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Synthesis, Growth and Structural aspects of DCTZ single crystals

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Abstract: In the present work, single crystals of $[(NH_4)_2]$ $[Zn(NCS)_4].2C_{12}H_{24}O_6.H_2O]$; [DCTZ] were grown using slow solvent evaporation technique and presented. The cell parameters of the grown crystals were confirmed by SXRD technique. In DCTZ, the ammonium cations are contained within the bowl of macro cycle via extensive N-H...O hydrogen bonding, In addition, Zn atom, two of the thiocyanate chains and a water molecule, disordered over two positions, lie on a mirror plane. The sample of DCTZ were subjected to spectral, optical and thermal studies and the results are reported.

Keywords: XRD, optical crystals, Crown ether, FT-IR, thiocyanate, supramolecular structure, centro symmetric.

Introduction

In recent years, material scientists have thirst to synthesize and grow crystals with an optically good quality and better physicochemical properties so that they can be used for device fabrications in modern industries including photonics. In this context, the feasibility of forming metal-thiocyanate with crown-ether is an attractive strategy for obtaining good quality linear and non-linear optical crystals. There is currently significant interest in crown-ethers because of their ability to form non-covalent, hydrogen bonding complexes with ammonium cations both in the solid state and in solution [1].

Experimental

The title compound, $[(NH_4)_2]$ $[Zn(NCS)_4].2C_{12}H_{24}O_6.H_2O$, the result of the reaction of ammonium thiocyanate, 18-crown-6 and zinc(II) chloride in aqueous solution, exhibits and unusual supramolecular structure. The Zn atom, two of the thiocyanate chains and a water molecule, disordered over two positions, lie on a mirror plane. A mixture of 18-crown-6, ammonium thiocyanate and zinc(II) chloride were dissolved in an aqueous solution in the molar ratio 2:4:1 and thoroughly mixed for two hours to obtain a homogeneous mixture. The solution was allowed to evaporate slowly at ambient temperature. Colorless single crystals (Fig. 1)suitable for single-crystal X-ray diffraction analysis were obtained in a week.

Results and Discussion

Single Crystal XRD

Single crystal X-ray diffraction (XRD) analysis was carried out DZCTC using Bruker Kappa APEXII CCD diffractometer with graphite monochromated M_0 - K_{oc} radiation ($\lambda = 0.71073$ Å). DCTZ crystallize in a centrosymmetricOrthorhombic crystal system with the space group Pnma. The unit cell parameters of DCTZ are a=22.7875(12) Å, b=23.6254 (12) Å and c=8.5593 (5) Å, V=4608.0 (4) Å³ and Z=4.In DCTZ, the Zn atom, two thiocyanatechains and water molecule, disordered over two positions lie on a mirror plane. The ammonium molecules are confined within in the bowl of the macrocyclevia extensive N-H...O hydrogen bonding. The incorporation of NH₄⁺cation within the cavity of 18-crown-6 ether has already been well established [2].

FT-IR studies

The FT-IR spectral profile of DCTZrecorded using BRUKER IFS 66V FI-IR spectrometer to confirm the presence of functional groups and coordination of ligands in the wave number range 400-4000 cm⁻¹as shown in Fig.2. The prominent absorption peaks of DCTZ were found to be shifted when compared with pure 18-crown-6-ether. The sharp and intense bands observed at 1105 21 and 958.62 cm⁻¹ were shifted from 1037 and 940 cm⁻¹ of pure 18-crown-6-ether respectively, which is due to asymmetric c-o-c stretching vibration. In addition, the sharp and intense band observed at 1350.17 was shifted from 1349 cm⁻¹ of CLTC [24], which is due to - CH₂ – stretching vibration. The CN stretching vibration mode of SCN appears as a very strong and highly intense sharp bond at 2088and 2069.62 cm⁻¹. Interestingly the CN stretching vibration of DCTZ (2088.91 cm⁻¹) was shifted from 2048.99cm⁻¹ of pureNH₄ SCN. It is worth noting that the NH₄⁺vibration at 3167.12, 3072.60 cm⁻¹ and shift in C-O-C vibration of the crown ether indicate the coordination of the crown ether to the NH₄⁺cation.

FT-Raman studies

The FT-Raman spectrum of DCTZ was recorded in the range of 40-4000 cm⁻¹ usingBRUKER RFS 27 Raman spectrometer. The Raman spectrum clearly shows the bending vibration modes of Zn metal ions at 278.6 and 256.7 cm⁻¹, respectively. These modes confirm the coordination of Zn with the SCN ligand. In addition, the presence of the SCN is well identified as a strong peak at 2128 cm⁻¹, which corresponds to the CN stretching vibration of SCN. From the structural point of view[1], it is also clearly evident that the Zn atoms are tetrahedrally coordinated with four nitrogen atoms.

Thermal studies

The TG-DSC analysis of DCTZ was carried out using SDT Q600 V20.9 thermal analyzer instrument in the temperature range 30-1000 °Cat a heating rate of 10 K/min (Fig. 3& 4). The experiment was performed in a nitrogen atmosphere. The TG curve of DCTZ shows the decomposition of the DCTZ sample at various temperatures. The DSC profile proves that the sample is stable up to $144^{\circ}5$ °C. DCTZ undergoes decomposition in three different stages. The first stage of decomposition in TG curve is the fragmentation of DCTZ including the loss of water molecule (onset temperature at about 105° C in DSC trace). The second stage of decomposition in TG curve is a overlapping stage in which the breakdown of $[(NH_4)_2]$ [Zn(NCS)₄].2C₁₂H₂₄O₆.H₂Ointo 18C₆, NH₄SCN and Zn (SCN)₂ may happen.Further, loss of two 18-crown-6 ether molecules and NH₄SCN may take place successively in the secondstage itself whose theoretical total value (77.15%) is comparable with the experimentally observed weight loss(78.48%). This fact clearly shows that there are two 18-crown-6-ether molecules in the DCTZ crystalline compound.Thermal analysis revealed that the sample is thermally stable up to 144.5 °C,

Fig1 As grown single crystals of DCTZ















Conclusions

This paper reports the growth of high quality single crystals of DCTZ by slow evaporation technique for the first time. The cell parameters of grown crystal were confirmed using single crystal XRD, which reveal that the DCTZ crystallizes in a space group Pnmawith cell parameters a=22.7875 (12)Å,b=23.6254 (12)Å,c=8.5593(5)Å. The functional groups of 18-crown-6-ether and thiocyanate in DCTZ crystal were well identified. The TG-DSC thermal analysis of DCTZ revealed that the sample is thermally stable up to 144.5°c.

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