

FT-IR Spectroscopic Study of $M(1,2\text{-Ethanedithiol})Ni(CN)_4 \cdot \text{Benzene}$ ($M = \text{Co}, \text{Cd}$) Clathrates

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Abstract

New Hofmann-ethanedithiol-type clathrates, $M(1,2\text{-Ethanedithiol})Ni(CN)_4 \cdot \text{Benzene}$ ($M = \text{Cd}, \text{Co}$), have been obtained in the powdered form. By vibrational spectroscopy of these two new compounds, it is exhibited that their structures are similar to those of the other Hofmann-type clathrates.

Introduction

It is well-known that infrared spectroscopy is one of the most powerful tools for investigation of the host–guest interactions in Hofmann-type clathrates. These clathrates have cage structures and inclusion behaviours. Therefore they are used as catalysts, anti-oxidants and stabilizing agents in various industrial areas [1]. The general formula for Hofmann-type clathrates is expressed as $ML_2Ni(CN)_4 \cdot G$ where M is a transition metal atom having the valence of +2, L is either a bidentate or two monodentates ligand molecule and G is the guest molecule [2].

The Hofmann-type host framework, $ML_2Ni(CN)_4$, is built of infinite $[M-Ni(CN)_4]_\infty$ layers with four planar coordination around Ni atom [3]. For the guest molecules this structure provides the α -type (rectangular boxes) cavities [4].

For bulk 1,2-ethanedithiol (EDT) which has been used as a ligand in the present work the infrared vibration modes and frequencies were given by Allinger and Fan [5]. In this study two Hofmann-ethanedithiol-type clathrates $M(EDT)Ni(CN)_4 \cdot \text{Benzene}$ ($M = \text{Cd}, \text{Co}$) were prepared and their infrared spectra are reported for the first time.

Experimental

Sample preparation

1,2-Ethanedithiol liquid of 98% purity and potassium tetracyanonickelate (II) hydrate used in this study were obtained from commercial sources (Fluka and Aldrich,

respectively) and were used without any purification. First, 1 mmol of $K_2Ni(CN)_4$ was dissolved in distilled water and 1 mmol of liquid EDT was dropped into the mixture and stirred rapidly during 2–3 min. Then, 10 mmol of benzene and the MCl_2 ($M = \text{Cd}$ or Co) solution in distilled water added to this mixture, and the whole was stirred during 3 days. The precipitates formed were filtered and washed with distilled water, ethylalcohol and diethylether successively and kept in a desiccator containing molecular sieves and saturated benzene vapour. The colour of the obtained clathrate containing Cd was yellow while the other including Co was dark brown.

On the other hand the host complexes, $Cd(C_2H_6S_2)Ni(CN)_4$ and $Co(C_2H_6S_2)Ni(CN)_4$, were prepared by a similar method to that given above in the absence of benzene.

Elemental analysis

The prepared compounds were analysed by using a LECO CHNS 932 model analyzer for C, H, N and S with the following results (found %/calculated %).

$Cd(C_2H_6S_2)Ni(CN)_4$: C: 12,41/19,51 H: 1,84/1,64 N: 8,35/15,38 S: 19,85/17,36
 $Cd(C_2H_6S_2)Ni(CN)_4 \cdot \text{Benzene}$: C: 14,03/32,21 H: 2,60/2,70 N: 6,43/12,52 S: 12,59/14,33
 $Co(C_2H_6S_2)Ni(CN)_4$: C: 12,51/22,81 H: 2,90/1,91 N: 9,96/17,74 S: 9,41/20,3
 $Co(C_2H_6S_2)Ni(CN)_4 \cdot \text{Benzene}$: C: 14,12/36,58 H: 3,57/3,07 N: 9,90/14,22 S: 7,91/16,28

It is well-known that these analytical results are often poor for the samples obtainable in powder form owing to partial decomposition.

