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A STUDY OF A HOST-GUEST INTERACTION IN HOFMANN-TYPE CLATHRATES

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SUMMARY

A host-guest interaction in a series of Hofmann-type clathrates : $M(NH_3)_2Ni(CN)_4 \cdot 2C_6H_6$ where M = Ni, Fe, Co, Zn, Mn and Cd has been studied using IR spectroscopy. The influence of the guest molecules (enclathrate benzene molecules) has been studied through the changes of the shape of the bands due to C-H out-of-plane deformations. In some of the clathrates, a considerable splitting of these bands has been observed at low temperature. This is especially true for the band near 980 cm^{-1}. The splitting of this band increases as the volume of the unit cell decreases in the order : Cd, Mn, Zn, Co, Fe, Ni. An attempt has been made to interpret this in terms of tunneling effect, using a simple model based on a double-minimum potential function.

INTRODUCTION

Hofmann-type clathrates give the isostructural series of metal complex hosts with regard to both octahedral M(II) and square-planar M'(II) metal with a general formula : $M(NH_3)_2M'(CN)_4 \cdot 2G$, where M could be any divalent metal with octahedral coordination as Zn, Cu, Mn, Cd, Ni, Co etc., M' could be Ni, Pd, Pt, with square-planar coordination and G is an aromathic molecule, such as C_6H_6, $C_6H_5NH_2$, C_4H_4S etc. We have studied a series of Hofmann-type clathrates in which M' was always Ni, G was always C_6H_6 and M was Ni, Fe, Co, Zn, Mn or Cd. These compounds consist of host layers of the composition $M(NH_3)_2Ni(CN)_4$ and guest molecules trapped in cavities between these sheets. In each sheet the $Ni(CN)_4$ group has a planar structure and an octahedral configuration of ligands around M(II) is attained by four nitrogen atoms of the CN groups in plane and by two ammonia molecules, up and above this plane (cf. Fig. 1).

The crystal structure of some of these compounds has been determined by three-dimensional X-ray methods [1,2], while some of them have been determined by X-ray diffractional patterns [3]. All these clathrates belong to tetragonal system, space group *P4/m* with

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Z = 1, with a slight variation of the cell constants *a* and *b*. There is no direct chemical bond between the host lattice and the enclathrate benzene molecule. The closest contact between them occurs between the C atom of the benzene molecule and NH_3 of the host lattice. The C(benzene)-N(ammonia) distance is almost always around 360 pm [2] indicating a van der Waals contact. According to the crystallographic data, there are two possible orientations of the benzene molecules, which are mirror images of each other with respect to the *a*-axis of the unit cell [1,2].

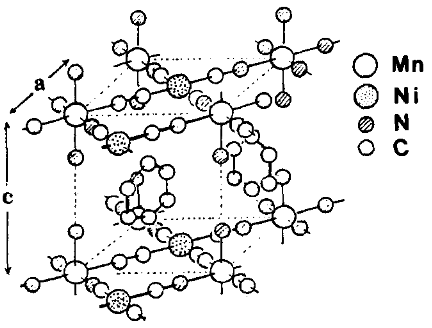

Fig. 1. The crystal structure of $Mn(NH_3)_2Ni(CN)_4 \cdot 2C_6H_6$ (ref. 2).

In this paper an attempt has been made to detect a possible host-guest interaction using IR spectroscopy.

The IR spectra of some of these compounds at RT have been published more than 20 years ago [4]. The authors found out that the only interaction between guest molecules and host lattice was the shift of all out-of-plane vibrations from those in gaseous and liquid state, and they concluded that the host-guest interaction in those clathrates was based solely on the van der Waals forces. Our recently recorded (at RT and LNT) IR spectra of these compounds, confirmed the previous findings. Furthermore, the LNT-IR spectra indicated that in some of the clathrates, these interactions may be stronger at low temperature.

EXPERIMENTAL

The clathrates and their residual host lattices were prepared by the methods reported by Iwamoto *et al.* [5]. The C and H microanalyses were carried out for the clathrates in glass vails, on the COLEMAN C-H analyser, while N was determined by the method of Dumas.

The IR spectra were recorded on Perkin-Elmer 580 spectrophotometer. The samples were measured as KBr pellets and mulls in nujol. The low-temperature VLT-2 cell was used for LNT-IR studies. The calibration was carried out with water vapour and polystyrene film. The resolution at 1000 cm^{-1} was about 2 cm^{-1}.

