



Vibrational spectroscopic study on some Hofmann type clathrates: $M(2-(1\text{-cyclohexenyl)ethylamine})_2Ni(CN)_4 \cdot 2\text{benzene}$ ($M = Ni$ and Cd)

Tekin İzgi^{a,*}, Cemal Parlak^b, Mustafa Şenyel^c

^a Department of Physics, Arts and Science Faculty, Inonu University, Malatya 44069, Turkey

^b Department of Physics, Arts and Science Faculty, Dumlupınar University, Kütahya 43100, Turkey

^c Department of Physics, Science Faculty, Anadolu University, Eskişehir 26470, Turkey

ARTICLE INFO

Article history:

Received 15 June 2009

Received in revised form

23 November 2010

Accepted 14 December 2010

Keywords:

Hofmann type clathrates

Inclusion compounds

2-(1-Cyclohexenyl)ethylamine

Benzene

IR and Raman spectra

ABSTRACT

New Hofmann type benzene clathrates in the form of $M(\text{CyHEA})_2Ni(\text{CN})_4 \cdot 2\text{benzene}$ (where $\text{CyHEA} = 2-(1\text{-cyclohexenyl)ethylamine}$ and $M = Ni$ or Cd) have been prepared in powder form and FT-IR and Raman spectra have been reported. The results suggest that title compounds are similar in structure to Hofmann type clathrates and their structures consist of polymeric layers of $[M-Ni(\text{CN})_4]_{\infty}$ with the CyHEA molecule bounded to the metal atoms (M).

© 2011 Published by Elsevier B.V.

1. Introduction

The Hofmann type clathrates are two component inclusion compounds consisting of a host lattice and a guest molecule which are associated without ordinary chemical union, but throughout complete enclosure of one set of molecules in a suitable structure formed by another [1,2]. Their general formula is $M(\text{II})L_2M'(\text{II})(\text{CN})_4 \cdot nG$ where, M is octahedrally coordinated metal: Mn, Fe, Co, Ni, Cu, Zn or Cd ; M' is square-planar coordinated metal: Ni, Pd or Pt ; L is a unidentate ligand molecule and n is the number of G (guest) molecules depending on the bulkiness of the ligand and the guest molecule [1–8]. The host framework consists of two dimensional polymeric layers composed of ML_2 cations and $M'(\text{CN})_4$ anions. The M' atoms are coordinated to four C atoms of the CN groups in a square planar environment. M atoms are octahedrally surrounded by six N atoms, two of which are from ligands and the rest are from cyanide groups. The ligand molecules lie above and below the layers. This structure provides α -type cavity similar to rectangular box for the guest molecules [1–8].

In our previous study, we reported the infrared spectroscopic investigation of $M(\text{CyHEA})_2Ni(\text{CN})_4$ ($M = Ni$ and Co) Hofmann type complexes [9]. In the present work, we have synthesized two new $M(\text{CyHEA})_2Ni(\text{CN})_4 \cdot 2\text{benzene}$ clathrates (abbreviated hereafter as

$M\text{-CyHEA-Ni-Bz}$) using benzene as a guest molecule, where $M = Ni$ or Cd and $Bz = \text{benzene}$, for the first time and investigated their FT-IR and Raman spectra.

2. Experimental

All the chemicals were purchased from Aldrich and used without further purification. The $M\text{-CyHEA-Ni-Bz}$ ($M = Ni$ and Cd) compounds were prepared as follows: firstly 1 mmol of $K_2Ni(\text{CN})_4$ was dissolved in distilled water, then slightly more than 2 mmol of CyHEA were added to this solution under stirring. After a short time, 3 mmol of benzene was added to prepared solution. Finally, 1 mmol of MCl_2 dissolved in distilled water was added drop wise to the prepared mixture, again under stirring. The final mixture was left for stirring for a week at room temperature. The obtained products were filtered and washed with water, ethanol and ether successively and stored in a desiccator containing guest benzene vapour.