Thermal analysis

For the melting point measurements of the title complexes, a LA 9100 electrothermal digital melting point

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apparatus (at the range of 0–350 °C) was used. Since the samples did not melt at this temperature interval the decomposition points for our sample were obtained as follows. The decompositions occurred at 245, 260, 170 and 180°C for the Cd(EDT)Ni(CN)₄, Cd(EDT)Ni(CN)₄·Benzene, Co(EDT)Ni(CN)₄ and Co(EDT)Ni(CN)₄·Benzene complexes, respectively. From these values we conclude that two results should be considered. Firstly, the decompositions of the complexes with the guest benzene molecules occur at higher degrees than other two host structures. This indicates that when the benzene molecules are connected to the polymeric structure, the decompositions go up higher temperature region. Secondly, lower decomposition points show that Co(EDT)Ni(CN)₄ and Co(EDT)Ni(CN)₄·Benzene complexes have shorter polymeric chain than the Cd(EDT)Ni(CN)₄ and Cd(EDT)Ni(CN)₄·Benzene complexes.

Infrared spectroscopy

IR spectra were recorded at room temperature on a Perkin-Elmer Spectrum One FT-IR (Fourier Transformed Infrared) Spectrometer with a resolution of 4 cm⁻¹ in the transmission mode. The prepared samples were compressed into self-supporting pellet and introduced into an IR cell equipped with KBr windows.

X-ray diffraction

XRD patterns were recorded using a Pananalytical BV (PW 3050/60 Model) powder diffractometer with CuKα (1.54060 Å, 40 mA, 45 kV) at 0.02 steps at the rate of 0.5 per second over the range 5 < 2θ < 75.

Results and discussion

X-ray structure determination

Powder X-ray diffraction patterns of M(EDT)Ni(CN)₄·Benzene (M = Cd, Co) complexes are not efficiently distinguished from each other and are shown in Figures 1 and 2, respectively. By considering the XRD patterns exhibited in Figures 1 and 2, the structures of the title complexes were referenced and solved from ICSD using POWD-12⁺⁺ [6]. In the results of these searchings, it is understood that the structures of the title complexes have the orthorhombic crystal systems with Pnma space groups [7–8]. On the other hand the Ni(CN)₄ units which are two-dimensional structures have a square-planar arrangement and are linked to octahedral metal (M = Cd, Co) centers by coordination through the cyanide N atom [9]. The structure of Co(EDT)Ni(CN)₄·Benzene which is isostructural with Cd(EDT)Ni(CN)₄·Benzene is roughly depicted in Figure 3.

As a result we conclude that the structure of the title complexes are composed of alternating nickel cyanide sheets and layers of sulphur-bonded ethanedithiol (ligand) molecules that alternate along the *a*-axis [8].

Infrared spectra

The IR spectra of Cd(EDT)Ni(CN)₄·Benzene and Co(EDT)Ni(CN)₄·Benzene clathrates are shown in Figures 4 and 5, respectively. Analysis of the results obtained from IR spectral data can be achieved three parts by considering the vibrations of ligand molecules, the Ni(CN)₄⁻² ion units and the guest benzene molecules.

