J. Environ. Nanotechnol.
Volume 2, No.4 pp. 06-10
ISSN (Print) : 2279-0748
ISSN (Online) : 2319-5541
doi : 10.13074/jent.2013.12.132038

Synthesis and Characterisation of Teterkis (Hydrazine) Barium (II) Chloride Monohydrate Crystals

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Received: 04.07.2013 Accepted: 12.12.2013

Abstract

The title compound,Tetrakis(hydrazine) barium(II) chloride monohydrate (TBCM) was crystallised by solvent evaporation- solution growth technique. Energy dispersive analysis of X-ray (EDAX) and elemental analysis confirmed the stoichiometry of the compound. FTIR spectral study has been performed to identify the presence of various functional groups. The optical transmittance window and the lower cut off wavelength of the TBCM have been identified by UV-Vis-NIR studies. The proton configuration of TBCM is confirmed by ^1H NMR Spectroscopy. The sharp Bragg peaks of powder X-ray diffraction pattern show crystalline nature of the compound. Thermogravimetry (TG), Differential thermal analysis (DTA) and low temperature differential scanning calorimetry (DSC) were used to study thermal properties of the compound. Kurtz powder test with Nd:YAG laser radiation shows a considerable second harmonic generation by TBCM.

Keywords: *FT-IR; NLO; NMR; Solvent evaporation; Thermogravimetry.*

1. INTRODUCTION

The organic NLO crystals can have very large nonlinear susceptibilities compared to inorganic crystals, but their use is impeded by their low optical transparencies, poor mechanical properties, low laser damage threshold, an inability to produce and progress large crystals. But inorganic NLO materials typically have excellent mechanical and thermal properties. The synthesis of crystalline complexes via insitu ligand reactions has been a rapidly developing area of coordination chemistry due to its simplicity, slow lig and formation to promote single crystal growth, and a novel pathway to synthesize new materials (Pasupathi *et al.* 2008; Singh *et al.* 2013). In this paper, we report the growth and characterization of a new inorganic material, tetrakis(hydrazine) barium(II) chloride monohydrate.

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2. SYNTHESIS AND CRYSTAL GROWTH

The single crystals of tetrakis(hydrazine) barium(II) chloride monohydrate (TBCM) were grown by slow evaporation of saturated aqueous solution at ambient temperature. A saturated aqueous solution was prepared by mixing of Analytical grade hydrazine dihydrochloride and barium nitrate using triply distilled water. The two solutions were mixed thoroughly using mechanical stirrer. The resulting solution was filtered and the filtrate was kept aside for crystal growth. Bright, transparent and colourless tetrakis(hydrazine)

barium(II) chloride monohydratecrystalswere obtained within 7-10 days. The net chemical reaction is as follows:

$$4\,(N_2H_4.2HCl) + Ba(NO_3)_2 \xrightarrow{H_2O} [Ba\,(N_2H_4)_4]\,Cl_2..H_2O$$

TBCM

$$+2NHO_3+6HCl$$

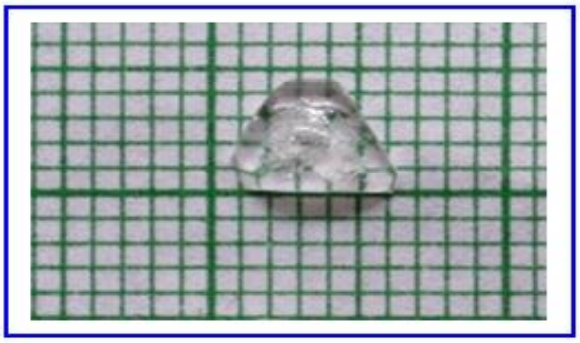

Fig. 1: Photograph of TBCM crystals

3. RESULTS & DISCUSSION

3.1 Appearance and elemental analysis

The grown TBCM crystals are colourless and transparent having well defined faces. The photograph of the crystal is given in Fig.1. The elemental analysis shows that the compound contains nitrogen: 31.23% (31.60) and hydrogen: 4.75% (6.02). Theoretical values are given in brackets.

