

THE NH₃ DEFORMATION VIBRATIONS IN THE HOFMANN-TYPE CLATHRATES

L. Andreeva and B. Minčeva-Šukarova

Institute of Chemistry, Faculty of Science, University "Cyril and Methodius", Arhimedova 5, 91000 Skopje, Yugoslavia

The infrared spectra of Hofmann-type clathrates $M(\text{NH}_3)_2\text{Ni}(\text{CN})_4 \cdot 2\text{C}_6\text{H}_6$, where $M = \text{Mg}, \text{Ni}, \text{Co}, \text{Zn}, \text{Mn}$, and Cd were studied in the region $1600\text{--}400 \text{ cm}^{-1}$ and were compared with the corresponding spectra of the "empty clathrates": $M(\text{NH}_3)_2\text{Ni}(\text{CN})_4$.

In all studied clathrates, a considerable splitting of the bands in the region of symmetric NH₃ deformation vibrations ($1250\text{--}1100 \text{ cm}^{-1}$) has been observed. The magnitude of this splitting and the ratio of the intensities of these bands varies depending on a metal $M(\text{II})$ attached to the ammonia molecules. The origin of this splitting has been discussed in terms of second-order transitions due to increased anharmonicity of $\rho(\text{NH}_3)$ motions.

INTRODUCTION

The series of Hofmann-type clathrates formed between a diammine- $M(\text{II})$ tetracyanonickellate(II), as the host lattice and an aromatic compound C_6H_6 , as a guest molecule, have been prepared. The general formula of the studied compounds is $M(\text{NH}_3)_2\text{Ni}(\text{CN})_4 \cdot 2\text{C}_6\text{H}_6$, where $M = \text{Mg}, \text{Ni}, \text{Co}, \text{Zn}, \text{Mn}$ and Cd .

The crystal structure of most of these clathrates has been determined by X-ray methods [1, 2], while the crystal data of some of them have been determined by X-ray diffractational patterns [3]. The Hofmann-type clathrates belong to tetragonal system, space group $P4/m$, with $Z = 1$. The basic structure consists of host layers $M(\text{NH}_3)_2\text{Ni}(\text{CN})_4$ and of benzene guest molecules which are trapped in the cavities between these sheets. The closest host-guest contact is 360 pm, and corresponds to the distance of the NH₃ ligands from the host

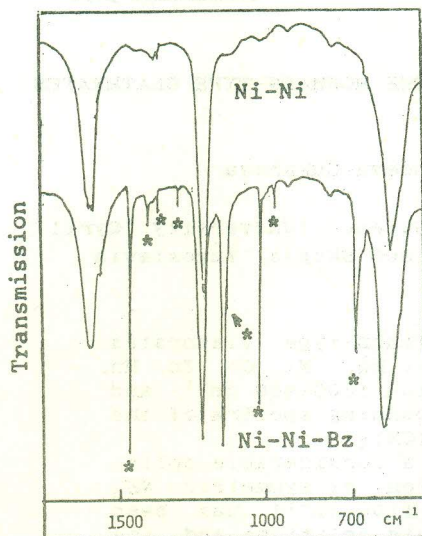


Fig. 1 : The IR spectra of Ni-Ni ("empty" clathrate) and Ni-Ni-Bz clathrate in the 1600-500 cm^{-1} region.

transmission minimum. The schematic representation, shown on Table I, confirms this clearly.

The estimated position of the $2\rho(\text{NH}_3)$ vibration in the studied clathrates is either nearer to the high frequency or to the low frequency band, but there are some clathrates (like Cd-Ni-Bz and Mn-Ni-Bz) in which it "falls" outside this region.

Although the possibility of Fermi resonance interaction can not be ruled out, it seems that some other effects have to be considered in order to explain the existence of the two strong infrared bands in the 1250-1100 cm^{-1} region of the studied clathrates.

The point group symmetry of the $\text{M}(\text{NH}_3)_2$ group, in which the NH_3 molecules can be considered to have free rotation, is $D_{\infty h}$, while the point group isomorphous with the factor group of the crystal is C_{4h} . The correlation made between these two groups [8] reveals that there are two librational NH_3 modes which are doubly degenerated (having E_U and E_g symmetry) and four deformational modes (having A_U , A_g , E_U and E_g symmetry).