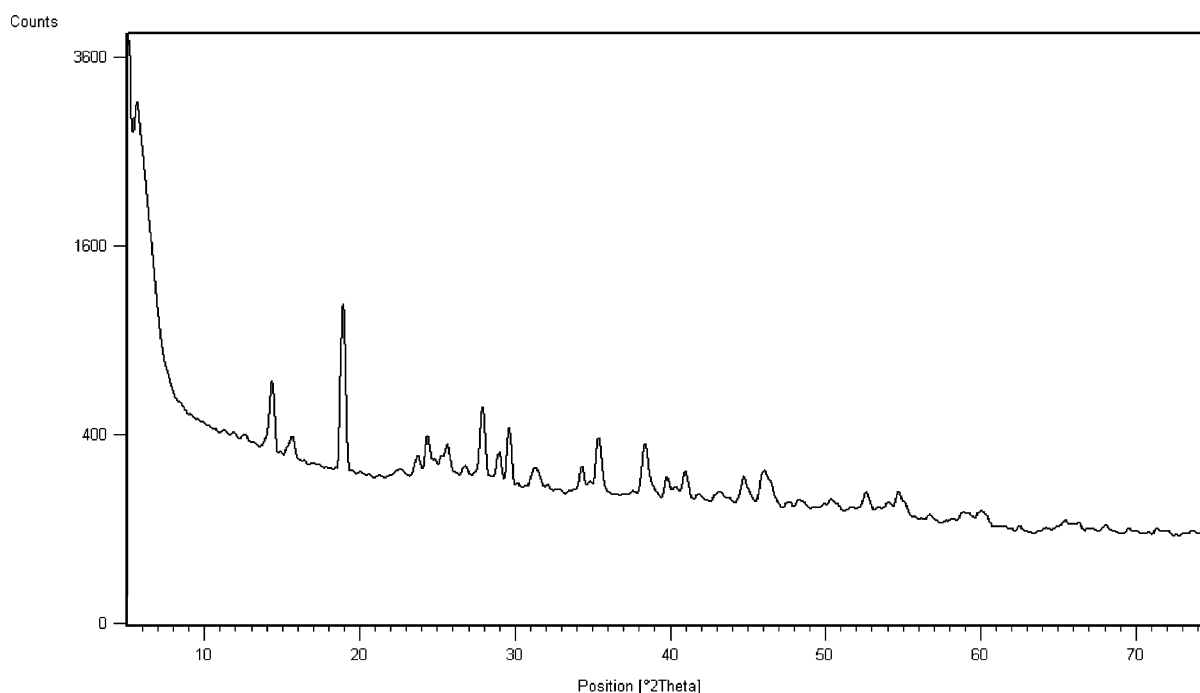


Figure 1. Powder X-ray diffraction pattern of Cd(EDT)Ni(CN)₄·Benzene clathrate.

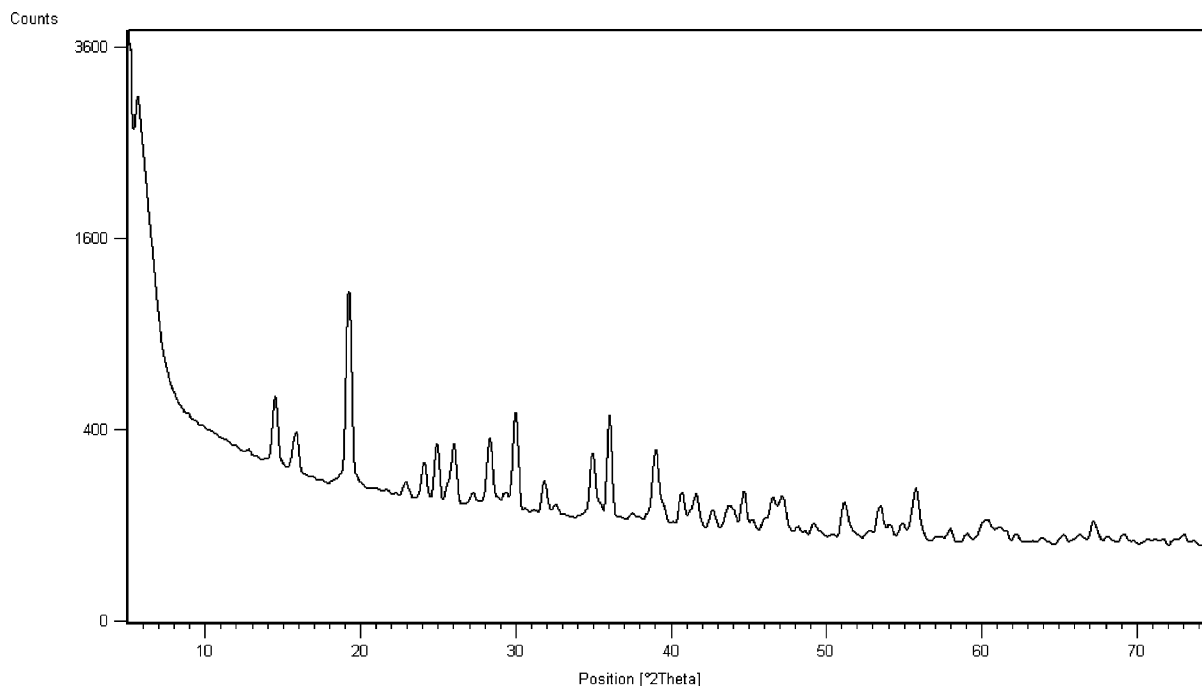


Figure 2. Powder X-ray diffraction pattern of Co(EDT)Ni(CN)₄·Benzene clathrate.

Ligand vibrations

The explicit form of EDT which is used as the ligand molecule in our work is C₂H₆S₂ and its synonym is dithioethyleneglycol. IR spectral data of EDT as a ligand molecule are summarized in Table 1.