3.2 Energy Dispersive X-Ray Spectroscopy

The EDX pattern of TBCM crystals Fig. 2 reveals the presence of barium, nitrogen, chlorine and oxygen. The presence of hydrogen was also detected.

3.3 Infrared spectroscopy

The FT-IR spectrum of TBCM crystals is shown in the Fig. 3 and the absorption frequencies

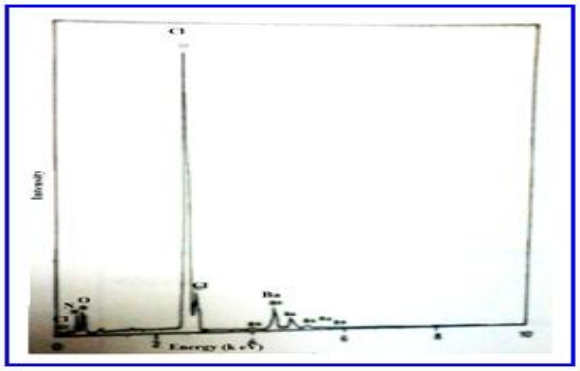

Fig. 2: EDX spectrum of TBCM

is analysed. The frequency observed at 3524 cm^{-1} is due to the intermolecular hydrogen bonding as well as asymmetric O-H stretching vibration present in the compound. The absorption frequency at 3324 cm^{-1} is due to symmetric O-H stretching vibration mode as well as N-H asymmetric stretching present in the compound (Vikram *et al.* 2007). The intermolecular hydrogen bonding in the compound might be due to the presence of N-group in the compound as well as the presence of water of hydration in the crystal. The absorption frequency at 3177 cm^{-1} is due to the N-H symmetric stretching present in the compound. The frequency at 1615 cm^{-1} is due to NH_2 deformation in the compound.

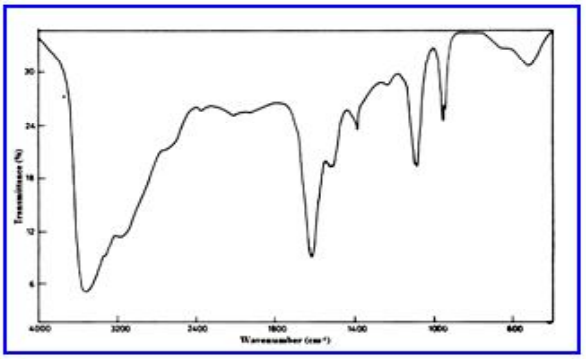

Fig. 3: FT-IR Spectrum of TBCM crystals

The observations coincide with the already published results (Bernalte-Garcia *et al.* 1997;

Yasodhai *et al.* 1999). The frequency at 1085 cm^{-1} is due to H-O-H deformation. The absorption frequencies at 950 cm^{-1} is due to N-N stretching in the compound. The absorption frequency at 515 cm^{-1} is due to Ba-N bonding (Nakamoto *et al.* 1978). The absorption frequencies at 2363, 1385 and 1230 cm^{-1} could not be accounted for.

3.4 NMR spectroscopy

The ^1H NMR spectrum of TBCM is shown in the Fig.4. The chemical formula of the compound is $[Ba(N_2H_4)_4]Cl_2.H_2O$. The ^1H NMR spectrum exhibits a single proton signal at δ 4.72 ppm indicating the presence of N-H proton in the compound.In general, hydrazine complexes are expected toexhibit two signals one at 2 ppm range and the other one at 4 ppm range in $CDCl_2$ and methanol solvents. The absence of one signal in the compound might be due to the change of solvent namely, D_2O. This has been reported for similar type of compounds (Heaton *et al.* 1996).

