

## Synthesis and characterization of tetraethylammonium tetrachlorocobaltate crystals

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**Abstract.** Single crystals of tetraethylammonium tetrachlorocobaltate were grown by solution method and characterized through single crystal X-ray diffraction, thermogravimetric analysis (TGA), differential scanning calorimetric studies (DSC) and infrared spectroscopic technique (IR). The crystals were bright, transparent and blue coloured. The unit cell parameters were found to be  $a = b = 9.0363 \text{ \AA}$  and  $c = 14.9879 \text{ \AA}$  and  $\alpha = \beta = \gamma = 90^\circ$ , showing tetragonal lattice from the XRD data. Thermogravimetric analysis showed a loss of weight at 683 K from which the decomposition reaction was formulated. Thermal anomalies were found for this crystal at temperatures 200 K, 220 K in the cooling cycle and at temperatures 200 K, 240 K in the heating cycle, respectively which showed that this crystal was associated with first order phase transition. All the vibrational frequencies corresponding to  $(\text{TEA})^+$  ions and  $\text{CoCl}_4^{2-}$  ions were assigned from the IR spectral data of this crystal.

**Keywords.** Single crystals; unit cell parameters; first order phase transition; thermal anomaly; tetragonal lattice.

### 1. Introduction

Tetraethylammonium tetrachlorocobaltate (TEATC–Co) belongs to the family of crystals  $(\text{TEA})_2\text{BX}_4$  with B = first *d* transition elements like Co, Cu, Ni, Zn, Fe and with X = Cl or Br, respectively. The crystal structure of tetraethylammonium compounds  $[(\text{C}_2\text{H}_5)_4]_2\text{NiCl}_4$  and  $[(\text{C}_2\text{H}_5)_4]_2\text{CoCl}_4$  had been determined (Stucky *et al* 1967). The space group of these crystals is  $P42/nmc$  with  $n = 2$  and cell dimensions are about  $a = b = 9.08537 \text{ \AA}$  and  $c = 16.60003 \text{ \AA}$  at room temperature. Organic groups as well as the anion tetrahedra were found to be distorted at room temperature. Although the ethyl groups have additional degrees of freedom compared to the methyl group, compounds containing them have shown at most two phase transitions at low temperatures. Most crystals in the TMA and TEA families are isomorphous. However, some differences have been found in their behaviour at low temperatures (Melia and Merrifield 1970; Wolthuis *et al* 1986). Structural phase transition in  $(\text{TEA})_2\text{CdX}_4$  compounds were carried out by Kahrizi and Stinitz (1989) through thermal expansion measurements. Iwata and Ishibashi (1991) carried out dielectric dispersion in  $(\text{TEA})_2\text{ZnCl}_4$  crystals. In all these crystals, generally large thermal hysteresis was observed with thermal anomaly, indicating the first order nature of phase transition. For most of the crystals with different metal

ions, the room temperature crystal structure itself is not available.

This paper deals with the preliminary study of the synthesis and characterization of  $[(\text{C}_2\text{H}_5)_4]_2\text{CoCl}_4$  (TEATC–Co) crystals through X-ray powder and single crystal diffraction, DSC, TGA and infrared spectroscopy, with a view to study structural phase transition through Raman spectroscopy in this crystal.

### 2. Experimental

Single crystals of TEATC–Co were obtained by slow evaporation of saturated aqueous solution of analytical grade tetraethylammonium chloride and cobaltous chloride mixed in the stoichiometric 2 : 1 molar proportions. The grown crystals were bright, transparent and blue coloured which is an indication of the presence of  $\text{CoCl}_4^{2-}$  group in TEATC–Co. The X-ray powder diffraction pattern for this sample was obtained using X-ray diffractometer (Rich Seifert unit, Germany) and the single crystal X-ray diffraction data was collected using Rigaku AFC7S diffractometer with graphite monochromated Mo- $K_\alpha$  radiation. The TG and DTA analyses were done using Mettler TA 3000 system. The DSC curves were obtained by employing Perkin-Elmer differential scanning calorimeter. The FTIR absorption spectra and FT-Far IR absorption spectra for this crystal were taken using BRUKER IFS66V FT-IR Spectrometer. The visible absorption data was obtained using HITACHI U-2000 ultra violet-visible Spectrometer.