The assignments of IR vibrational frequencies for liquid EDT have been obtained from Allinger and Fan [5]. As seen in Table 1 the symmetric CH stretching vibration band of bulk EDT at the 2837 cm⁻¹ is shifted to 2852 and 2859 cm⁻¹ for Cd(EDT)Ni(CN)₄·Benzene and Co(EDT)Ni(CN)₄·Benzene complexes (denoted with arrows in Figures 4 and 5), respectively. However the medium band at 2906 cm⁻¹ in Cd(EDT) Ni(CN)₄·Benzene clathrate and the weak band at 2924 cm⁻¹ in Co(EDT)Ni(CN)₄·Benzene clathrate can be assigned to

the CH asymmetric stretching modes of EDT ligand molecule. In a similar way the methylene (CH₂) bending, wagging and twisting vibration modes of the bulk EDT are observed at the slightly shifted values for both clathrate as seen in Table 1. These bands mentioned above are the most characteristic bands which are those of the (CH₂) groups attached to the unoxidized sulfur atom in the EDT ligand molecules [10]. On the other hand the S-H stretching vibrations of bulk EDT is observed at 2550 cm⁻¹ while this mode is shifted to a weak band at 2302 cm⁻¹ (shown with an arrow) in low frequency region for Cd(EDT)Ni(CN)₄·Benzene complex. However the SH vibration mode of ligand EDT molecule in Co(EDT)Ni(CN)₄·Benzene complex is observed at the same value. Furthermore the ν(CS) stretching modes of bulk EDT can be attributed to the very strong band at 693 cm⁻¹ and the strong band at 635 cm⁻¹. But for the ligand EDT molecules of Cd(EDT)Ni(CN)₄·Benzene and Co(EDT)Ni(CN)₄·Benzene clathrates the ν(CS) stretching modes are slightly shifted to low frequency region at 691, 690, and 629 and 630 cm⁻¹, respectively. Then it is obvious that the changes in the surroundings of EDT ligand molecules in the complexes under study cause the observation of frequency shifts because of the formation of a new compound.

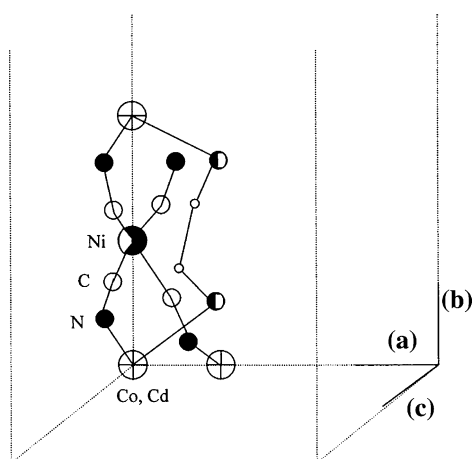


Figure 3. A roughly depiction of the arrangements of MNi(CN)₄ (M = Cd, Co) and EDT sheets.

Ni(CN)₄⁻² group vibrations

The vibrational wave numbers of the Ni(CN)₄⁻² anions in our complexes studied are given in Table 2. The assignments of IR vibrational modes of K₂Ni(CN)₄ have been based on those of the work done by McCullough and co-worker in the tetracyanonickelate group in the salt Na₂Ni(CN)₄ [11].