Infrared spectra of the clathrates were recorded in the region of $4000\text{--}400\text{ cm}^{-1}$ with Perkin-Elmer FT-IR 2000 spectrometer at a resolution of 4 cm^{-1} . In order to provide better identifications for the vibrational bands of the compounds prepared in this study, two different mulls (in nujol and hexachloro-1,3-butadiene) were used. In the MIR region of spectrum, bands of nujol were reported at 1377 cm^{-1} , 1461 cm^{-1} , 2858 cm^{-1} , 2925 cm^{-1} and of hexachloro-1,3-butadiene 655 cm^{-1} , 793 cm^{-1} , 852 cm^{-1} , 941 cm^{-1} , 981 cm^{-1} , 1170 cm^{-1} , 1564 cm^{-1} , 1610 cm^{-1} , respectively. Raman spectra of

* Corresponding author. Tel.: +90 422 341 00 10x3764; fax: +90 422 341 00 37.
E-mail address: tizgi@inonu.edu.tr (T. İzgi).

the compounds were recorded in the region of 2800–1650 cm⁻¹ with Bruker Senterra Dispersive Raman Microscope using the 532 nm line of a 3B diode laser having 3 cm⁻¹ resolution.

The compounds were analyzed for Ni and Cd metals with Perkin Elmer 4300 ICP-OES and for C, H and N with Fisons EA-1108 elemental analyzer. Ni and Cd metals were investigated at 231.604 nm and 228.802 nm. The results are as follows: (found %/calculated %) Ni(C₈H₁₅N)₂Ni(CN)₄·2C₆H₆ (M_r = 628.10): C(61.05/61.19), H(6.62/6.74), N(13.13/13.38), Ni(18.38/18.69) and Cd(C₈H₁₅N)₂Ni(CN)₄·2C₆H₆ (M_r = 681.82): C(56.18/56.37), H(6.08/6.21), N(12.17/12.32), Ni(8.49/8.61), Cd(16.26/16.49). All the analyses of these clathrates were carried out immediately to avoid any declathration.

3. Results and discussion

The infrared and Raman spectra of the M–CyHEA–Ni–Bz (M = Ni and Cd) clathrates are compatible with each other which implies that the compounds have similar spectral features. Infrared spectra of the clathrates are given in Fig. 1. Raman spectrum of the Cd–CyHEA–Ni–Bz clathrate is given in Fig. 2 as an example. The spectral analysis of each compound has been performed by taking into account the CyHEA ligand molecule, Ni(CN)₄ ions and guest benzene molecule individually.

3.1. CyHEA vibrations

In our previous study, we reported the vibrational assignments and frequencies of the free CyHEA both theoretically and experimentally in the region of 4000–400 cm⁻¹ [10]. The assignments and frequencies for CyHEA in the infrared spectra of the clathrates under study are given in Table 1, together with our previous data, for comparison.

The spectral data for CyHEA in the clathrates exhibit characteristics of a coordinated ligand (Table 1, Fig. 1). On coordination, the NH stretching frequencies attributed to ethylamine within the CyHEA should decrease and CH stretching frequencies arise from both ethylamine and cyclohexene within the CyHEA increase due to the consecutive inductive effects, respectively (on coordination, NH and CN bonds should become weaker and CH bonds should become stronger) [11]. It is clearly observed in Table 1 and Fig. 1 that these requirements are fulfilled for CyHEA in our compounds. These shifts in frequencies have been explained in terms of coupling of the internal vibration of CyHEA ligand with M–N vibrations [2–9]. The observed small shifts for vibrational frequencies of CyHEA are also resulting from the environment changes upon coordination.

3.2. Ni(CN)₄ group vibrations

Assignments of the bands for Ni(CN)₄ ion in the spectra of the present compounds have been carried out by means of vibrational data of Ni(CN)₄ ion in Na₂Ni(CN)₄ reported by McCullough et al. [12]. Since the ion is not coordinated to cations, it can be treated as an isolated unit. Therefore, we have used it as a reference for finding out whether coordination to the M is taking place. The vibrational data for Ni(CN)₄ groups in our clathrates are given in Table 2 along with McCullough et al.'s data.

The assigned IR and Raman wavenumbers for Ni(CN)₄ group in the compounds studied appear to be much higher than those for isolated Ni(CN)₄ units (Table 2, Figs. 1 and 2). Such frequency shifts have been observed for other Hofmann type clathrates [2–8] and are attributed to the mechanical coupling of the internal modes of Ni(CN)₄ with the M–NC vibrations. The characteristic frequencies of Ni(CN)₄ group are found to be similar to those of the Hofmann

Table 1

The vibrational wavenumbers (cm⁻¹) of CyHEA in the M–CyHEA–Ni (M = Ni or Cd) clathrates.

