

FT-IR Spectroscopic Study of the Hofmann- T_d -type Clathrates: $\text{Ni}(1,9\text{-diaminononane})\text{M}'(\text{CN})_4 \cdot 2\text{G}$ ($\text{M}' = \text{Cd}$ or Hg , $\text{G} = \text{Benzene}$, $1,2\text{-Dichlorobenzene}$ or $1,4\text{-Dichlorobenzene}$)

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Keywords New Hofmann T_d -type clathrates in the form of $\text{Ni}(1,9\text{-diaminononane})\text{M}'(\text{CN})_4 \cdot 2\text{G}$ ($\text{M}' = \text{Cd}$ or Hg , $\text{G} = \text{benzene}$, $1,2\text{-dichlorobenzene}$ or $1,4\text{-dichlorobenzene}$) were prepared in powder form and their infrared spectra are reported in the range of $4000\text{--}200\text{ cm}^{-1}$. As seen from the spectral features, the present compounds are similar in structure to the Hofmann T_d -type clathrates.

1,9-diaminononane
1,2-dichlorobenzene
1,4-dichlorobenzene
benzene
Hofmann T_d -type clathrates
infrared spectra

INTRODUCTION

Hofmann- T_d -type clathrates are defined by the general formula $\text{M}(\text{L}_2)\text{M}'(\text{CN})_4 \cdot n\text{G}$, where M is the transition metal, L_2 is a bidentate ligand or a pair of unidentate ligand molecules, M' is Zn , Cd or Hg and G is the guest molecule of an n amount.^{1,2} In the host framework of the compounds $[\text{M}(\text{L}_2)\text{M}'(\text{CN})_4]$, the M' atom is tetrahedrally coordinated to the carbon atoms of the four cyanide groups while the M atom is octahedrally surrounded by six nitrogen atoms, two of which are from the ligand molecules attached to the Zn , Cd or Hg atom in the position *trans* to each other and the other four are from cyanide groups.^{1–3} The $\text{M}'(\text{CN})_4$ groups are linked by the $\text{M}(\text{L}_2)$ moieties to form a three-dimensional network.⁴ These structures provide two kinds of cavities, α and β , for guest

molecules. The α cavity approximates to a rectangular box and the β cavity is a biprismatic cage.^{2,3} Various studies have shown that a host structure of this kind can accommodate various molecules as guests, which in turn provides information on the inclusion ability of the host structure.^{5–9}

In the present study, six compounds were prepared in the form of $\text{Ni}(\text{L})\text{M}'(\text{CN})_4 \cdot 2\text{G}$ [$\text{M}' = \text{Cd}$ or Hg , $\text{G} = \text{benzene}$ (Bz), $1,2\text{-dichlorobenzene}$ ($1,2\text{ClBz}$) or $1,4\text{-dichlorobenzene}$ ($1,4\text{ClBz}$), $\text{L} = 1,9\text{-diaminononane}$ (danon)] for the first time and their spectral properties (abbreviated henceforth as $\text{Ni-danon-M}'\text{-}2\text{G}$) were studied in the IR region. The spectral data are structurally correlated with those of the corresponding T_d type clathrates, whose structures are known from single crystal X-ray studies.^{1–4}