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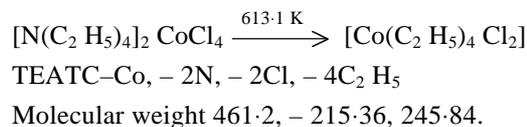
### 3. Results and discussion

The grown crystals of TEATC-Co is shown in figure 1. The X-ray powder diffraction pattern for this crystal is shown in figure 2. The unit cell parameters were found to be  $a = b = 9.0363 \text{ \AA}$  and  $c = 14.9879 \text{ \AA}$  employing least square refinement and the cell volume is  $1223.9 (\text{ \AA})^3$  from single crystal X-ray studies. The data were collected at a temperature of  $30 \pm 1^\circ\text{C}$  using the  $w-2\theta$  technique to a maximum of  $2\theta$  value of  $50-0^\circ$ . These values were found to be in good agreement with the lattice parameters reported for  $(\text{TEA})_2\text{BX}_4$  type materials (Stucky *et al* 1967). The thermograms (figure 3) of TG and DTA show a loss of 46.97% by weight at 613 K. When the sample is



Figure 1. Photograph of the grown crystals of TEATC-Co.

heated from 594 K to 673 K there is a loss of 216.7 units which can be accounted for by formulating the decomposition reaction as



The DSC for this crystal shows thermal anomalies at temperatures 200 K, 240 K in the heating cycle and 200 K, 220 K in the cooling cycle, respectively (figure 4). The thermal anomaly found in this crystal shows that it exhibits first order phase transition.

The infrared and far infrared absorption spectra of the grown TEATC-Co crystals were recorded using the KBr pellet technique. The IR spectra of this crystal at 300 K is shown in figure 5. The various absorption frequencies of the compound are assigned and are shown in table 1.

The infrared and far infrared spectra of TEATC-Co crystal (figure 5) do not contain absorption bands due to water molecules in any form. The CH<sub>3</sub> and CH<sub>2</sub> groups have their asymmetric and symmetric frequencies around  $2992 \text{ cm}^{-1}$ . The *d* asymmetric and *d* symmetric CH<sub>2</sub> frequencies are found at  $1462 \text{ cm}^{-1}$  and  $1404 \text{ cm}^{-1}$ , respectively. The CH<sub>2</sub> twist mode is seen at  $1308 \text{ cm}^{-1}$ . The peak at  $1184 \text{ cm}^{-1}$  represents the CH<sub>3</sub> rocking mode of C<sub>2</sub>H<sub>5</sub> group in TEATC-Co. The C-C asymmetric and C-N asymmetric absorption frequencies are represented by the peaks at  $1078 \text{ cm}^{-1}$  and  $1033 \text{ cm}^{-1}$ , respectively. Another CH<sub>3</sub> rocking mode is found at  $1008 \text{ cm}^{-1}$ . The peak at  $896 \text{ cm}^{-1}$  is due to C-C symmetric vibration. The CH<sub>2</sub> rocking mode is represented by  $793 \text{ cm}^{-1}$  and