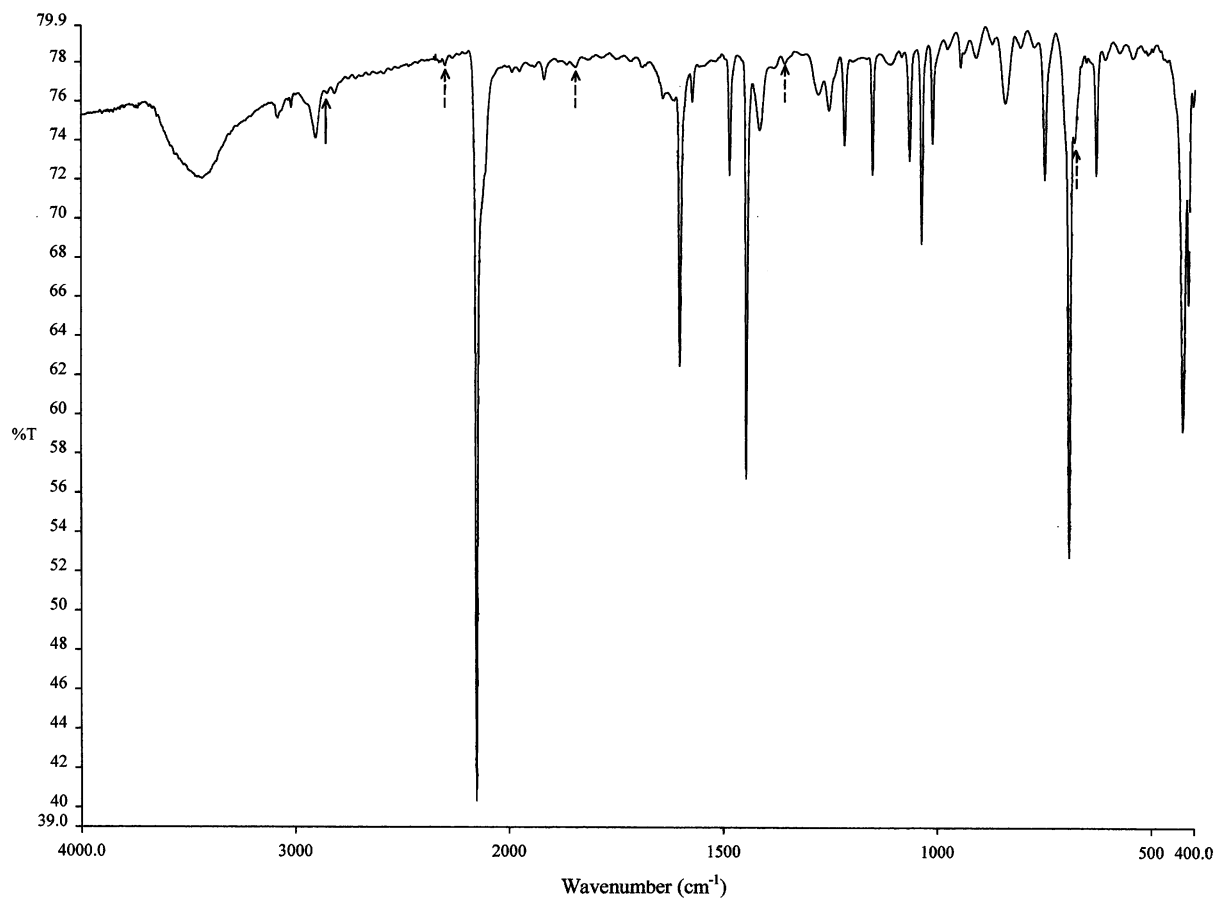


Figure 4. The infrared spectrum of Cd(EDT)Ni(CN)₄·Benzene clathrate.