RESULTS

The IR spectra of the studied clathrates (at RT and LNT) confirmed the results obtained from crystallographic experiments (there is no direct chemical bond between host lattice and guest molecules). The comparison between the IR spectra of an "empty" lattice : $Ni(NH_3)_2Ni(CN)_4$ (denoted as Ni-Ni) and Hofmann-type clathrate : $Ni(NH_3)_2Ni(CN)_4 \cdot 2C_6H_6$ (Ni-Ni-Bz), which are given as an example on Fig. 2, confirm that clearly.

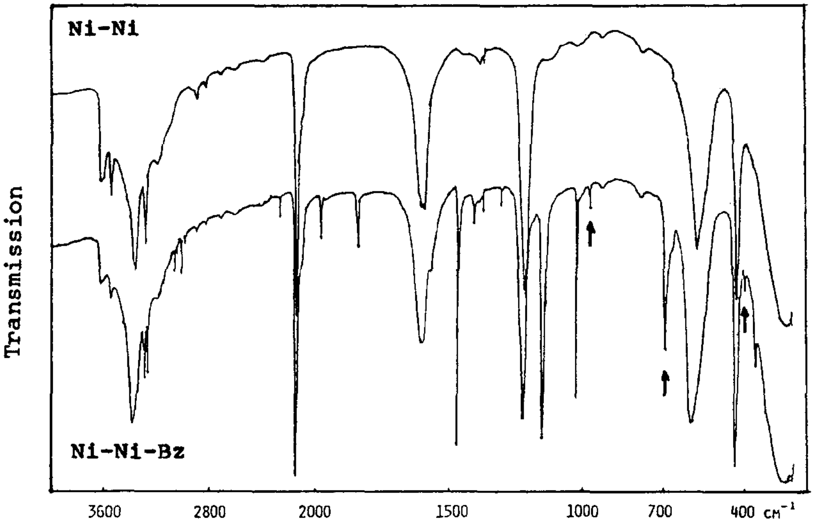

Fig. 2. The IR spectra of Ni-Ni and Ni-Ni-Bz at LNT. The CH out-of-plane vibrations are marked with arrows.

The dynamics of the guest molecules has been studied through the changes of the frequencies and the shape of the bands due to CH out-of-plane vibrations at RT and at LNT. There are several bands in the IR spectra of the clathrates that are expected to originate from this type of vibration : a weak band at around 405 cm^{-1}, a strong band at around 700 cm^{-1} and a weak band around 985 cm^{-1}. In addition, there are two bands at around 1850 and 1990 cm^{-1} which are, most probably, due to combinations of at least one of these types of vibrations. All these bands are shifted to higher frequencies with respect to gaseous and liquid state.

We focused our attention on the band around 985 cm^{-1} because it exhibited the most prominent changes on cooling. The IR spectra of this band, in all studied clathrates are shown on Fig. 3.

In some of the clathrates, like in the case of Ni-Ni-Bz, the effect of temperature caused a considerable splitting of this band. A well defined high frequency band appears in addition to the main maximum, the separation being about 5 cm^{-1}. In Fe-Ni-Bz, Co-Ni-Bz and Zn-Ni-Bz, this separation is less pronounced (the high frequency shoulder appears 3-4 cm^{-1} above the main maximum). Finally, in Mn-Ni-Bz and Cd-Ni-Bz, this band does not change its shape when cooled from RT to LNT. In Mn-Ni-Bz there is no detectable splitting of this band at low temperatures, although its halfwidth increases by 1 cm^{-1}. A slight decrease of the halfwidth of this band was detected only in the case of Cd-Ni-Bz. The overall increase in the halfwidth of these bands, from RT to LNT, in all studied clathrates is between 1 and 2 cm^{-1}.