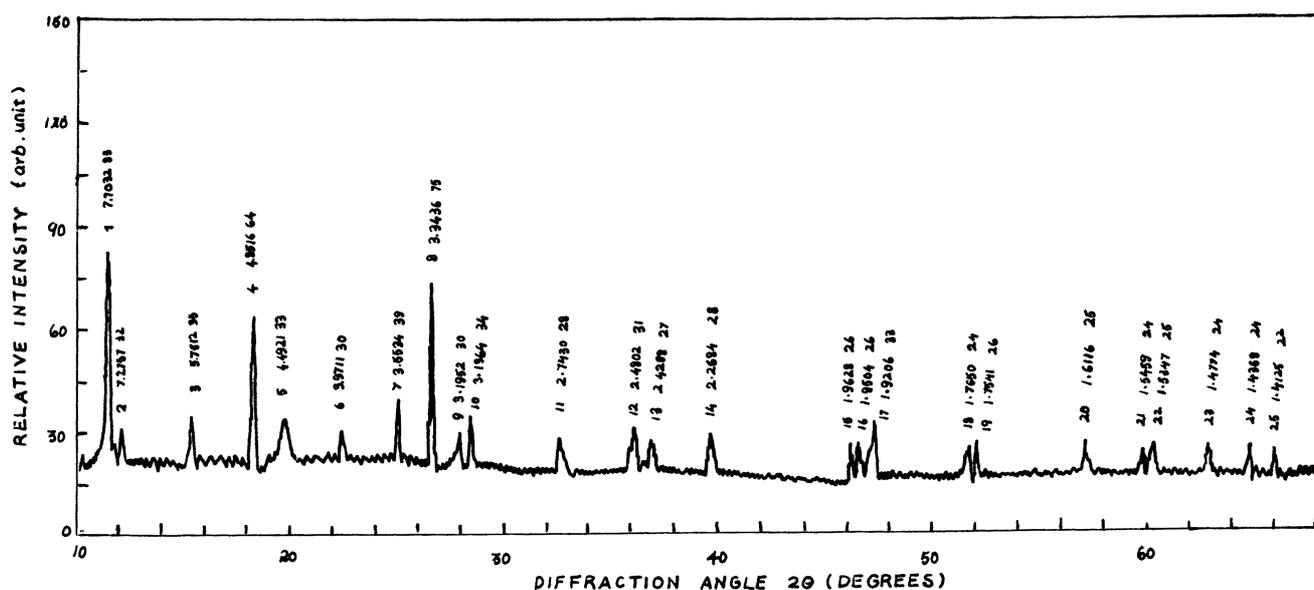


Figure 2. X-ray powder diffraction pattern of TEATC-Co.

the peak at  $470\text{ cm}^{-1}$  is due to  $d\text{C-C-N}$  vibration. The far infrared absorption spectrum of TEATC-Co contains the lattice modes at  $72.1\text{ cm}^{-1}$ ,  $84.3\text{ cm}^{-1}$  and  $35.8\text{ cm}^{-1}$  and  $\text{CoCl}_4^{2-}$  internal vibrations at  $125.8\text{ cm}^{-1}$ ,  $291.9\text{ cm}^{-1}$  and  $385.6\text{ cm}^{-1}$ , respectively. A very broad band covering a range of frequencies from  $350\text{--}250\text{ cm}^{-1}$  is observed with peak intensities at  $291.9\text{ cm}^{-1}$ . Similar absorption frequen-

cies have been observed in other compounds of this family (deBeer and Heyns 1981; Richter and Clask 1981).

The visible absorption spectrum (figure 6) of TEATC-Co crystals dissolved in water, shows that the radiation of wavelength of  $510.5\text{ nm}$  at  $0.320\text{ Abs}$  is absorbed. This may be the reason why the Raman spectrum of TEATC-Co in this work, employing  $\text{Ar}^+$  ion laser beam of

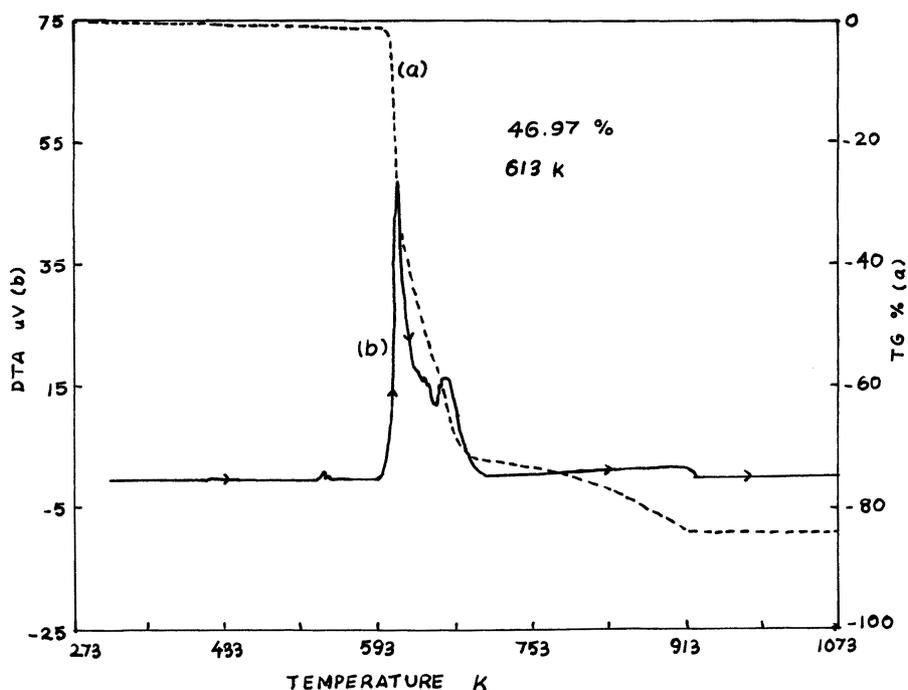


Figure 3. Thermograms of TG and DTG for TEATC-Co.