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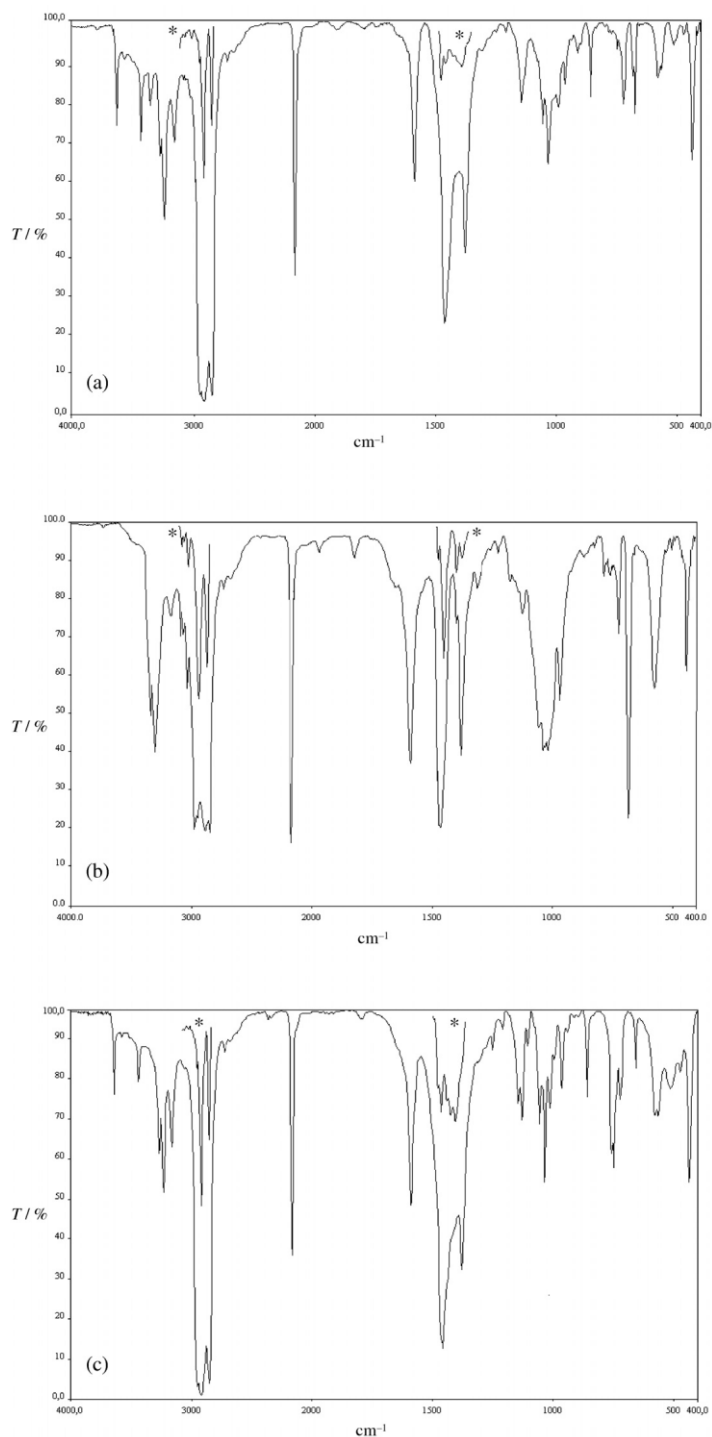


Figure 1, cont. ⇒

EXPERIMENTAL

All the chemicals used were of reagent grade (Merck) and were used without further purification. The Ni-danon-M'-2G (M' = Cd or Hg) compounds were prepared using a method analogous to that given in the literature.^{10,11} The compounds were prepared as follows: 1 mmol of K₂M(CN)₄ (M = Cd or Hg) was dissolved in distilled water and left under stirring with a magnetic stirrer. After a short time, slightly more than 1 mmol of danon dissolved in ethanol was added drop-

wise to the solution and then 3 mmoles of the guest molecule G (G = Bz, 1,2ClBz or 1,4ClBz) was added to the prepared solution. Finally, 1 mmol of NiCl₂ dissolved in distilled water was added to the mixture prepared dropwise, again under stirring. The final mixtures of all compounds were then stirred for a week at room temperature. The obtained precipitates were filtered and washed successively with water, ethanol and ether, and kept in a desiccator containing saturated guest vapour.