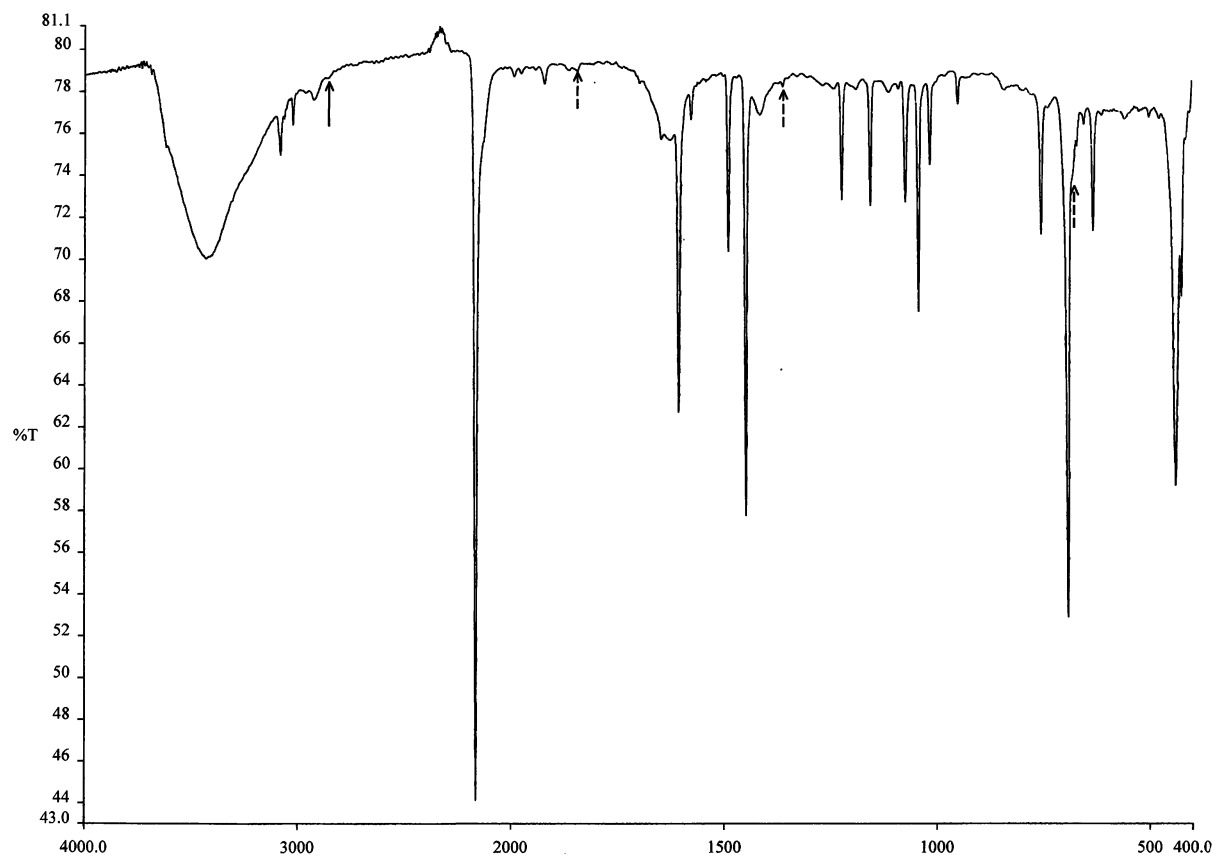


Figure 5. The infrared spectrum of Co(EDT)Ni(CN)₄·Benzene clathrate.

Table 1. The IR vibrational wavenumbers (cm^{-1}) of bulk EDT in $\text{M}(\text{EDT})\text{Ni}(\text{CN})_4\cdot\text{Benzene}$ ($\text{M} = \text{Cd}$ and Co) complexes

Assignments	Liquid EDT	Cd-(EDT)-Ni-Bz	Co-(EDT)-Ni-Bz
Asym. CH stretch	2922 s	2906 m	2924 w
Sym. CH stretch	2837 m	2852 w	2859 w
SH stretch	2550 s	2302 vw	–
CH2 bend	1418 s	1447 s	1447 s
CH2 wag	1273 s	1253 w	–
CH2 wag	1216 s	1216 m	1219 m
CH2 twist	1146 s	1152 m	1153 m
CC stretch	1032 m	1060 m	1070 m
CC stretch	974 s	1012 m	1013 m
CSH def	892 m	945 w	947 w
CSH def	767 s	749 m	749 m
CS stretch	693 vs	691 s	690 s
CS stretch	635 s	629 m	630 m

Where s: strong, vs: very strong, m: medium, w: weak, vw: very weak.

The diagnostic wave numbers of the (CN) and (Ni-CN) modes are found to be similar those of Hofmann-type clathrates [12–13]. The $\nu(\text{CN})$ E_u and $\delta(\text{Ni-CN})$ E_u modes are both observed as strong bands at 2152 and 2163 cm^{-1} and as weak bands 414 and 424 cm^{-1} in the IR spectra of the $\text{Cd}(\text{EDT})\text{Ni}(\text{CN})_4\cdot\text{Benzene}$ and $\text{Co}(\text{EDT})\text{Ni}(\text{CN})_4\cdot\text{Benzene}$ clathrates, respectively. On the other hand the $\nu(\text{Ni-CN})$ modes of the $\text{Ni}(\text{CN})_4^{2-}$ groups are shifted to the bands at 544 and 555 cm^{-1} in high frequency region while the $\pi(\text{Ni-CN})$ modes are shifted to the low frequency region at and 438 cm^{-1} for both clathrates, respectively. As seen in Table 2 the (CN) frequencies are metal dependent and increase in the order $\text{Cd} < \text{Co}$. These frequency shifts can arise from the pairing between the CN stretching vibrations and the metal-nitrogen bond stretching vibration. By considering these data it can be stated that the $\{\text{M-Ni}(\text{CN})_4\}_P$ layers were preserved and these polymeric layers are held in the parallel by van der Waals interactions between the methylene (CH_2) groups in the EDT ligand molecules [14].

