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Single crystal growth, spectroscopic and surface studies of A novel organic-inorganic compound: BCTZ

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Abstract

In the present work, good quality single crystals of $[(18C_6)K]_2[Zn(SCN)_4]$;[BCTZ] were grown using slow solvent evaporation technique at room temperature. The cell parameters of the grown crystals were confirmed by SXRD technique. The grown crystal found to be crystallized in a non-centrosymmetric space group p_{na21} of an orthorhombic system. The samples of BCTZ were subjected to spectral and surface studies and the results are reported. The functional groups were identified through FT-IR studies. Surface features were studied through SEM analysis. The NMR profile indicates that the crystalline compound contains one type of carbon which is due to the incorporation of Zn with SCN ligand in the BCTZ. The etching study indicates the occurrence of different types of etch pit patterns. The purity of the compound was confirmed by HPLC studies.

Keywords: SXRD, SEM, HPLC

Introduction:

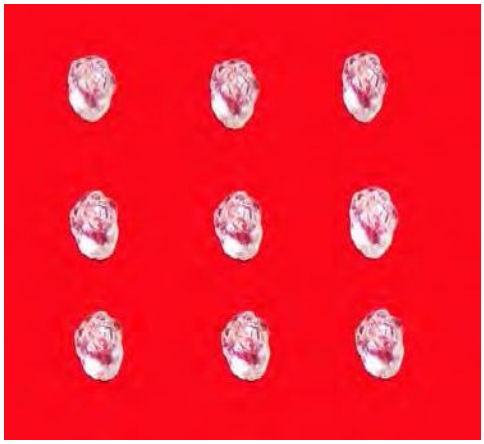
Crystal growth is very important and fundamental part of material science and engineering. The metal-organic and coordination compounds offer a variety of molecular structure by changing the metals, ligands, coordination numbers and so on. This diversity of molecular structure gives opportunity to tune the electronic properties of the molecules, and hence to exploit the linear and nonlinear optical properties [1-3]. In metal thiocyanate complex the thiocyanate (SCN) plays a crucial role in combining the versatile ambidentate ligand with two donor atoms. The modes of metal coordination with thiocyanates are best understood in terms of the Hard-Soft Acid-Base (HSAB) concept developed by pearson, Balarew and Duhlew [4,5]. The metal-thiocyanate complexes have all the good characteristics such as crystallizing in a non-centro symmetric space group 14 , pale colours and high thermal stability [6-7].

In the present work, the title compound Bis[(18-crown-6) potassium] Tetrakis (isothiocynato) zinc(II) ;$[18C_6(K)]_2[Zn(SCN)_4]$;BCTZ has been synthesized. The structural aspects of BCTZ were reported by A.N. Cheskhlov . However, the characterization aspects and surface analysis studies were not reported elsewhere. Hence, in the present work, efforts were made to synthesize good quality single crystals and their by the spectral and surface studies were carried out on the sample and reported.

Experimental

The calculated amounts of analytical grade reagent materials were

used. To grow the single crystals of BCTZ, crown either, potassium thiocyanate and zinc chloride were chosen in the molar ratio 2:4:1and dissolved in an aqueous solution and thoroughly stirred for three hours to obtain a homogeneous solution. The filtered solution was allowed to evaporate at room temperature. .Colorless single crystals of BCTZ were obtained within 10 days which are shown in Figure 1.



3. Characterization studies

The crystal structure was studied using X-ray diffraction analysis by means of a CAD4 automated single crystal diffractometer. FT-IR studies were carried out through BRUKER IFS 66 V FT-IR spectrometer. FT- Raman spectrum was recorded in the range 40-4000 cm^{-1} BRUKER RFS 27 Raman Spectrometer. The sample was subjected to High performance liquid chromatography study using HPLC instrument. Surface morphology studies were undertaken with the help of JOEL JSM 6610 LV scanning electron microscope. The itch pits were observed through the optical microscope. The NMR spectrum was recorded using BRUKER SPECT instrument at room temperature operating at 400 MHz.

