound is the standard testing method that has been previously described in greater detail in some papers and is described as follows: After pre-incubation lasting 24 h at 37°C in a 5% CO_2 atmosphere and 100% humidity, the tested compound in the concentration range of 0.1 to 28 µM for STFTCB, 0.1 to 20 µM for STFTCB was added.

The incubation lasted for 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 for the compound concentrations lethal for 90 and 50% of the tumor cells were determined both in control and in compound concentrations lethal for both in compound-treated cultures. The compound was first dissolved in DMSO and then filtrated. The corresponding 50 and 90% inhibitory dose (IC_{50} and IC_{90}) values are shown in Table 3. After the incubation periods, 72 h for all cell lines, the

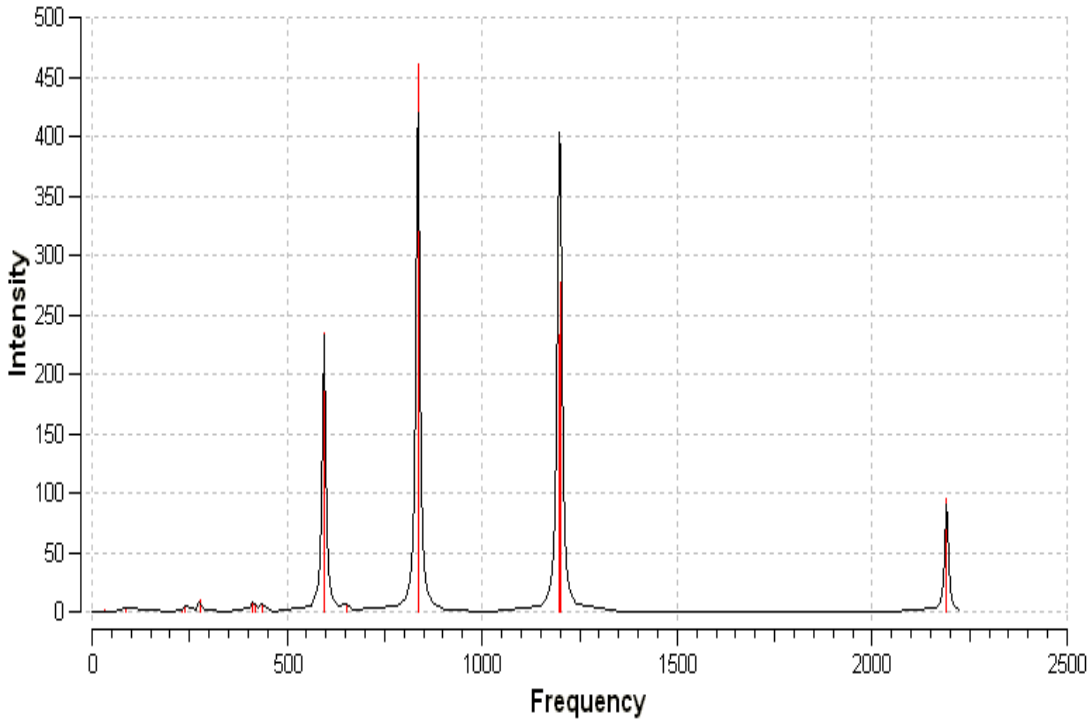

Figure 6. The calculated IR spectrum of the $[BF_3(SCN)]^-$, (anion part).

Table 2. Comparison of the experimental and calculated data of frequencies for $BF_3[(SCN)]^-$.

Bond	Experimental	Calculated
C≡N	2094	2191.01
B-F	1030	1201
B-S	742	835.39
S-C	521	651.77

Table 3. The calculated bond lengths [Å] and bond angles [°] $[BF_3(SCN)]^-$.

Bond	Bond lengths (Å)	Angles	Bond angles (°)
R (B1, F2)	1.4139	A (F2, B1, F3)	112.8026
R (B1, F3)	1.4079	A (F2, B1, F4)	112.8018
R (B1, F4)	1.4079	A (F2, B1, S5)	101.2471
R (B1, S5)	2.1085	A (F3, B1, F4)	112.1651
R (S5, C6)	1.7406	A (F3, B1, S5)	108.55
R (C6, N7)	1.1817	A (F4, B1, S5)	108.5529
		A (B1, S5, C6)	104.8267

cell concentrations were determined both in control and in drug-treated cultures. All experiments were done for six times.

Table 4. IR data obtained from calculations for $[BF_3(SCN)]^-$.

Bond	Vibration
C≡N	2191.01
B-F	1201
B-S	835.39
S-C	651.77

DISCUSSION

Synthetic method

We present the mentioned results as recommendations in order to increase information with respect to potassium trifluorothiocyanoborate (III) and continue the quest for more details. A new method for synthesis of potassium trifluorothiocyanoborate (III) was used. The compound was obtained by reaction of BF_3 and KSCN on the base of an addition reaction from metathesis type substitution. In better words, this compound was synthesized through a one-step reaction. The procedure for producing compound has some advantages. For example, there is no side product in preparing PTFTCB 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.

Table 5. *In vitro* antibacterial studies of the $K[BF_3(SCN)]$.

Compound	*Escherichia coli*	*Estreptococo* B	*Staphylococcus epidermidis*	*Staphylococcus aureus*	*Shigella*
PTFTCB	-	0.2	0.1	-	-

Table 6. 72 h IC_{50} and IC_{90} values (m) obtained for $K[BF_3(SCN)]$.

Compound	IC_{50} for cell line	IC_{90} for cell line
$K[BF_3(SCN)]$	>0.1 mM	>0.01 M

Characterization

In summary, the molecular structure is confirmed by presence of functional groups in FTIR spectra. In the case of PTFTCB, we observed the following changes. The bands appeared around 2094, 1030, 742 and 521 cm^{-1} due to v CN, v B-F, v B-S, v B-F and v S-C. Mass spectrometer was used for characterization of molecule compartments. The signals appeared at m/e 98, 49, 95, 85 and 105 that related to Na $[F_4]$, Na $[BF_3]$, $[BF_4]$, Na $[F_3]$ and NaF compartments.

Theoretical study

Quantum calculations have been used for prediction and extraction of structural and spectral data of PTFTCB. 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. 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 PTFTCB and the infrared spectra of this salt tell about the structure of compound. Figure 6 shows the final optimized structure of PTFTCB that is obtained after calculations. Molecular parameters can depict molecular structure.

Biological properties

According to the results of biological tests, potassium trifluorothiocyanoborate (III) showed antitumor activity against one kind of cancer cells that is human cancer cell lines: K742. The IC_{50} cytotoxicity values of the complex was compared to that found for the starting organic bases, and is far from some of the anti-cancer agents used nowadays, that is, cisplatin and oxaplatin compounds, and shows less anticancer properties of this compound. 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 and is described as follows: 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 that are the compounds concentrations lethal for >0.1 mM and >0.01 M of the tumor cells were determined both in control and in compounds.

This compound also was tested against the bacterial species *S epidermidis, Estreptococo B* and *Shigella* This compound was shown little antibacterial activity.

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