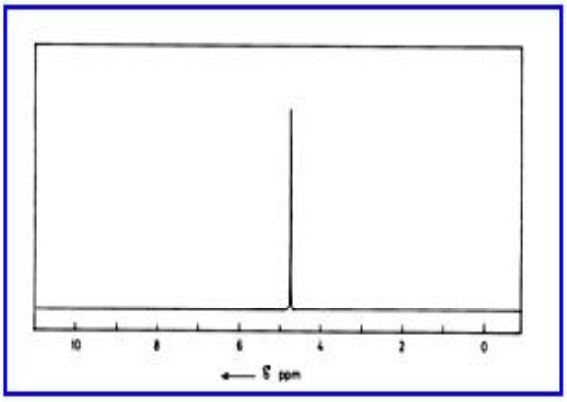

Fig. 4: ^1H spectrum of TBCM

3.5 Thermal analysis

The TG curve of TBCM crystal is shown in the Fig. 5. When the sample is heated from 40 to 1000 ºC, a two step decomposition pattern with 52% residue is observed. In the first step, one water molecule of crystallisation from the compound gets eliminated at 100 ºC. An experimental weight loss of 5% due to elimination one water molecule (equal to 18 molecular mass units) matches with the theoretical weight loss in the first step (5.08%). The second stage decomposition starts at 500 ºC and ends at 750 ºC. In this step, the original complex decomposes and reforms the barium nitride residue along with elimination of smaller fragments such as N_2, H_2 and Cl_2. The total weight loss in the second stage is around 43%. Inabalanced decompositionpattern proposed in the second stage, the weight loss is equal to 569 molecular units out of 1008. This can be accounted for the loss of 11 moles of nitrogen, 3 moles of chlorine and 24 moles of hydrogen. The residue is barium nitride which is formed at this temperature during decomposition of the TBCM crystal. The decomposition pattern formulated is as given below (Hargis *et al.* 1988).

The difference in weight loss between theory and experiment was nearly 13% shown in Fig.6 the peak at 100 ºC was due to elimination of

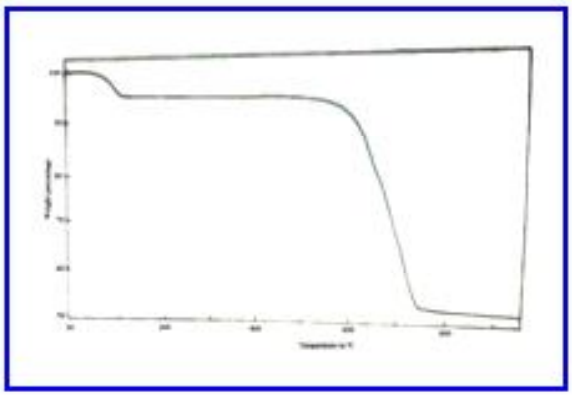

Fig. 5: Thermogram of TBCM

water molecule.The ex othermic peak at 500 ºC was due to the melting of the compound. At 750 ºC, there is a broad exothermic peak due to the decomposition of the compound and simultaneous formation of barium nitride. The broad peak indicates the large energy requirement of decomposition process. The DTA results are complementary to the TG results.

I Step

$$[Ba(N_2H_4)_4]Cl_2.H_2O \xrightarrow{100\ ^oC} [Ba(N_2H_4)_4]Cl_2 + H_2O\uparrow$$

Formula weight: 354.32 336.32

Theoretical Loss : 5.08%

Experimental Loss : 5 %

II Step

$$3[Ba(N_2H_4)_4]Cl_2 \xrightarrow{500\text{-}750\ ^oC} Ba_3N_2 + 3Cl_2\uparrow + 11N_2\uparrow + 24H_2\uparrow$$