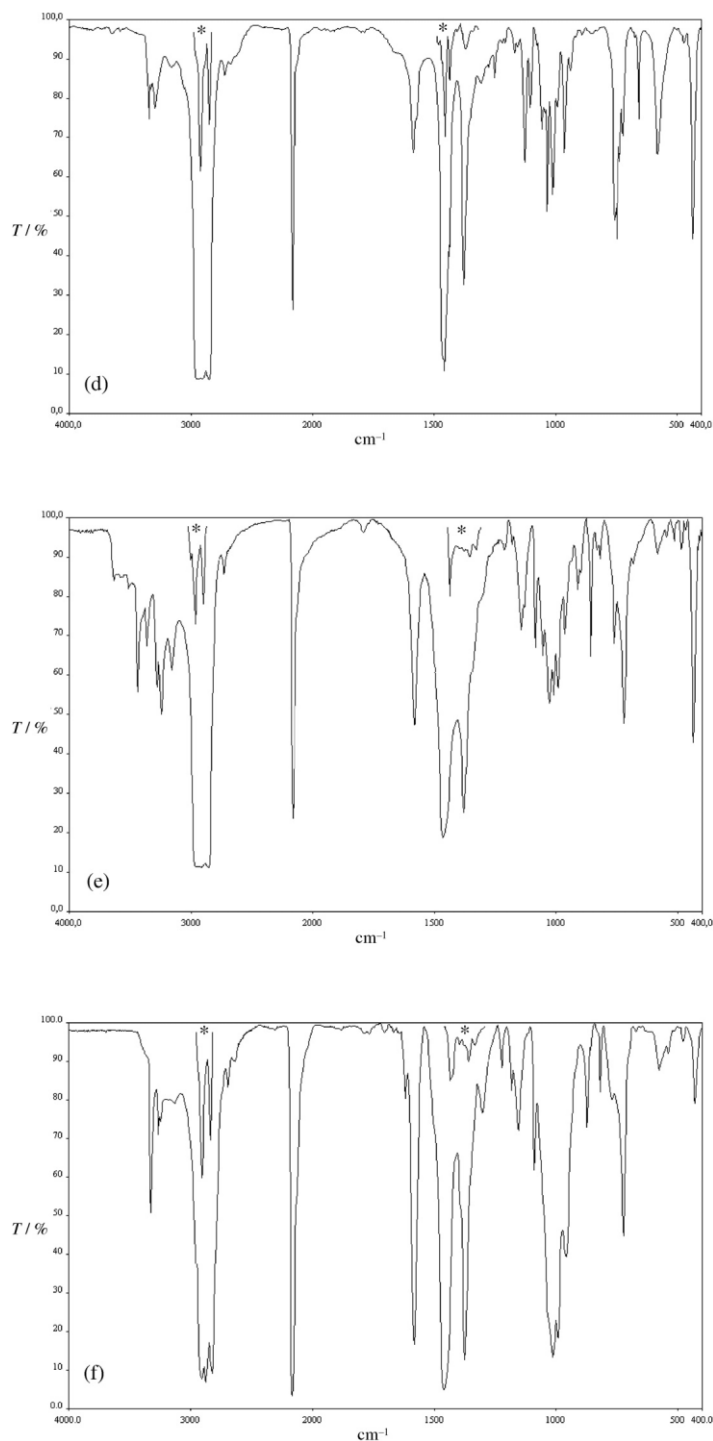


Figure 1. Infrared spectrum of Ni-Cd-Bz (a), Ni-Hg-Bz (b), Ni-Cd-1,2ClBz (c), Ni-Hg-1,2ClBz (d), Ni-Cd-1,4ClBz (e) and Ni-Hg-1,4ClBz (f) clathrates in nujol (*, in hexachloro-1,3-butadiene).

Infrared spectra of the compounds were recorded in the range of 4000–200 cm^{-1} using a Perkin Elmer FTIR 2000 spectrometer with the resolution of about 4 cm^{-1} . The spectrometer was calibrated using polystyrene and indene. The samples were prepared as mulls in nujol and hexachloro-1,3-butadiene between CsI cells. The prepared samples were analyzed for Ni, Cd and Hg with a Perkin Elmer 4300 ICP-OES and for C, H and N with a LECO, CHNS-932 ele-

mental analyzer. The analytical results indicate that the number of guest molecules in the compounds is 2; see Table I. A similar n number was reported for the Hofmann T_d -type clathrates.^{5–9} In addition to the IR study, methods of thermal analysis (DTA and TGA) were also applied for one of the present compounds $[\text{Ni}(\text{danon})\text{Cd}(\text{CN})_4 \cdot 2\text{Bz}]$ to find out whether clathration takes place. Differential thermal analysis (DTA) and thermo-gravimetric analysis (TGA) curves for the

TABLE I. Elemental analyses of compounds: the calculated and found data expressed in percents^(a)

