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## A Report on the Synthesis, Growth and Structural aspects of DPCI single crystals

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**Abstract:** In the present work, single crystals of Di(potassium crown-ether cadmium tri-iodide) [ $\{K(C_{12}H_{24}O_6)\}_2Cd_2I_6$ ]; (DPCI) were grown using slow solvent evaporation technique. In the structure of the title compound, the potassium lies approximately in the plane of the crown ether, coordinated by six crown ether O atoms and also by an iodide anion bound to a cadmium atom. The cell parameters of the DPCI were confirmed by SXRD, which are found to be  $a=10.627(2) \text{ \AA}$ ,  $b=14.986(2) \text{ \AA}$ ,  $c=15.190(3) \text{ \AA}$ . It belongs to monoclinic crystal system with the space group  $P2_1/c$ . The functional groups were well identified by FT-IR spectral analysis. The crystalline samples of DPCI were also subjected to FT-Raman, UV-Vis-NIR and TG-DSC analysis and the results are presented.

**Key words:** Single crystal, slow evaporation, organic-inorganic, TG-DSC.

### 1. Introduction and Experimental

Recent research is focused mainly on materials which exhibit nonlinear optical property as they have wide applications in various fields such as telecommunications, optical computing, optical information processing, optical data storage, laser remote sensing, etc., In photonics, a growing need continues for low cost, high quality and highly nonlinear efficient crystalline materials for optical frequency conversion[1-3]. It is interesting to note that the organic-inorganic crystals belonging to a new class of family Inorganic polymers with organic spacers (IPOS) have received renewed attention as they possess superior qualities of organic, inorganic and polymeric materials [1]. Very recently, Ramesh and Rajarajan et al have reported the synthesis, structure and physicochemical properties of Ammonium (18-crown-6-ether) cadmium(II) trithiocyanate (ACCTC) [4]. In the present work, effort was made to synthesize and characterize Di(potassium crown-ether cadmium tri-iodide) (DPCI);  $[K(C_{12}H_{24}O_6)]_2[(CdI_3)_2]$  single crystals [5]. The single crystals of DPCI were subjected to single crystal X-ray diffraction, FT-IR, UV-Vis-NIR and TG-DSC analysis and reported.

## 2. Synthesis and crystal growth

A mixture of 18-crown-6 ( $C_{12}H_{24}O_6$ ),  $CdCl_2$  and KI (molar ratio 1:1:3) was thoroughly dissolved in de-ionized water and stirred for 4 h to obtain a homogeneous mixture. Colorless single crystals were obtained after the filtrate had been allowed to stand at room temperature for two weeks.

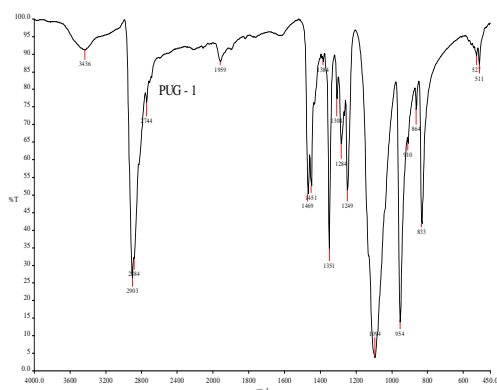
## 3. Results and Discussions

### 3.1 Single Crystal XRD and structure of DPCI

Single crystal X-ray diffraction (SXRD) analysis was carried out on DPCI single crystal using a Bruker Kappa APEXII CCD diffractometer with graphite monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). DPCI crystallizes in monoclinic system with the space group  $P2_1/c$ . The unit cell parameters of DPCI are  $a = 10.627 (2) \text{ \AA}$ ,  $b = 14.986 (2) \text{ \AA}$ ,  $c = 15.190 (3) \text{ \AA}$ ,  $V = 2347.7 (7) \text{ \AA}^3$ , and  $Z = 4$ . The reaction of  $CdCl_2$ , 18-crown-6 and KI in water yields the title coordination polymer,  $[K(C_{12}H_{24}O_6)_2Cd_2I_6]$ . The potassium ion lies approximately in the plane of the crown ether, coordinated by all six crown ether O atoms and also by an iodide anion bound to a cadmium atom. A C atom of the crown ether is disordered over two positions with site occupancies of 0.77(2) and 0.23 (2). Two  $K(18\text{-crown-6})^+$  units are linked by inversion symmetry, forming [bis(18-crown-6) dipotassium] system with approximately squareplanar  $K_2O_2$  units. Inversion symmetry also generates the  $Cd_2I_6$  fragment and the polymeric system is extended along the  $c$  axis by the formation of  $K-I-Cd$  bridges.

### 3.2 FT-IR studies

The FT-IR spectral profile of DPCI was recorded using BRUKER IFS 66 V FT-IR spectrometer in the range  $400 - 4,000 \text{ cm}^{-1}$  to confirm the presence of functional groups of the compound as shown in (Fig 1). The functional groups of DPCI were compared with 18-crown-6-ether. The absorption peaks of DPCI were found to be shifted with reference to the free 18-crown-6. The asymmetric and symmetric C-O-C stretching vibrations of pure 18-crown-6-ether ( $1037 \text{ cm}^{-1}$  and  $940 \text{ cm}^{-1}$ ) were shifted to  $1094 \text{ cm}^{-1}$  and  $954 \text{ cm}^{-1}$  respectively. In addition the sharp and intense band observed at  $1351 \text{ cm}^{-1}$  was shifted from  $1333 \text{ cm}^{-1}$  which intern evidences  $CH_2$  stretching vibration.