3.1 SXRD

The crystal structure of BCTZ is studied by CAD4 automated diffractometer, MoK_{α} radiation. The compound consists of three complex ions: one $[Zn(NCS)_4]^{2-}$ anion and two host–guest cations $[K(18\text{-crown-}6)]^{+}$ [8], all linked through one bridging anionic ligand SCN^{-} into a tri nuclear complex molecule $[[K(18\text{-crown-}6)]_2[Zn(NCS)_4]]$ (**I**).The crystals of BCTZ are Ortho rhombic with the cell parameters a=17.604(4) Å, b=14.190(3) Å, c=17.625(6) Å, V=4403(2) $Å^3$, z=4, space group $pna2_1$. [9]

3.2 SEM analysis

The scanning electron microscope is used for studying the surface morphology of the synthesized samples. The accelerating voltage of the electron beam is 15kV and the image is magnified to 25,000 times than its original size. The particle morphology and elemental analysis of the grown crystal BCTZ are observed by using JOEL JSM-6610LV scanning electron microscope, Oxford Instruments, Inca Penta FETX3.JPG connected with energy dispersive spectra. The surface morphology image of crystals of the title compound is shown in Figure 2 and 3. It is clear from the SEM micrographs of the sample that the crystal surface contains voids of irregular size and dendrites like growth pattern of micro crystals. The presence of valleys and cracks are predominantly seen on the surface of the crystal. It is believed that the grown crystals can be subjected to such defects unless growth parameters like temperature and pH is carefully optimized [10]. Few micro crystals are viewed on magnification. The shape of the crystals is pyramidal, which is the actual shape of the grown crystal of BCTZ.

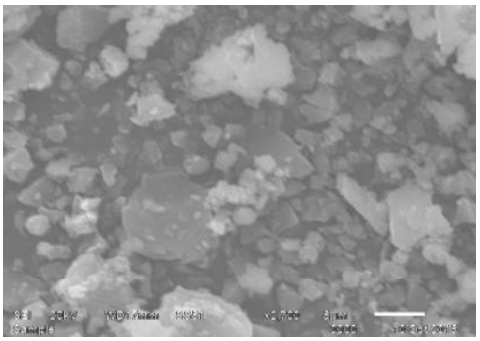


Figure 2

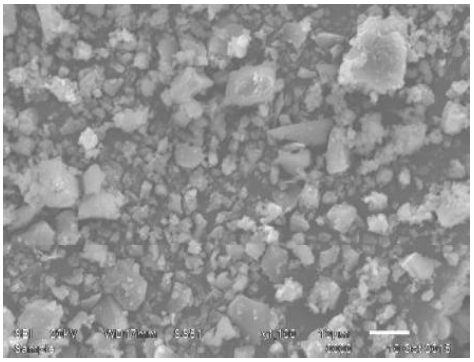


Figure 3

3.3 Etching studies

The crystals with defects can destroy the mechanical and electrical properties which damage the usefulness of the crystals. The nonlinear optical properties depend upon the crystalline perfection. Etching is one of the desirable study to identify defects in the grown crystal. When the sample is dissolved in a solvent, the reversal of the growth takes place by giving the well-defined etch pits. Etching of surface using desirable solvent gives information about the surface features.

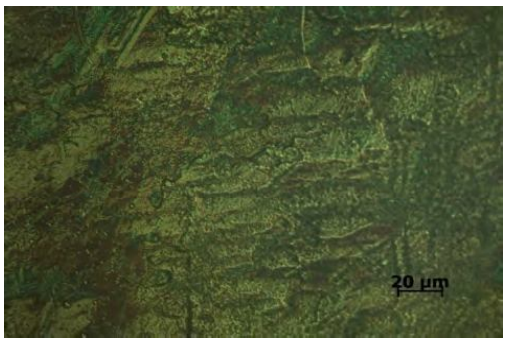


Figure 4

3.4 NMR Studies

H^1 NMR: The proton magnetic resonance spectrum of the BCTZ crystal was recorded using BRUKER SPECT instrument at room temperature and operating at 400MHz. Single crystals of

Optical microscopy was employed to study the surface features of grown crystal BCTZ. The crystal was immersed in water for an etching period of 5s and 10s. The crystal was taken out gently and cleaned with the tissue paper and instantly placed under the optical microscopy. For the etching periods of 5s, 10s, layer type patterns were observed. The Figure 4 depicts the itching patterns. The etching study revealed the formation of layer pattern, which is an indicative of two dimensional mechanism [11].