The possible candidate "responsible" for the appearance of the strong infrared band at around 1150-1100 cm^{-1} (see

However, our infrared spectra of the studied clathrates, indicate that a slightly different approach has to be adopted in the interpretation of the bands in this region for at least two reasons : Firstly, the frequency of the symmetric NH_3 deformation vibration (around 1250 to 1200 cm^{-1}) does not change (or changes insignificantly) compared to the corresponding frequency of the "empty" clathrates, which is something one should expect if Fermi resonance is present. This is also the case with the frequencies of the antisymmetric NH_3 deformation vibration and librational mode. Secondly, the estimated position of the "overtone" of NH_3 rocking vibration deviates considerably from the frequency of the

lattice and CH groups from the benzene molecules. The NH_3 ligands are attached to the metal, M(II) , forming an infinite chain along the c -axis of the crystal.

As a part of a study on Hofmann (and Hofmann- T_d)-type clathrates [4,5], we recorded their infrared spectra in the region of NH_3 deformation vibrations and librational motions.

The only infrared spectra on these compounds were published more than 20 years ago [6]. The splitting of the bands in the region of the NH_3 symmetric vibrations was discussed in terms of Fermi resonance interaction between the rocking NH_3 vibration and the symmetric deformation of the NH_3 molecules. However, after a more careful investigation of the infrared spectra of Hofmann-type clathrates, we propose somewhat different explanation for the "splitting" of the bands in this region.

EXPERIMENTAL

The Hofmann-type clathrates and their residual host lattices have been prepared by the methods reported previously [4,7]. In order to ensure that the clathrates consist of two benzene molecules, the C and H microanalyses were carried out on the COLEMAN C-H analyser.

The infrared spectra were recorded on Perkin-Elmer 580 spectrophotometer, from KBr pellets or mulls in Nujol. The low-temperature VLT-2 cell was used for LNT-IR studies.

RESULTS AND DISCUSSION

The infrared spectra of one of the studied clathrates and its corresponding "empty" clathrate in the region of antisymmetric, symmetric deformation and librational modes of the NH_3 molecules are shown on Fig. 1. Apart from the IR bands due to the guest molecules (marked with asterisks on Fig. 1.), all other bands are due to the modes of the host lattice.

Attention was paid to the splitting of the strong infrared band in the $1250\text{-}1100\text{ cm}^{-1}$ region which has been observed only in the spectra of clathrates, but not in the spectra of "empty" clathrates. The splitting of this band, as mentioned in the introduction, has been suggested [6] to originate from the Fermi resonance interaction of the NH_3 symmetric deformation vibrations with the overtone of the NH_3 rocking vibration.

Table I : Schematic representation of the frequency distribution of the antisymmetric and symmetric deformation and $\rho(\text{NH}_3)$ vibrations (full lines) and the estimated position for the "overtone" of the $\rho(\text{NH}_3)$ vibrations (arrows)

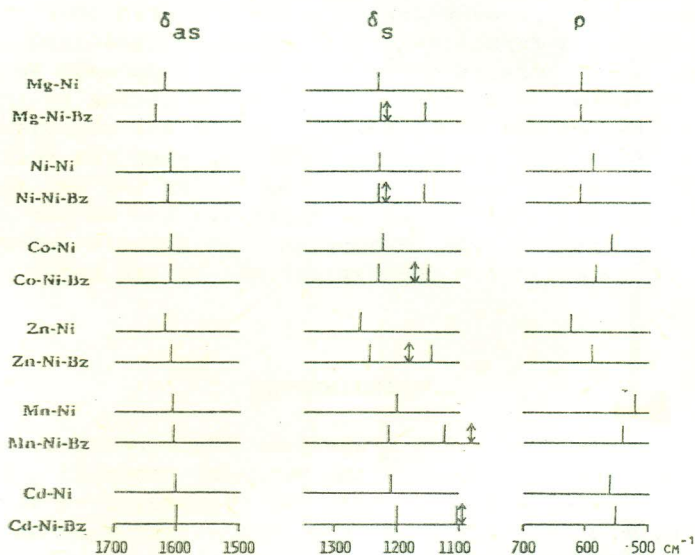


Table I) could be the combination band originating from the sum of the two fundamental librational modes of the NH_3 molecules in the $\text{M}(\text{NH}_3)_2$ group, i. e. $E_U + E_G$. The frequency of one component of this summation band is known from our infrared spectra, while the other is Raman active. Unfortunately, we did not have success in recording the Raman spectra of these compounds and no literature data have yet been found. Nevertheless, it is expected that the Raman active mode of the NH_3 rocking vibration will be somewhere around the corresponding infrared active mode (from 600 to 500 cm^{-1}). Therefore, the sum $E_U + E_G$ is expected to fall in the 1150 - 1100 cm^{-1} region (see Fig. 1 and Table I).