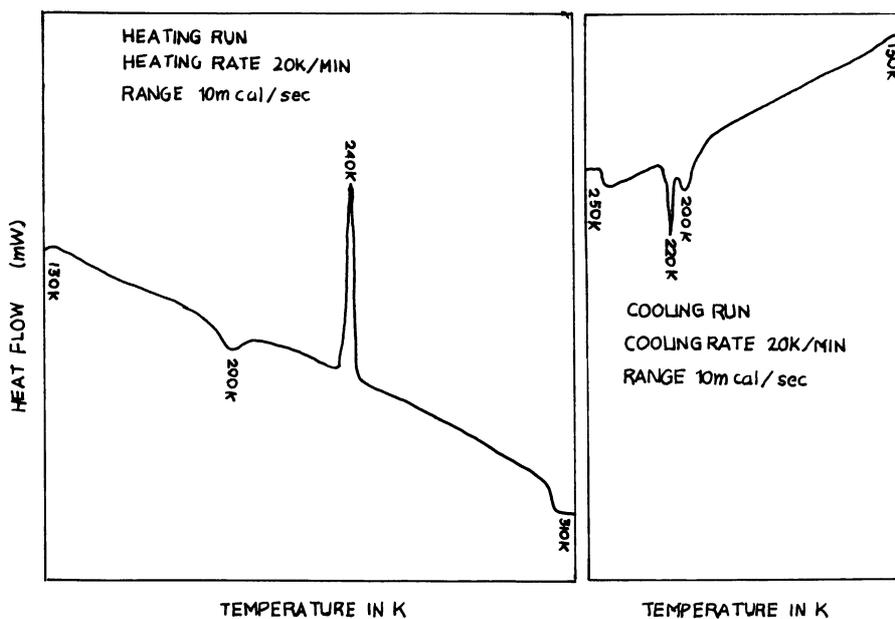


Figure 4. DSC thermogram for TEATC-Co.