Samples and M_r	C	H	N	Ni	Cd	Hg
Ni(C ₉ H ₂₂ N ₂)Cd(CN) ₄ · 2C ₆ H ₆ $M_r = 589.68$	50.92 (50.51)	5.81 (5.67)	14.25 (14.12)	9.95 (9.85)	19.06 (18.95)	–
Ni(C ₉ H ₂₂ N ₂)Hg(CN) ₄ · 2C ₆ H ₆ $M_r = 677.86$	44.30 (43.98)	5.05 (4.88)	12.40 (12.21)	8.66 (8.23)	–	29.59 (29.27)
Ni(C ₉ H ₂₂ N ₂)Cd(CN) ₄ · 2(1,2-C ₆ H ₄ Cl ₂) $M_r = 727.46$	41.27 (41.07)	4.16 (4.03)	11.55 (11.15)	8.07 (7.83)	15.45 (15.27)	–
Ni(C ₉ H ₂₂ N ₂)Hg(CN) ₄ · 2(1,2-C ₆ H ₄ Cl ₂) $M_r = 815.64$	36.81 (36.46)	3.71 (3.49)	10.30 (10.03)	7.20 (7.01)	–	24.60 (24.21)
Ni(C ₉ H ₂₂ N ₂)Cd(CN) ₄ · 2(1,4-C ₆ H ₄ Cl ₂) $M_r = 727.46$	41.27 (41.02)	4.16 (3.98)	11.55 (11.20)	8.07 (7.91)	15.45 (15.21)	–
Ni(C ₉ H ₂₂ N ₂)Hg(CN) ₄ · 2(1,4-C ₆ H ₄ Cl ₂) $M_r = 815.64$	36.81 (36.53)	3.71 (3.55)	10.30 (10.10)	7.20 (7.07)	–	24.60 (24.37)

^(a) Found data are in the parentheses.

compound were recorded using a Setaram Labsys TG/DTA with *ca.* 6.2 mg of sample and a scanning rate of 5° min⁻¹ under argon.

RESULTS AND DISCUSSION

The infrared spectra obtained for the Ni-danon-M'-2G (M' = Cd or Hg) are similar, indicating that the compounds have analogous spectral features; see Figure 1 for each spectrum. Spectral analysis was performed for each compound considering the danon molecule, M'(CN)₄ (M' = Cd and Hg) ions and guest molecules individually, as explained below starting with the ligand molecule vibrations.

The thermal analysis results for Ni(danon)Cd(CN)₄ · 2Bz are presented in Figure 2. The TGA method data indicate that on heating, the compound gradually loses two guest molecules and one ligand in a single step between about 40 and 120 °C. On the basis of the DTA curve, guest molecules leave the host structure at around 63.64 °C and this is followed by the leaving of the ligand molecule at about 98.23 °C. After this temperature, the structure of the compound decomposes. The results manifest the formation of clathrating.

1,9-Diaminononane Vibrations

Assignments and wavenumbers of the vibrational bands for the danon molecule observed in the infrared spectra of the Ni-danon-M'-2G (M' = Cd or Hg) clathrates are given in Table II together with the wavenumbers of danon in CCl₄ solution,^{12–13} in which assignments were made.

As seen from Table II, the NH₂ stretching frequencies of danon molecules in the compounds are lower than

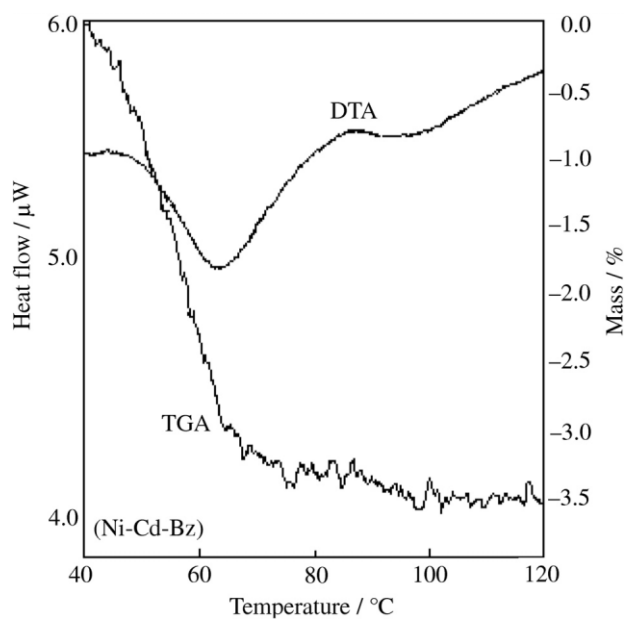


Figure 2. TGA and DSC curves of the Ni(danon)Cd(CN)₄ · 2Bz.

