

## Vibrational Spectroscopic Studies on the $T_d$ -Type Clathrates: $M(N,N'$ -Dimethylethylenediamine) $M'(CN)_4.C_6H_6$ ( $M = Mn, M' = Zn, Cd$ or $Hg; M = Cd, M' = Cd$ or $Hg$ )

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In this study, the  $M(N,N'$ -dimethylethylenediamine) $M'(CN)_4.C_6H_6$  ( $M = Mn, M' = Zn, Cd$  or  $Hg; M = Cd, M' = Cd$  or  $Hg$ ) clathrates of  $N,N'$ -dimethylethylenediamine (DMEDA) were prepared for the first time and their FT-IR and FT-Raman spectra were investigated. The infrared spectra of the clathrates were recorded in the range  $4000$ - $500\text{ cm}^{-1}$  and FT-Raman spectra of the clathrates (Cd-DMEDA-Cd-Bz and Cd-DMEDA-Hg-Bz) were recorded  $4000$ - $70\text{ cm}^{-1}$  and its fundamental vibrational wavenumbers were obtained (Fig. 1). All the vibrational modes of coordinated DMEDA were characterised. Several modes of coordinated DMEDA have upward shifts in frequencies compared to those in the free molecule, these shifts being metal dependent.

The assigned wavenumbers for the  $M(CN)_4$  group in the compounds studies appeared to be much higher than those for the  $M(CN)_4$  ion  $K_2M(CN)_4$  ( $M = Zn, Cd$  or  $Hg$ ) salts. The CH out-of-plane mode ( $A_{2U}$ ) of benzene in the infrared spectra of the clathrates was located at ca.  $693\text{ cm}^{-1}$  and observed as a very intense single band. This band in the spectra of the clathrates was found shifting to higher frequency ( $693\text{ cm}^{-1}$ ) from that of liquid benzene ( $670\text{ cm}^{-1}$ ). Similar positive frequency shifts were observed for Hofmann- $T_d$ -type and Hofmann-type clathrates.

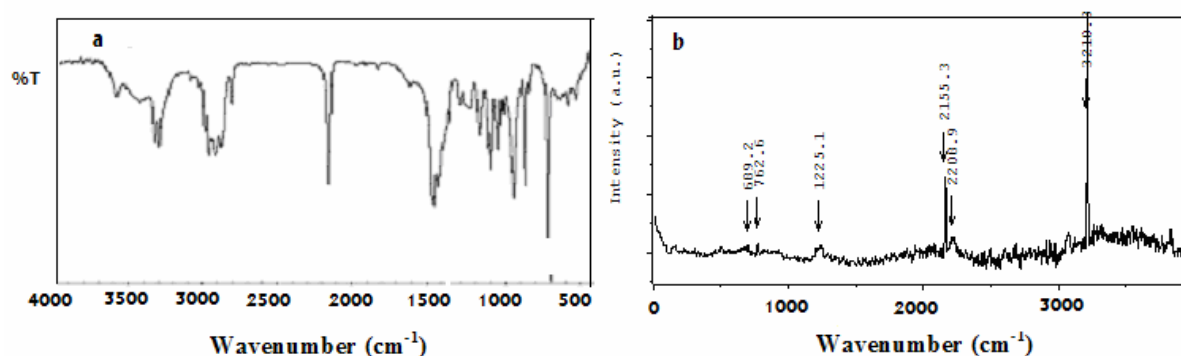


Fig. 1: FT-IR (in KBr) (a) and FT-Raman spectra (b) of Cd-DMEDA-Cd-Bz clathrate.