Formula weight: 1008.96

439.96 569

Theoretical Loss : 56.39%

Experimental Loss : 43%

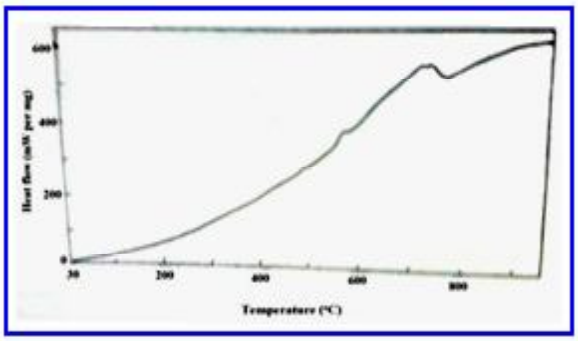

Fig. 6: DTA of TBCM crystal

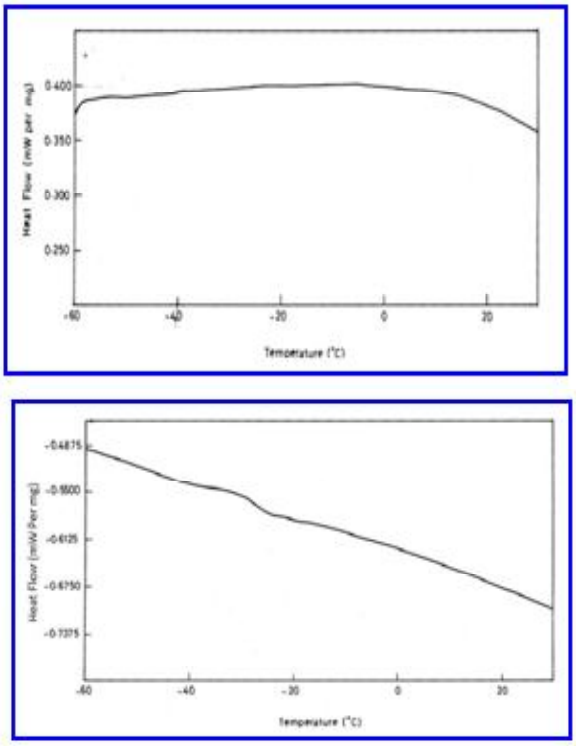

Fig. 7: Heating and cooling curve of DSC

3.6 Low Temperature Differential Scanning Calorimetry

Low Temperature DSC curves of the compound were shown in the Fig.7. The curves were recorded in the cooling run from RT to -70 °C. The cooling curve was run from -70 °C to RT. There is a thermal anomaly observed in heating curve at -28.36 °C. But there is no thermal anomaly observed in cooling curve (West, 1987). This indicates that there is occurrence of first order phase transition in the crystal.

3.7 Powder X-ray diffraction

The powder X-ray diffraction pattern of the TBCM crystal is shown in the Fig. 8. The sharp and well defined Bragg peaks in the powder XRD pattern confirm the crystalline nature of the compound (Cheetham *et al.* 1987). The compound crystallizes in tetragonal system. The unit cell parameters are a =18.247300Å, b=18.247300Å and c=14.614340 Å . The

values of $\alpha = \beta = \gamma = 90^{o}$. Volume of the unit cell is 4866.05 $Å^3$

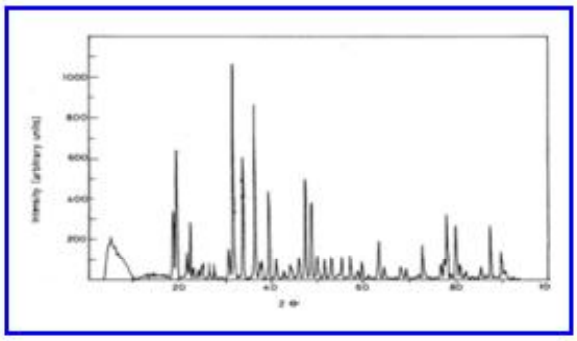

Fig. 8: Powder X-ray diffraction pattern of TBCM crystal

3.8 Non Linear Optical Property

Kurtz and Perry second harmonic generation (SHG) test was performed to measure the NLO efficiency of the grown TBCM single crystals. The powdered crystalline sample was illuminated using Spectra Physics Quanta Ray DHS-2, Nd:YAG laser using the first harmonics output of 1064 nm with pulse width of 8 ns and repetition rate of 10 Hz. It is found that the SHG of the compound is 0.20 times equal to that of KDP.

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