**Fig 1.** FT-IR spectrum of DPCI

### 3.3 FT-Raman studies

The FT-Raman spectrum of DPCI was recorded on the powder sample of DPCI in the range of  $50 - 4,000 \text{ cm}^{-1}$  using BRUKER RES 27 Raman spectrometer. It identifies the vibration modes of cadmium metal ions at  $267 \text{ cm}^{-1}$ ,  $168 \text{ cm}^{-1}$  respectively. These modes confirm the coordination of cadmium with iodine ion.

### 3.4 Thermal studies

The TG-DSC analysis of DPCI was carried out using NETZSCH STA 449 F3 thermal analyzer instrument in the temperature range  $25 - 1,400 \text{ }^\circ\text{C}$  at a heating rate of  $10 \text{ K/min}$ . The experiment was carried out in a nitrogen atmosphere. The TG curve of DPCI shows (Fig.2) that the sample undergoes decomposition at three different stages. However the major decomposition happens during the first and second stages respectively. During the above stages the fragments of crown-ether and cadmium iodide may take place. The DSC profile of DPCI shows (Fig.3) that the first decomposition temperature of DPCI is about  $227.8^\circ\text{C}$ . Hence it is clearly evident that DPCI thermally stable up to  $227.8^\circ\text{C}$ .

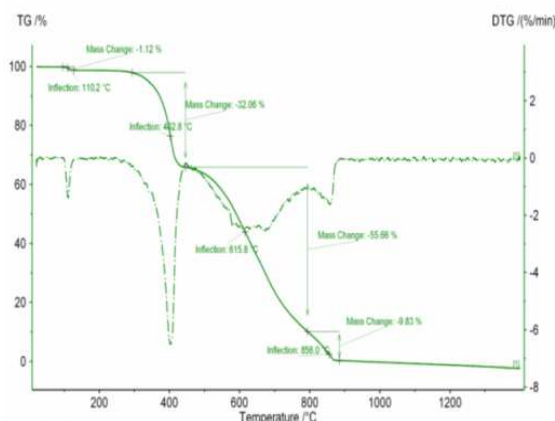


Fig 2. TG curve of DPCI

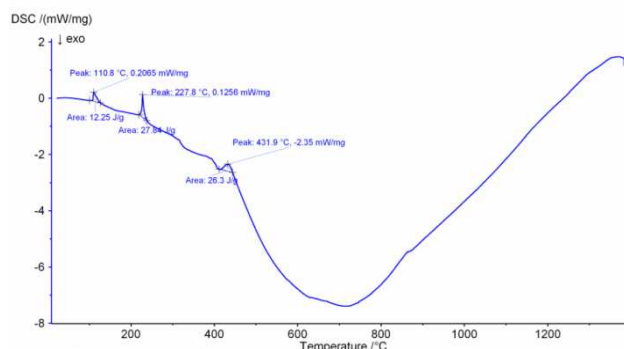


Fig 3. DSC curve of DPCI

### 3.5 Optical Studies

The optical absorbance spectrum of DPCI was recorded in the range 190-1200nm using Thermo Scientific Evolution 201 Spectrophotometer. The UV cut off wavelength in an aqueous solution is found to be 257nm. The coefficient of absorbance is less than 0.1 over the entire visible and part of IR region.

### 4. Conclusions

The single crystals of DPCI were grown using slow solvent evaporation techniques and the cell parameters were confirmed using SXRD. The functional groups were confirmed using both FT-IR and FT-Raman technique, the thermal stability of DPCI is found to be 227.8°C. The UV cut off wavelength in an aqueous solution is found to be 257nm. The DPCI single crystals may be used for third harmonic generations.

### 5. Acknowledgement

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### References

1. Jianjun Zhanga, Xiangqun Shu, Growth and characterization of a new nonlinear optical crystal [(18C6)Li][Cd(SCN)3], Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 2009, 74, 532-535
2. Hong Zhang, David E. Zelmon, Crystal growth of a new hybrid nonlinear optical compound [(18C6)K][Cd(SCN)3] from aqueous solution, Journal of crystal growth, 2002, 234, 529-532
3. Chekhlor. A.N, Bis[(18-Crown-6) Potassium] Tetrakis (iso-thioryanato) Zinc(II): Synthesis and Crystal Structure, 2008, 53, 845-849
4. Ramesh. V, Rajarajan. K, Crystal growth and characterization of a novel inorganic-organic hybrid NLO crystal: (NH4)[Cd(NCS)3] C12H24O6, Applied Physics B
5. Rajarajan.K, Pugazhenth. A, Nizammohideen.M, Catena-Poly[[bis(μ-1,4,7,10,13,16-hexaoxa cyclo octadecane)dipotassium]-μ2-iodo-(iodidocadmium)-di-μ2-iodido-(iodido cadmium)-μ2-iodido], Acta Crystallographica section E, 2013, E69, m125.

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