Growth and comparison of physicochemical properties of Lewis base adduct of MMTC and CMTC: Efficient non-linear optical single crystals

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Abstract. In the present investigation, single crystals of CMTG and MMTG were conveniently grown by slow evaporation technique. The grown crystals were confirmed by single crystal XRD. The physicochemical properties of the grown crystals were analyzed and compared. The SHG efficiency of CMTG is found to be three times higher than that of urea and for MMTG, it is equal to that of urea. Thermal stability of CMTG and MMTG was found to be 105 ºC and 145 ºC.

1. Introduction
Organometallic 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 non linear optical properties [1-3]. Chinese scientists have developed a few interesting coordination compounds such as MHg(SCN)4·nH2O (where M = Co, Cu, Zn, Cd, Ni, Fe, Mn) and demonstrated them as the useful SONLO materials [4]. Among these crystals, Cadmium mercury thiocyanate [CdHg(SCN)4] (CMTC) [5] and manganese mercury thiocyanate [MnHg(SCN)4] (MMTC) [4] shows high second harmonic intensity and attractive features that are suitable for blue / green laser light generation. Along with these crystals, few Lewis base adducts has also been investigated in recent past due to the interesting variations seen not only in their structures but also in their properties, particularly the relatively high SHG efficiency. Lewis base adducts are ones of the interesting themes of structural chemistry [6]. They have chain structures in which respective side-by-side metal atoms are bridged by thiocyanate ions. Their structural features bestow on them usefulness in nonlinear optics [7], chemical analysis [8], chemical, electrochemical metal sulfide thin film deposition [9]. Recently, some physicochemical properties of CMTG and MMTG have been reported by Duan et al, Xing Qiang Wang et al and Vetha Potheher et al [10,11, 12] respectively. In the present investigation, physicochemical properties of CMTG and MMTG were studied and compared.

2. Experimental
2.1. Synthesis of CMTC
During first stage of experiment, CMTC was synthesized by using CdCl2, HgCl2 and KSCN taken in stoichiometric ratio and dissolved in millipore water. The solution was stirred till the completion of reaction. After the completion of reaction, a white precipitate was formed which was further separated and dried. In order to increase the purity of the synthesized material the product was washed in millipore water three to four times and then dried. The chemical reaction is as follows:

\[
\text{CdCl}_2 + \text{HgCl}_2 + 4\text{KSCN} \rightarrow \text{CdHg(SCN)}_4 + 4\text{KCl}
\]
2.2 Synthesis of MMTC
In first stage, manganese mercury thiocyanate was synthesized by mixing manganese chloride, mercury chloride and potassium thiocyanate in millipore water. The following reaction is used for synthesis:

\[
\text{MnCl}_2 + \text{HgCl}_2 + 4 \text{KSCN} \rightarrow \text{MnHg(SCN)}_4 + 4\text{KCl}
\]

2.3 Growth of CMTG and MMTG crystals
In the second stage, the synthesized salt of CMTC and MMTC were dissolved in glycol monomethyl ether taken with millipore water in the ratio 3:1. Glycol monomethyl ether (GME) acts as a ligand to react with the CMTC and MMTC salt. The chemical reaction is given as follows:

\[
\begin{align*}
\text{CdHg(SCN)}_4 + \text{CH}_3\text{OC}_2\text{H}_5\text{O} & \rightarrow \text{CdHg(SCN)}_4(\text{CH}_3\text{OC}_2\text{H}_5\text{O}) \\
\text{MnHg(SCN)}_4 + \text{CH}_3\text{OC}_2\text{H}_5\text{O} & \rightarrow \text{MnHg(SCN)}_4(\text{CH}_3\text{OC}_2\text{H}_5\text{O})
\end{align*}
\]

To avoid the precipitation, the pH of the solutions was adjusted to be in between 2 and 3 by adding a few drops of HCl to the mixed solutions. The solution was vigorously stirred for about 6 hours and then filtered. The filtered solutions were kept for nucleation. The solutions were allowed to evaporate in room temperature. Single crystals of CMTG and MMTG were grown in a period of 35 – 40 days and 40 – 45 days respectively, with dimensions up to 17 x 18 x 6 mm³ and 11 x 10 x 6 mm³ respectively by slow evaporation technique. Figure 1 and 2 shows the photographs of as grown single crystal of CMTG and MMTG. The grown crystals exhibits hygroscopic nature, hence to avoid the loss of optical transparency, the crystals was kept in a dark place.