Benzene (guest molecule) vibrations

In assigning the band attributable to the enclathrated benzene observed in spectra of studied complexes we

Table 2. The IR vibrational wave numbers (cm^{-1}) of $\text{Ni}(\text{CN})_4$ groups in the $\text{Cd}(\text{EDT})\text{Ni}(\text{CN})_4\cdot\text{Benzene}$ and $\text{Co}(\text{EDPT})\text{Ni}(\text{CN})_4\cdot\text{Benzene}$ clathrates

Assignment	$\text{K}_2\text{Ni}(\text{CN})_4$	Cd-Ni-(EDT)-Bz	Co-Ni-(EDT)-Bz
$\nu(\text{CN})$	2121	2152 s	2163 s
$\nu(\text{Ni-CN})$	539	544 w	555 w
$\pi(\text{Ni-CN})$	443	427 m	438 m
$\delta(\text{Ni-CN})$	416	414 w	424 w

Where s: strong, m: medium, w: weak, v: stretching, π : out of plane bending, δ : in plane bending.

Table 3. The IR vibrational wavenumbers (cm^{-1}) of benzene in the $\text{Cd}(\text{EDT})\text{Ni}(\text{CN})_4\cdot\text{Benzene}$ and $\text{Co}(\text{EDT})\text{Ni}(\text{CN})_4\cdot\text{Benzene}$ clathrates

Assignment	Liquid benzene	Cd-(EDT)-Ni-Bz	Co-(EDT)-Ni-Bz
ν_{20}, E_{1u}	3071	3081 m	3082 m
ν_{13}, B_{1u}	3035	3019 m	3022 m
$\nu_5 + \nu_{17}, E_{1u}$	1960	1976 w	1974 w
$\nu_{10} + \nu_{17}$	1815	1847 w	1841 w
ν_8, E_{2g}	1528	1574 m	1573 m
ν_{19}, E_{1u}	1477	1486 s	1487 s
ν_{14}, B_{2u}	1393	1357 w	1358 w
ν_{18}, E_{1u}	1035	1037 s	1039 s
ν_{17}, E_{2u}	849	842 m	838 w
ν_{11}, A_{2u}	670	679 vw	679 sh

Where b: broad, s: strong, m: medium, sh: shoulder, w: weak, vw: very weak, v: stretching.

refer to the work of Painter and Koenig [15] and IR vibrational wavenumbers of benzene in these compounds are given in Table 3. It is expected that the benzene molecules should lose their own intrinsic (D_{6h}) symmetries due to the changes of their surroundings in the clathrates [13]. Structurally the most informative spectral features are the following.

The A_{2u} (the CH-out-of plane) mode at 670 cm^{-1} for the bulk benzene is slightly shifted to higher frequency region (the bands at 679 cm^{-1} which are denoted with a dashed arrow on the Figures 4 and 5) for both complex. Similarly the ν_{19} mode of guest benzene molecules in the $\text{Cd}(\text{EDT})\text{Ni}(\text{CN})_4\cdot\text{Benzene}$ and $\text{Co}(\text{EDT})\text{Ni}(\text{CN})_4\cdot\text{Benzene}$ complexes are observed in the strong bands at 1486 and 1487 cm^{-1} (shown with dashed arrows on the Figures 4 and 5), respectively. In other words, these bands are shifted to higher frequency region as seen in Table 3. On the other hand the ν_{14}, B_{2u} mode for guest benzene molecule in both compounds appears as the weak bands at 1357 and 1358 cm^{-1} , respectively (denoted with the dashed arrows on Figures 4 and 5) as seen in Table 3 and are shifted to lower frequency region. Meanwhile the strong bands at 1037 and 1039 cm^{-1} in the $\text{Cd}(\text{EDT})\text{Ni}(\text{CN})_4\cdot\text{Benzene}$ and $\text{Co}(\text{EDT})\text{Ni}(\text{CN})_4\cdot\text{Benzene}$ complexes, respectively can be attributed to the ν_{18}, E_{1u} mode of enclathrated benzene. These frequency shifts for the guest benzene molecule in the mentioned complexes are arised from the interactions of guest benzene molecules with the host molecules of these compounds.

As a conclusion, the preceding discussion considered as a whole declares that the $\text{Cd}(\text{EDTT})_2\text{Ni}(\text{CN})_4\cdot\text{Benzene}$ and $\text{Co}(\text{EDTT})_2\text{Ni}(\text{CN})_4\cdot\text{Benzene}$ complexes are two new Hofmann-type clathrates.

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