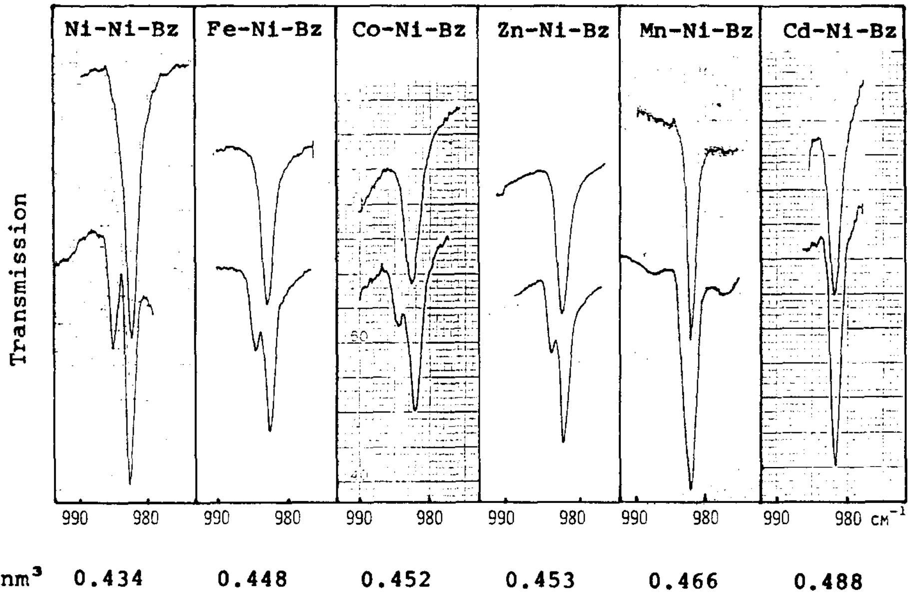

Fig. 3. The CH out-of-plane bending vibrations in the IR spectra of various clathrates at RT (upper) and LNT (lower curve). Data for the cell-volumes are taken from refs. 1, 2 and 3.

DISCUSSION

It is obvious that the only difference in the M-Ni-Bz type of clathrates is due to the nature of M(II) metal. As a consequence of this, the following physical properties can be changed : (i) the covalent radius of the metal; (ii) the bonding ability, i.e. the electronic configuration and (iii) the crystal structure of the clathrate. It was already mentioned that these compounds belong to the tetragonal system, the only difference between them being the variation of the cell-constants *a* and *b*, i.e. the volumes of the unit-cells, interatomic distances etc.

The possible explanation for the different behaviour of the *same* type of vibration in series of Hofmann-type clathrates could be ascribed to any of the above mentioned properties. However, there is a certain decreasing order in the splitting of the CH out-of-plane bands at LNT, following the metal-sequence from Ni to Cd. This corresponds quite well to the order of increasing of the volume of the unit-cells of the series of clathrates (cf. Fig. 3). On the other hand, no such clear trend was found for the covalent radia and the bonding ability of the metal, which beyond doubdt influence the crystal structure.

In order to explain the behaviour of the band due to CH out-of-plane bending vibrations in the enclathrate benzene molecules (E_{2u} species; two H-atoms are at rest), a simple model based on a double-minimum potential function was proposed.

The splitting of the bands may be explained in terms of a tunneling motion of the benzene molecules in the host lattice.

The potential energy function of the benzene γ_{CH} vibration may be approximated by :

$$U(x) = a\begin{cases}(x + x_0)^2 , & x < 0 \\ (x - x_0)^2 , & x > 0\end{cases} , \qquad a = m\cdot\omega^2/2 \qquad (1)$$

where $2x_0$ is the effective distance between the two energetically equivalent states; ω is the angular frequency and m is the effective mass of the oscilator. This equation describes the motion of a particle in a symmetric double-minimum potential. The magnitude of the splitting (due to the tunneling motion) in the WKB approximation can be represented [6] with :

$$\Delta\tilde{\nu} = \frac{\tilde{\nu}}{\pi}\cdot\exp[-\frac{2E}{h}\sqrt{\frac{2m}{a}}(\frac{x_0}{2}\sqrt{\frac{a}{E}}\sqrt{x_0^2\frac{a}{E} - 1} - \ln|x_0\sqrt{\frac{a}{E}} + \sqrt{x_0^2\frac{a}{E} - 1}|)] \qquad (2)$$