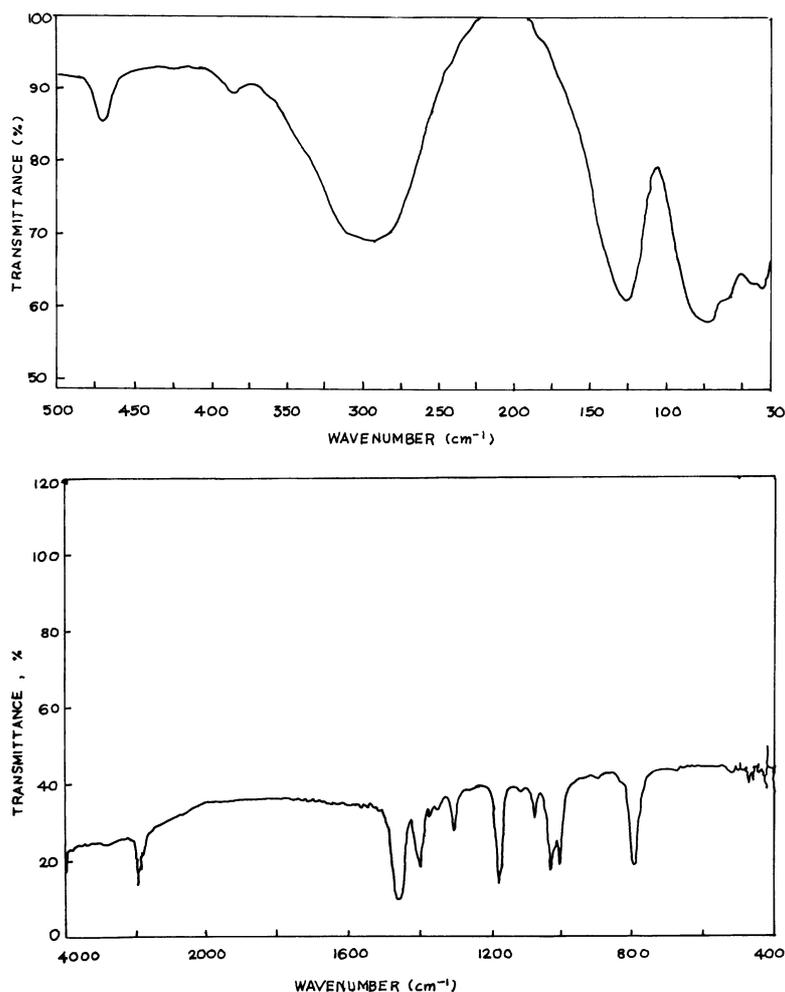


Figure 5. Infrared spectra (far IR and FTIR) of TEATC-Co.

Table 1. Infrared absorption frequencies of TEATC-Co.

| Wave number<br>( $\text{cm}^{-1}$ ) | Assignment   |
|-------------------------------------|--|
| 2992                                | Asymmetric $\text{CH}_2$ , symmetric $\text{CH}_2$ , asymmetric $\text{CH}_3$ and symmetric $\text{CH}_3$ (Cluster of peaks) |
| 1462                                | <i>d</i> asymmetric $\text{CH}_2$  |
| 1404                                | <i>d</i> symmetric $\text{CH}_2$   |
| 1372                                | <i>d</i> asymmetric $\text{CH}_3$  |
| 1353                                | <i>d</i> symmetric $\text{CH}_3$   |
| 1308                                | $\text{CH}_2$ twist  |
| 1184                                | $\text{CH}_3$ rock   |
| 1078                                | <i>n</i> asymmetric C-C  |
| 1033                                | <i>n</i> asymmetric C-N  |
| 1008                                | $\text{CH}_3$ rock   |
| 896                                 | <i>n</i> symmetric C-C   |
| 793                                 | $\text{CH}_2$ rock   |
| 470                                 | <i>d</i> C-C-N   |
| 385.6                               |  |
| 291.9                               | $\text{CoCl}_4^{2-}$ internal vibrations   |
| 125.8                               |  |
| 72.1                                |  |
| 43.3                                | $n_L$ lattice  |
| 35.8                                |  |

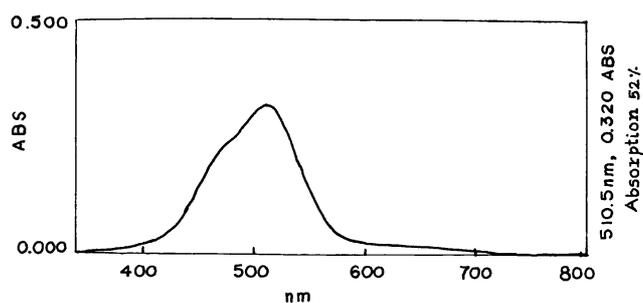


Figure 6. Visible absorption spectrum of TEATC-Co.

514.4 nm wavelength, shows the fluorescent lines and Raman scattered lines are found to merge in the vicinity of these fluorescent lines.

#### 4. Conclusions

Single crystals of TEATC-Co were obtained by solution technique. The crystals were found to be transparent and

deep blue in colour. X-ray powder diffractogram shows the well defined Bragg peaks at specific ( $2q$ ) angles indicating the crystallinity of the sample and the single crystal X-ray data shows the tetragonal character and the crystalline nature of the sample. From the TGA studies the decomposition reaction was formulated for this compound. DSC curves show thermal hysteresis behaviour, predicting that this sample exhibits first order structural phase transition. All the vibrational frequencies due to the tetraethylammonium group cation and the metal halide anion (both internal and external) have been identified by studying the infrared spectra of this crystal and the absorption peak was found at 510 Nm in the visible region for this sample. Laser Raman scattering studies for this crystal at low temperature is in progress and the single crystal X-ray structural studies are being published elsewhere.

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facilities. The authors are thankful to Prof. J Shashidhara Prasad, Department of Studies in Physics, University of Mysore, Mysore, for extending the National single crystal X-ray facility and obtaining the single crystal data for the sample. The authors' thanks are due to Prof. K J Rao, Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore, for the permission accorded for getting the DSC curves and the IR spectra of this sample. The authors thank Prof. P Ramasamy, Director, Crystal Growth Centre, Anna University, Chennai, for having provided facilities to grow the crystals at the Centre.

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