those of danon in the CCl₄ solution. The downward frequency shifts may be interpreted as a weakening of the N–H bonds resulting from the electron draining of the two N atoms on account of their bridging coordination between the two consecutive Ni atoms. Analogous shifts upon coordination were reported for the Hofmann T_d-type clathrates; see Kantarci *et al.* and references therein.⁹ Another spectral feature is that the asymmetric and symmetric stretching vibrations of the NH₂ groups appear as two single sharp bands; hence no splitting for these bands. This implies that the ligand molecule in the compounds

TABLE II. The vibrational wavenumbers (expressed in cm^{-1}) of danon in the Ni-danon- M' -2G clathrates

Assignment ^(a)	Danon in CCl_4 ^(b)	Ni-Cd-Bz	Ni-Hg-Bz	Ni-Cd-1,2ClBz	Ni-Hg-1,2ClBz	Ni-Cd-1,4ClBz	Ni-Hg-1,4ClBz
$\nu_d(\text{NH}_2)$	3361 vs	3284 vs	3333 vs	3284 vs	3348 s	3284 s	3335 vs
$\nu_s(\text{NH}_2)$	3325 vs	3249 vs	3295 vs	3248 vs	3297 s	3246 s	3290 s
$\nu_d(\text{CH}_2)$	2926 vs	2915 vs ^(c)	2923 vs ^(c)	2915 vs ^(c)	2926 vs ^(c)	2916 vs ^(c)	2920 vs ^(c)
$\nu_s(\text{CH}_2)$	2856 vs	2850 vs ^(c)	2853 vs ^(c)	2851 vs ^(c)	2853 vs ^(c)	2848 vs ^(c)	2851 vs ^(c)
$\delta(\text{NH}_2)$	1581 vs	1588 vs	1588 vs	1586 vs	1588 s	1586 vs	1583 vs
$\delta(\text{CH}_2)$	1489 vs	1466 s ^(c)	1467 s ^(c)	1465 s ^(c)	1460 s ^(c)	1475 vs ^(c)	1473 vs ^(c)
$\rho_t(\text{CH}_2)$	1313 m	1309 w	1310 m	–	1306 w	1307 w	1305 w
$\rho_t(\text{NH}_2)$	1225 w	1208 w	1223 w	1210 w	1219 w	1215 w	1223 m
$\nu(\text{CN})$	1097 vw	1102 sh	–	1105 w	1105 m	–	1110 sh
$\nu(\text{CN})$	1070 w	1057 m	1052 w	1057 m	1058 m	1058 m	1059 sh
$\rho_r(\text{CH}_2)$	931 m	964 m	968 m	964 m	966 s	964 m	960 m
$\rho_r(\text{CH}_2)$	877 m	859 m	864 w	859 s	860 w	858 s	873 m
$\rho_r(\text{CH}_2)$	721 m	722 s	723 s	723 m	724 m	723 s	724 s

(a),(b) Taken from Refs. 13, 12. (c) In hexachloro-1,3-butadiene. (d) vs = very strong, s = strong, m = medium, w = weak, vw = very weak, sh = shoulder.

TABLE III. Vibrational wavenumbers (expressed in cm^{-1}) of the $M'(\text{CN})_4$ group for the Ni-danon- M' -2G clathrates

Assignment ^(a)	$\text{K}_2\text{Cd}(\text{CN})_4$ ^(a)	$\text{K}_2\text{Hg}(\text{CN})_4$ ^(a)	Ni-Cd-Bz	Ni-Hg-Bz
$\nu_5(\text{CN})\text{F}_2$	2145	2146	2165 vs	2165 vs
$\nu_6[\nu(\text{MC})+\delta(\text{NCM})]\text{F}_2$	316	330	353 s	352 s
$\nu_7[\nu(\text{MC})+\delta(\text{NCM})]\text{F}_2$	250	235	266 w	267 w
Assignment ^a	Ni-Cd-1,2ClBz	Ni-Hg-1,2ClBz	Ni-Cd-1,4ClBz	Ni-Hg-1,4ClBz
$\nu_5(\text{CN})\text{F}_2$	2166 vs	2162 vs	2166 s	2165 s
$\nu_6[\nu(\text{MC})+\delta(\text{NCM})]\text{F}_2$	353 s	353 s	350 s	350 s
$\nu_7[\nu(\text{MC})+\delta(\text{NCM})]\text{F}_2$	267 w	267 w	265 w	265 w

(a) Taken from Ref. 14.

behaves as a bridge (bidentate coordination). From the present spectral data, it is not possible to give an account of the danon molecule conformation in the compounds.