However, the intensity of this combination band (or second-order transition band) is extremely high with respect to the theoretically expected one. The origin of this unusually high infrared intensity may be understood in terms of strong mechanical (and probably electrical) anharmonicity connected with the motions of the NH_3 molecules which have librational,

rather than deformational character. The question arises naturally, why these vibrations are more sensitive to mechanical anharmonicity than the others and why the "splitting" of the band at around $1150-1100\text{ cm}^{-1}$ is not visible in the "empty" clathrate? One of the possible answers for both of these questions may be the existence of some kind of host-guest interaction in the $M(\text{NH}_3)_2\text{Ni}(\text{CN})_4 \cdot 2\text{C}_6\text{H}_6$ type of compound.

An evidence for a host-guest interaction has already been detected in the infrared spectra of the studied clathrates [4, 5] at LNT. It was found that the C-H out-of-plane deformation vibration in guest benzene molecules splits into two bands as the volume of the unit cell decreases in the order: Cd, Mn, Zn, Co, Fe, Ni and Mg. It is therefore, not surprising that the host-guest interaction will also have influence on the infrared spectra on the host lattice. This influence will probably be most prominent in the type of vibrations which are mainly dependant on the motion of H atoms in NH_3 molecules, thus resulting in their high anharmonicity.

The above conclusion is supported by the results from the X-ray data [3] in which it was found (as mentioned in the introduction) that the nearest host-guest contact is 360 pm and is between the NH_3 molecules from the $M(\text{NH}_3)_2$ group and the CH from the benzene molecules. In view of this result, one would presume that the CH out-of-plane vibrations in the benzene (guest) molecules and the rocking vibrations of the NH_3 molecules (from the host lattice) will be the first to exhibit the influence of host-guest interaction in the Hofmann-type clathrates.

The proton magnetic resonance spectra of $\text{Cd}(\text{NH}_3)_2\text{Ni}(\text{CN})_4 \cdot 2\text{C}_6\text{D}_6$ showed [9] that there is a considerable proton-proton repulsion around the protons of an ammonia molecules. The p-p distance have been obtained to be 178 pm which is 16 pm longer than in gaseous ammonia. In addition to this, the π -electron system of the surrounding benzene molecules may attract the protons of ammonia towards the benzene molecules thus forming weak H-bond. The observed strong anharmonicity in the studied clathrates may be caused by at least one of these factors.

The X-ray diffractational data and the NMR spectra, as well as our infrared spectra of these compounds seems to impose the idea that non-bonded proton-proton interactions have a considerable influence on those types of vibrations in which the motions of H atoms are dominant, such as NH_3 rocking vibrations in the host lattice and CH out-of-plane vibrations in the guest (benzene) molecules.

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ИЗВОД

ОБЛАСТ НА ДЕФОРМАЦИОНИ NH_3 ВИБРАЦИИ ВО HOFMANN-ОВ ТИП НА КЛАТРАТИ

Л. Андреева и Б. Минчева-Шукарова

Институт за хемија, Природно-математички факултет, Пошт. фах 162, 91000 Скопје

Испитувани се инфрацрвените спектри на Hofmann-ов тип на клатрати со општа формула : $\text{M}(\text{NH}_3)_2\text{Ni}(\text{CN})_4 \cdot 2\text{C}_6\text{H}_6$ каде што $\text{M} = \text{Mg}, \text{Ni}, \text{Co}, \text{Fe}, \text{Zn}, \text{Mn}$ и Cd , во областа од 1600 до 400 cm^{-1} и споредувани се со таканаречените "празни клатрати", со општа формула : $\text{M}(\text{NH}_3)_2\text{Ni}(\text{CN})_4$.

Во инфрацрвените спектри на испитуваните клатрати забележено е расцепување на лентите во областа $1250-1100 \text{ cm}^{-1}$. Големината на расцепувањето помеѓу обие две ленти и распределбата на нивните интензитети е различна кај различни клатрати и зависи од металот за којшто се координирани молекулите на амонијак.

Ваквото расцепување најверојатно е резултат на премин од втор ред настанат како резултат на силна анхармоничност на либрационите движења на NH_3 молекулите.