BCTZ were dissolved in methanol solvent and the recorded spectrum is shown in the Figure 5. It is observed that the spectrum has double bonded C-H protons or CH_2 protons attached to the end groups .The single signal peak is observed at 1.823ppm

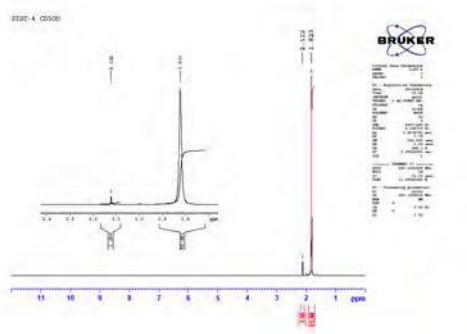


Figure 5

C^{13} NMR: Carbon NMR spectrum has been used to find out the carbon atoms present in the sample and to confirm the grown crystal BCTZ. The chemical shift values of the carbons were plotted on the x axis and the intensity on the Y axis. C^{13} NMR spectrum is shown in the Figure 6. The signal at 68.4ppm was assigned to the single carbon lying in methoxy group. The remaing methoxy group carbons produced a single peaks at 25 and 65 ppm. These observations indicate the incorporation of one type of SCN ligand in the grown crystal BCTZ.

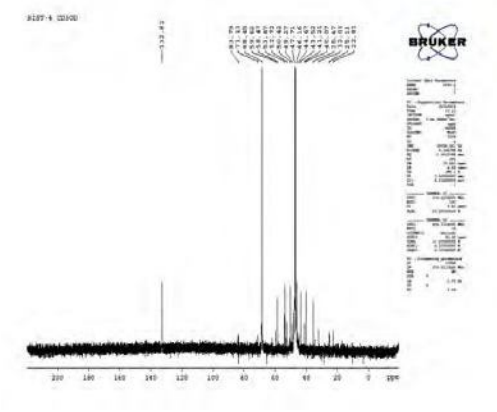


Figure 6

HPLC Studies

To find out the purity of the crystalline materials of BCTZ, the sample was subjected to High Performance Liquid Chromotography study using HPLC instrument with mobile phase : 100 pecentage methanol, flow rate 1 ml/min. Injection per sample :20ul, wavelength 210 nm. The recorded BCTZ chromatogram is presented in the Figure 7. The spectrum shows single peak with the retention time of 3.969 minutes with the peak voltage of 490mV.The signal peak with high resolution clearly shows that BCTZ sample is pure.

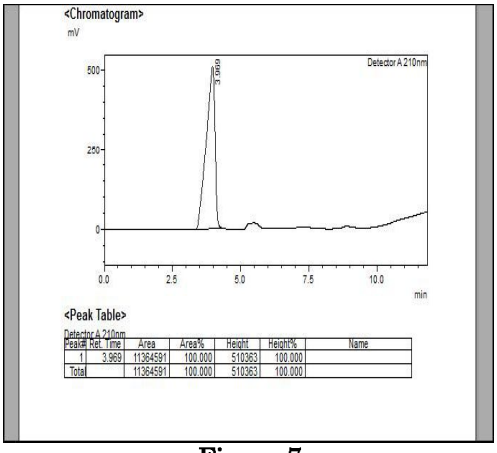


Figure 7

4. Conclusion

Single crystals of BCTZ were grown by slow evaporation method. The surface properties of the crystals were investigated by SEM and itching studies and the results are discussed. BCTZ with water and ethanol as etchants suggests that the crystal growth is progressed with different growth pattern. The purity of the compound was confirmed by HPLC studies. The signal obtained from NMR spectrum at 132.82 ppm indicates the incorporation of ZinC in the resulting compound of BCTZ.

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