Assignment ^a	CyHEA ^a	Ni–CyHEA–Ni–Bz	Cd–CyHEA–Ni–Bz
NH a-str	3366 s	3354 s	3355 s
NH s-str	3288 s	3286 m	3286 m
ν_1	3043 m	3043 w ^b	3040 w ^b
ν_2 + CH str	2926 vs	2928 vs ^b	2929 vs ^b
ν_{27} + CH str	2857 vs	2857 m ^b	2859 m ^b
ν_5 + CH str	2836 vs	2838 vs ^b	2837 vs ^b
ν_6	1666 m	1666 m	1663 m
NH ₂ sciss	1600 mb	1591 vs	1590 vs
CH ₂ sciss	1505 vw	1510 w	1509 w
CH bend	1473 vw	1461 m ^b	1460 m ^b
ν_8	1438 s	1438 s ^b	1437 s ^b
CH ₂ wag	1384 w	1386 vw ^b	1386 w ^b
ν_9 + CH bend	1370 vw	1361 m ^b	1363 w ^b
ν_{10}	1344 m	1343 vw ^b	1344 w ^b
ν_{30}	1334 w	1320 vw ^b	1319 w ^b
NH ₂ twist	1307 w	1306 w	1307 w
ν_{32}	1269 m	1270 m	1270 m
ν_{11} + CH ₂ twist	1242 w	1243 w	1242 w
ν_{12}	1215 w	1218 m	1221 m
ν_{34}	1136 m	1138 s	1138 s
(CC, CN) a-str	1086 w	1093 s	1097 s
ν_{15}	1066 w	1063 m	1063 m
ν_{16}	966 w	985 s	977 s
ν_{37}	919 m	919 m	920 m
ν_{17}	906 vw	902 vw	910 m
ν_{38}	857 w	869 w	851 w
ν_{18} + CH ₂ rock	829 m	821 w	821 w
ν_{19} + NH ₂ wag	800 m	801 m	801 m
ν_{39}	720 sh	724 w	723 m
ν_{20}	497 vw	497 w	495 vw
ν_{41}	448 w	–	451 w

^a Taken from Ref. [10].

^b In hexachloro-1,3-butadiene. vs: very strong, s: strong, m: medium, w: weak, b: broad, str: stretching, bend: bending, sciss: scissoring, twist: twisting, wag: wagging, rock: rocking.

type clathrates suggesting that coordination around the Ni atom is square planar, and that |M–Ni(CN)₄|_∞ layers have been preserved.

3.3. Benzene vibrations

The assignments and frequencies of the vibrational bands for benzene of the clathrates are given in Table 3 along with the frequencies of benzene in the liquid phase [13,14]. Most of the vibrational bands of the isolated benzene molecules are observed in the infrared spectra of the clathrates (Table 3). According to the chemical results, the number of guest molecules in the present compounds is two ($n=2$). This result has also been observed for other Hofmann-type [2,6,15] and T_d-type [16–18] clathrates.

It is clearly observed in Table 3 and Fig. 1 that the CH out of plane band (ν_{11} –A_{2u}) of the benzene in the clathrates is shifted to higher frequency than that of liquid benzene (670 cm⁻¹) for both compounds. Similar positive frequency shifts have been reported for the Hofmann-type [2–5,7,8] and T_d-type [16–18] clathrates. This case is attributed to the formation of weak hydrogen bonding between

Table 2

The vibrational wavenumbers (cm⁻¹) of Ni(CN)₄ group in the M–CyHEA–Ni–Bz (M = Ni or Cd) clathrates.

Assignment ^a	Na ₂ Ni(CN) ₄ ^a	Ni–CyHEA–Ni–Bz	Cd–CyHEA–Ni–Bz
ν_1 (CN), A _{1g}	(2149)	(2186) vs	(2167) vs
ν_4 (CN), B _{1g}	(2141)	(2176) vs	(2164) vs
ν_8 (CN), E _u	2132	2171 vs	2151 vs
ν_9 (NiC), E _u	543	555 m 580 s	538 s 566 s
δ (NiCN), E _u	433	440 vs	424 vs

^a Taken from Ref. [12]. The bands observed in the Raman spectra are given in parentheses. vs: very strong, s: strong, m: medium.

Download English Version:

<https://daneshyari.com/en/article/1235721>

Download Persian Version:

<https://daneshyari.com/article/1235721>

[Daneshyari.com](https://daneshyari.com)