where E and ν are the energy and the wavenumber of the degenerate state, respectively and $\Delta\nu$ is the splitting of the level at LNT. This approach seems to be consistent with our experimental results : the decrease of temperature causes continuous increase in $\Delta\nu$ (cf. Fig. 4). Thus, eq. (2) enables one to calculate x_0, for a given value of $\Delta\nu$ and m. As expected, x_0 decreases when $\Delta\nu$ increases and v.v. This is in agreement with the experiment; the decrease of temperature usually implies a contraction of the crystal lattice i.e. a decrease of the interatomic distances. Therefore, it follows from eq. (2), that a continuous increase in $\Delta\nu$, as well as the probability of tunneling motion is expected when the temperature decreases. A rough calculation (for $m = 4m_H$, which seems a realistic estimation for this type of motion) gives the following results : for $\Delta\nu = 4.6$, 2.0 and 0.8 cm^{-1}, x_0 equals to 26, 27.5 and 29 pm respectively. The calculated increase of x_0 is of the same order of magnitude as the increase of the unit cell parameters [3]. The values of $\Delta\nu$, used in eq. (2), are within the range of experemental results (Fig. 3). The resolution of the instrument was 2.0 cm^{-1} and this corresponds to $x_0 = 27.5$ pm. Therefore, according to the model, the splitting of the γ_{CH} band in the lattices with larger volumes of the unit cell, could not be observed, which was actually found to be the case

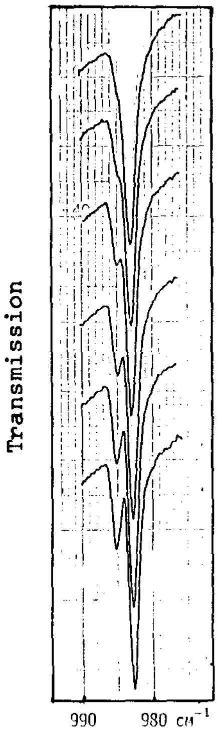

Fig. 4. Temperature dependence (RT-LNT) of γ_{CH} in Ni-Ni-Bz

in the studied clathrates (cf. Fig. 3).

CONCLUSIONS

In this work we did not consider other possibilities which can more or less affect the splitting of the γ_{CH} band. These are :

(1) "Free" rotation at RT, but hindered rotation at LNT; this may be expected in this type of clathrates, since the guest-host interactions are weak.

(2) Removing of the degeneracy of the γ_{CH} vibration (E_{2u} species for the "free" molecule), i.e. site-group splitting.

(3) Crystallographic data showed [1,2] that the benzene molecules can occupy two possible orientations which are mirror images of each other, with respect to the *a*-axis of the unit cell. Therefore, the splitting of the γ_{CH} band may appear as a result of "freezing" of the benzene molecules at LNT.

All these possibilities can not be rulled out. However, the decrease of temperature showed a continuous increase of the γ_{CH} band splitting (cf. Fig. 4) which seems to favour the model based on tunneling motion. In order to confirm or confute our conclusions, further experiments are needed. In the first place, some more clathrates can be synthetised, with smaller or bigger volumes of the unit cell. For instance, Pt and Pd can be used instead of Ni in $Ni(CN)_4$ plane, which will enlarge the unit cell of the clathrates [7].

Finally, we recorded the IR spectra of a series of Hofmann-T_d-type clathrates, in which a square-planar Ni atom is replaced by Cd or Hg. In those clathrates, the γ_{CH} of the C_6H_6 molecules showed similar effect to that found in Hofmann-type clathrates. The results of these studies will be published elsewhere.

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REFERENCES

[1] J.H. Rayner and H.M. Powell, *J. Chem. Soc.*, (1952) 319-329.
[2] R. Kuroda and Y. Sasaki, *Acta Crystallogr.*, B30 (1974) 687-691.
[3] T. Nakano, T. Miyoshi, T. Iwamoto and Y. Sasaki, *Bull. Chem. Soc. Japan*, 40 (1967) 1297.
[4] T. Miyoshi, T. Iwamoto and Y. Sasaki, *Inorg. Chim. Acta*, 1 (1967) 120-126.
[5] T. Iwamoto, T. Miyoshi, T. Miyamoto, Y. Sasaki and S. Fujiwara, *Bull. Chem. Soc. Japan*, 40 (1967) 1174-1178.
[6] L.D. Landau and E.M. Lifshic, *Kvantovaya Teoriya*, Ed., Fiz. Mat. Lit., Moskva, (1963) p. 213.
[7] M. Morita, T. Miyoshi, T. Miyamoto, T. Iwamoto and Y. Sasaki, *Bull. Soc. Chem. Japan*, 40 (1967) 1556.