$M'(\text{CN})_4$ ($M' = \text{Cd}$ or Hg) Vibrations

Assignments of bands for the $M'(\text{CN})_4$ ($M' = \text{Cd}$ or Hg) ions in the spectra of the compounds were made using the vibrational data of the $\text{K}_2\text{M}(\text{CN})_4$ ($M = \text{Cd}$ or Hg) salts in the solid phase reported by Jones, who assigned the vibrational data on the basis of T_d symmetry.¹⁴ Studies of these salts have shown that the K–CN distances are 2.9 Å in $\text{K}_2\text{Cd}(\text{CN})_4$ ¹⁵ and in $\text{K}_2\text{Hg}(\text{CN})_4$,¹⁶ while the Cd–NC distances are 2.3 Å in the T_d symmetry.⁴ We therefore used them as references to account for the vibrational changes when the stiffer M–NC bonding takes place. Vibrational data for the $M'(\text{CN})_4$ groups in the compounds are given in Table III along with the vibrational wavenumbers of $\text{K}_2\text{Cd}(\text{CN})_4$ and $\text{K}_2\text{Hg}(\text{CN})_4$.

As seen from Table III, vibrational frequencies of the $M'(\text{CN})_4$ groups in the compounds are shifted to higher frequencies compared to the $M'(\text{CN})_4$ groups in $\text{K}_2\text{Cd}(\text{CN})_4$ and $\text{K}_2\text{Hg}(\text{CN})_4$. Similar frequency shifts were observed for the Hofmann T_d -type compounds^{5–9,11,17} and indicated that the shifts arise from the mechanical coupling of the internal modes of $M'(\text{CN})_4$ with metals since both ends of the CN group are bounded to the transition metals. Accordingly, the shifts observed in the compounds can be attributed to the mechanical coupling of the internal modes of $M'(\text{CN})_4$ with metals.

Guest Vibrations

Assignments and wavenumbers of the vibrational bands for the guest molecules of the compounds are given in Tables IV–V along with the wavenumbers of benzene in the liquid phase,¹⁸ 1,2ClBz¹⁹ and 1,4ClBz in the liquid phase²⁰ for comparison.

TABLE IV. Vibrational wavenumbers (expressed in cm^{-1}) of benzene in the Ni-danon-M'-2Bz clathrates

Assignment ^(a)	Liquid benzene ^(a)	Ni-Cd-Bz	Ni-Hg-Bz
ν_{20} , E_{1u}	3073	3089 w	3088 m
$\nu_8 + \nu_{19}$, E_{1u}	3075	3071 vw	3068 w
B_{13} , B_{1u}	3048	3039 m ^(b)	3036 m
$\nu_5 + \nu_{17}$, E_{1u}	1955	1961 w	1966 m
$\nu_{10} + \nu_{17}$, E_{1u}	1815	1817 w	1819 m
ν_{19} , E_{1u}	1479	1477 s ^(b)	1479 s ^(b)
ν_{15} , B_{2u}	1149	1146 s	1138 m
ν_{18} , E_{1u}	1036	1035 s	1035 m
ν_{11} , A_{2u}	670	684 w 675 s	682 vs

^(a) Taken from Ref. 18. ^(b) In hexachloro-1,3-butadiene.

TABLE V. Vibrational wavenumbers (expressed in cm^{-1}) of 1,2ClBz and 1,4ClBz in the Ni-danon-M'-2G clathrates