3. Results and Discussion
3.1 Single crystal XRD
Crystal structure of CMTG was confirmed by single crystal X-ray diffraction analysis using ENRAF NONIUS CAD4-F diffractometer. The structure was solved by the direct method and refined by full matrix least square technique using the SHELXL program. From the data, it is observed that CMTG belongs to orthorhombic crystal system with the space group Pca2₁. The unit cell parameters are a = 16.6172 Å, b = 7.0143, c = 13.5602 Å and V = 1580.5501 Å³. There is no change in crystal structure when CdCl₂ replaced by MnCl₂. But there were changes in the lattice parameter. The unit cell parameter for MMTG are a = 16.2051 Å, b = 7.3012 Å, c = 13.5098 Å and V = 1598.4347 Å³.

3.2 Optical absorption spectrum
The absorption spectrum of the sample was recorded in the range 200 – 2500 nm using HITACHI U-2800 spectrophotometer. The optical absorption spectrum along with Tauc’s plot [13] of CMTG and MMTG is shown in Figure 3 and 4. It is evident from the spectrum that the absorbance of the sample is less than 0.1 units. The UV cut-off wavelength of CMTG and MMTG is about 370 nm and 365 nm respectively, which is comparable to other metal-organic compounds such as CMTC (371 nm) [5], MMTC (373 nm) [14] and MMTD (375 nm) [15]. A plot drawn between the photon energy (hν = E) and \((ahν)^2\) was used to estimate the band gap of the material. The band gap (E₉) is determined by extrapolating the straight line portion of the curve to \((ahν)^2 = 0\). From the plot, the
band gap of CMTG and MMTG is estimated as 3.99 eV and 3.5 eV. MMTG has better optical property compared to CMTG.

3.3 NLO Test

The NLO test was performed for CMTG and MMTG using Kurtz and Perry powder technique [16]. The SHG efficiency of the sample was compared with microcrystalline powder of KDP and urea. In the present investigation, the laser pulse of 8 ns with spot radius of 1mm was employed. The input laser beam was passed through the IR reflector and then directed on the microcrystalline powdered sample packed in a capillary tube of diameter 0.154 mm. When a laser beam of 1.35 mJ was passed through the sample, second harmonic signal of 532 nm was generated and the output of 55, 330, 998 and 354 mV were obtained from KDP, urea, CMTG and MMTG respectively. From the experimental data, it was observed that the efficiency of the MMTG is nearly equal to that of urea and the efficiency of CMTG is around 3 times higher than that of urea, which is better than Tetrathiourea mercury (II) tetrathiocyanato zinc (II) (TMTZ) [17], Tetrathiourea mercury (II) tetrathiocyanato manganese (II) (TMTM) [18] and Diaquatetrakis (thiocyanato) cobalt (II) mercury (II) N-methyl-2-pyrolidone (CMTWMP) [19].

3.4 Thermal Analysis

Thermal analysis was carried out by the instrument Perkin Elmer Thermal Analyzer in nitrogen atmosphere at a heating rate of 15 °C/min., from 28 to 1000 °C. Figure 5 and 6 show the TGA-DTA thermogram of CMTG and MMTG respectively. The TGA trace of CMTG and MMTG reveals the different stages of decomposition of the sample. The first stage of TGA shows the weight loss of GME molecules. The melting point of the CMTG and MMTG is 105 °C and 145 °C, which is high when compared with ATZC (58 °C) [20]. Further, the sharp peak observed at 263.14 °C and 358 °C confirms the decomposition of the three dimensional steric structure of CMTC and MMTC. The various DTA peaks observed in the temperature range 400 - 1000 °C correspond to the decomposition of metal sulphides (CdS, HgS), carbon bi sulphides (CS₂) and nitrogen (N₂), dicyanogen ((CN)₂).
4. Conclusion
Single crystals of CMTG and MMTG were grown by slow evaporation technique. The crystal systems of the grown crystals were confirmed by single crystal XRD. Both the crystals were belongs to orthorhombic crystal system with non centrosymmetric space group Pca2₁. Optical property of the crystals was studied and the band gap energy was found to be 3.99 eV and 3.5 eV. The samples possess good non linear optical property and the SHG efficiency of CMTG is three times higher than that of urea and MMTG is equal to that of urea. The thermal stability of the CMTG and MMTG was found to be 105 ºC and 145 ºC respectively.

5. References
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