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RAMAN SPECTRA OF HOFMANN AND HOFMANN-T_d TYPE CLATHRATES AND THEIR STRUCTURAL IDENTIFICATION

B. Minceva-Sukarova[1], L. Andreeva[1] and C.J. Chunnilall[2]

[1] Institute of Chemistry, Faculty of Science, University "St Cyril and Methodius", Arhimedova 5, POB 162, 91001 Skopje, MACEDONIA
2 National Physical Laboratories, Queens Road, Teddington, TW11 OLW, UK

Hofmann and Hofmann-T_d type clathrates belong to a class of inclusion compounds consisting of a host-lattice; diammine-M(II) tetracyano-M'(II) and a guest molecule, enclathrate aromatic molecule. General formula : $M(NH_3)_2M'(CN)_4 \cdot 2G$, where M is octahedrally coordinated metal; Ni, Zn, Fe, Co, Mn, Cd; M' is square-planar coordinated metal, such as Ni, Pt or Pd (for Hofmann clathrates) and tetrahedrally coordinated metal, such as Cd, Hg or Zn (for Hofmann-T_d clathrates); the aromatic compound is usually benzene, aniline, thiophene, etc. The crystal structures of these compounds are known, although considerably more data are available for Hofmann than for Hofmann-T_d clathrates. Hofmann clathrates are tetragonal, space group $P4/m$, $Z = 1$ [1-3] while Hofmann-T_d clathrates are triclinic (but pseudotetragonal), space group $P\bar{1}$, $Z = 2$ [4]. The main structural difference between these two clathrates is in the square-planar $M'(CN)_4$ group in Hofmann- and a tetragonal $M'(CN)_4$ group in Hofmann-T_d clathrates. This results in the existence of two-dimensional network of planar $M'(CN)_4$ groups with the NH_3 groups sticking out above and below the planes in Hofmann clathrates as opposed to three dimensional network of $M(NH_3)_2$ and $M'(CN)_4$ groups in Hofmann-T_d clathrates. Crystallographic data indicate that there is no direct chemical bond between the host lattice and the guest molecule; this was also confirmed by the study of infrared and Raman spectra of these clathrates, the so-called "empty" clathrates and the guest molecules.

In our previous studies on these clathrates, a host-guest interaction have been studied using mainly infrared spectroscopy [5,6]. In these studies comparisons were often made with the "empty" clathrates (host lattices). However, no crystal data for these "empty" clathrates have been reported up to date. Since it is of great importance for our further spectroscopic studies to establish the structure of these compounds, we recorded the FT Raman spectra and X-ray powder diagrams of Hofmann and Hofmann-T_d clathrates and corresponding "empty" clathrates. The Raman spectra and X-ray powder diagrams of typical representatives of Hofmann-T_d : $Cd(NH_3)_2Hg(CN)_4 \cdot 2C_6H_6$ (Cd-Hg-Bz), and Hofmann : $Cd(NH_3)_2Ni(CN)_4 \cdot 2C_6H_6$ (Cd-Ni-Bz) clathrates, and the corresponding "empty" clathrates : $Cd(NH_3)_2Hg(CN)_4$ (Cd-Hg) and $Cd(NH_3)_2Ni(CN)_4$ (Cd-Ni) are shown in Fig. 1a and Fig. 1b.

FT Raman spectra (Fig. 1a) of Hofmann-T_d clathrates and their corresponding "empty" clathrates are very similar. Nearly all Raman bands in the low frequency region (except for the band at 606 cm^{-1} due to vibration of benzene), are present in both Cd-Hg-Bz and in Cd-Hg clathrates. This is also true for their IR spectra

[7]. The X-ray powder diffraction patterns of Cd-Hg-Bz and Cd-Hg are also very similar (Fig. 1b). One should therefore conclude that the crystal structure of the host lattice was not significantly perturbed by the abandonment of the benzene molecules from Hofmann-T_d type clathrates.

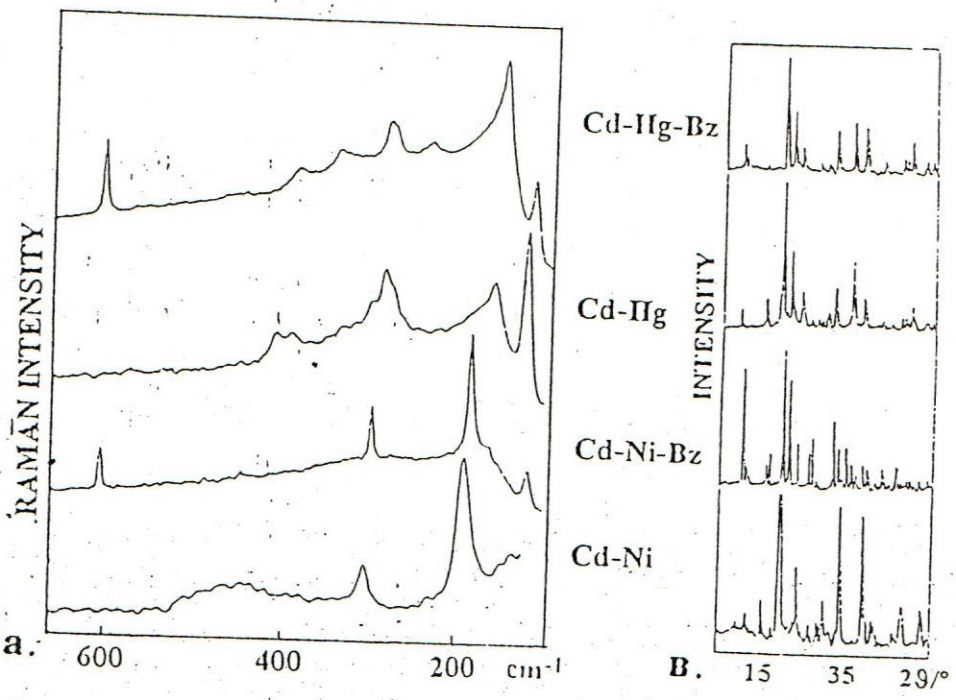

Fig.1. Room temperature FT Raman spectra (a) and X-ray powder diagrams (b) of Hofmann-T_d and Hofmann type clathrates and their corresponding "empty" clathrates.

The FT Raman spectra of Hofmann clathrates and their corresponding empty clathrates are also very similar (Fig. 1a), although there is a slight broadening and shift at higher frequencies of the two bands at 186 and 303 cm^{-1} in Cd-Ni-Bz compared to Cd-Ni. On the other hand, there is considerable difference between the X-ray powder diffraction patterns in Cd-Ni-Bz and Cd-Ni (Fig. 1b). This undoubtedly indicates that the host lattice in Hofmann clathrates exhibits changes upon abandonment of the guest molecules. One should therefore be careful when Raman and IR spectra are being compared with their corresponding empty clathrates. Since there is no structural data for empty clathrates there is a need for a thorough structure determination of empty Hofmann-T_d and, in particular, Hofmann type clathrates.

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