Assignment ^(a)	1,2ClBz ^(a)	Ni-Cd-1,2ClBz	Ni-Hg-1,2ClBz	Assignment ^(b)	1,4ClBz ^(b)	Ni-Cd-1,4ClBz	Ni-Hg-1,4ClBz
$\nu(\text{CH})$, A_1	3072	3071 w	3067 w	$\nu(\text{CC})$, B_{2u}	1394	1394 m ^(c)	1397 m ^(c)
$\nu(\text{CC})$, A_1	1576	1578 sh	1575 sh	$\alpha(\text{CCC})$, B_{2u}	1220	1218 sh	–
$\nu(\text{CC})$, A_1	1458	1458 w ^(c)	1465 w	X-sens, B_{1u}	1090	1088 m	1089 s
$\nu(\text{CC})$, B_2	1438	1434 m	1434 w	$\beta(\text{CH})$, B_{1u}	1015	1013 m	*
$\beta(\text{CH})$, B_2	1252	1251 m	1252 m	$\gamma(\text{CH})$, B_{3g}	934	934 w	930 sh
X-sens., A_1	1155	1146 w	1156 w	$\gamma(\text{CH})$, B_{3u}	819 ^(d)	819 w	818 m
X-sens., B_2	1130	1129 m	1127 s	X-sens, B_{1u}	550	548 m	547 w
$\beta(\text{CH})$, B_2	1038	1035 s	1036 s	$\phi(\text{CC})$, B_{3u}	485 ^(d)	485 w	483 m
$\gamma(\text{CH})$, B_1	940	939 w	940 w	$\phi(\text{CC})$, A_u	405	406 vw	
$\gamma(\text{CH})$, B_1	748	750 m	750 s				
X-sens., B_2	740	740 s	740 m				
X-sens., A_1	660	660 s	659 s				
X-sens., A_1	480	474 w	476 w				
$\phi(\text{CC})$, B_1	435	437 s	437 s				

^{(a),(b)} Taken from Refs. 19, 20. ^(c) In hexachloro-1,3-butadiene. ^(d) Band contour of vapour spectrum. ^(e) vs = very strong, s = strong, m = medium, w = weak, vw = very weak, sh = shoulder, * = overlap.

As seen from the spectral features, the CH out-of-plane mode (A_{2u}) of the benzene molecule in the clathrate spectra was shifted to higher frequencies (Table IV) than that of liquid benzene (670 cm^{-1}) for both compounds. The frequency shifts are due to the π electron donation from the benzene ring to the hydrogen atom of the NH_2 group of the ligand molecule. Similar positive frequency shifts were reported for the Hofmann T_d -type^{5–9} and Hofmann type clathrates.^{21–23} Moreover, the mode appears as a doublet for Ni-danon-Cd-2Bz and a singlet for Ni-danon-Hg-2Bz in the spectra, indicating that the host-guest interaction is strong for the former one (*i.e.*, crystal field effects) while the interaction is weak for the latter one. This vibrational mode appears as a singlet for $\text{Cd}(4,4'$ -bipyridyl) $\text{M}'(\text{CN})_4 \cdot 2\text{C}_6\text{H}_6$ ($\text{M}' = \text{Cd}, \text{Hg}$),²⁴ a doublet for

$\text{M}(\text{NH}_3)_2\text{M}'(\text{CN})_4 \cdot 2\text{C}_6\text{H}_6$ ($\text{M} = \text{Mn}$ or Cd , $\text{M}' = \text{Cd}$ or Hg),⁶ and a triplet in $\text{M}(\text{en})\text{M}'(\text{CN})_4 \cdot 2\text{C}_6\text{H}_6$ ($\text{M} = \text{Mn}$ or Cd , $\text{M}' = \text{Cd}$ or Hg).⁵ On the other hand, the out-of-plane CH vibration mode possesses lower positive frequency shifts compared to the benzene molecule (Table V). This comes from the geometry of the guest molecules.²⁵

For the present compounds, similarities of the spectral features with the Hofmann T_d -type structures have led us to conclude that the compounds are further examples of the Hofmann T_d -type clathrates. The spectral features from the IR spectra together with the methods of thermal analysis results also point to the inclusion ability of the host structure of the compounds for various guest molecules. The compounds then may be employed for selective enclathration.

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SAŽETAK

**Istraživanje Hofmannovih klatrata tipa T_d FT-IR spektroskopijom:
Ni(1,9-diaminononan) $M'(CN)_4 \cdot 2G$ ($M' = Cd$ ili Hg , $G =$ benzen, 1,2-diklorbenzen
ili 1,4-diklorbenzen)**

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Pripravljene su novi Hofmannovi klatrati tipa T_d u obliku Ni(1,9-diaminononan) $M'(CN)_4 \cdot 2G$ ($M' = Cd$ ili Hg , $G =$ benzen, 1,2-diklorbenzen ili 1,4-diklorbenzen). Infracrveni spektri praškastih uzoraka snimljeni su u području od 4000 cm^{-1} do 200 cm^{-1} . Na temelju spektralnih podataka zaključeno je da su ispitani spojevi strukturno slični Hofmannovim klatratima tipa T_d .