



VIBRATIONAL SPECTROSCOPIC INVESTIGATION ON SOME HOFMANN-T_d-TYPE CLATHRATES: Ni(1,9-DIAMINONONANE)M(CN)₄.2G (M = Cd OR Hg, G = 1,3-DICHLOROBENZENE)

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ABSTRACT

New Hofmann-T_d-type clathrates in the general form of Ni(1,9-diaminononane)M(CN)₄.2G (M = Cd or Hg, 1,9-diaminononane = danon, G = 1,3-dichlorobenzene) have been prepared in powder form and their FT-IR and Raman spectra have been reported in the range of (4000–200) cm⁻¹ and (2850–1650) cm⁻¹, respectively. The spectral results suggest that these compounds are similar in structure to the Hofmann-T_d-type clathrates.

Keywords: *Hofmann-T_d-type clathrate, Vibrational spectrum, 1,9-diaminononane, 1,3-dichlorobenzene.*

BAZI HOFMANN-T_d-TİPİ KLATRATLARIN TİTREŞİM SPEKTROSKOPİSİ İLE İNCELENMESİ: Ni(1,9-DİAMİNONONAN)M(CN)₄.2G (M = Cd VEYA Hg, G = 1,3-DİKLOROBENZEN)

ÖZET

Ni(1,9-diaminononan)M(CN)₄.2G (M = Cd veya Hg, 1,9-diaminononan = danon, G = 1,3-diklorobenzen) genel formülüne sahip Hofmann-T_d-tipi klatratlar toz halde hazırlanmakta ve bunların infrared ve Raman spektrumları sırasıyla (4000–200) cm⁻¹ ve (2850–1650) cm⁻¹ aralıklarında incelenmektedir. Spektrum sonuçları bu bileşiklerin yapısal olarak Hofmann-T_d-tipi klatratlara benzediğini ortaya koymaktadır.

Anahtar Kelimeler: *Hofmann-T_d-tipi klatrat; Titreşim spektrumu; 1,9-diaminononan, 1,3-diklorobenzen.*

1. INTRODUCTION

Vibrational spectroscopy has long been recognized as a valuable way of revealing the structural properties of the Hofmann-T_d type clathrates which have two components, namely inclusion compounds consisting of a host lattice and a guest molecule [1-4]. Their general formula is M(L)₂M'(CN)₄.nG where, M is one of the first-row transition metals; M' is tetrahedrally coordinated Cd, Hg or Zn; L corresponds to a bidentate ligand or a pair of unidentate ligand molecules and n is the number of guest (G) molecules. The host structure is formed by the chains of -M-L₂-M-L₂- extending along the a- and b-axes alternately and the tetrahedral M'(CN)₄ ions are arranged between the consecutive crossing chains with the N-ends bonded to the M atoms [1-4]. This structure possesses two kinds of cavities, namely α and β. The α cavity with the rectangular box is similar to those in the Hofmann type hosts while the β cavity is a twisted biprism. The cavities within the structure can act as hosts for the guest molecules [1-5].

Studies of the Hofmann type and Hofmann-T_d type clathrates of danon exhibit its coordination properties [4, 6]. In the present work, we have synthesized two new Ni(danon)M(CN)₄.2G clathrates (abbreviated hereafter as Ni-danon-M-2G), where M = Cd or Hg, G = 1,3-dichlorobenzene (1,3ClBz), for the first time and investigated their FT-IR and Raman spectra.

2. EXPERIMENTAL

All the chemicals used were reagent grade (Aldrich) and they were used without further purification. The Ni-danon-M-2G (M = Cd or Hg) compounds were prepared as follows: at first step 1 mmol of $K_2M(CN)_4$ (M = Cd or Hg) was dissolved in distilled water, then slightly more than 1 mmol of danon solved in the ethanol were added to this solution under stirring. After a short time, 3 mmoles of 1,3CIBz were added to prepared solution. Finally, 1 mmol of $NiCl_2$ 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 product were filtered and washed with water, ethanol and ether successively and stored in a desiccator containing guest vapour.

Infrared spectra of the clathrates were recorded in the region of $(4000-200) \text{ cm}^{-1}$ with Perkin-Elmer FT-IR 2000 and Bruker IFS 66v/S vacuum FT-IR spectrometers at a resolution of 4 cm^{-1} . In order to provide better identifications for the vibrational bands of the clathrates prepared in this study two different mulls (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 at 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 the compounds in powder form were recorded in the region of $(2850-1650) \text{ cm}^{-1}$ with Bruker Senterra Dispersive Raman Microscope using the 532 nm line of a 3B diode laser.

The compounds were analyzed for Ni, Cd and Hg metals with a Perkin Elmer 4300 ICP-OES and for C, H and N via a Fisons EA-1108 elemental analyser. Ni, Cd and Hg metals were investigated at 231.604 nm , 228.802 nm and 253.652 nm , respectively. The results are as following; (found % / calculated %) $Ni(C_9H_{22}N_2)Cd(CN)_4.2C_6H_4Cl_2$ ($M_w = 727.46$): C(41.05/41.27), H(4.05/4.16), N(11.21/11.55), Ni(7.85/8.07), Cd(15.25/15.45) and $Ni(C_9H_{22}N_2)Hg(CN)_4.2C_6H_4Cl_2$ ($M_w = 815.64$): C(36.51/36.81), H(3.61/3.71), N(10.05/10.30), Ni(7.03/7.20), Hg(24.35/24.60). All the analyses of these compounds were carried out immediately to avoid any declathration.

3. RESULTS AND DISCUSSION

The infrared and Raman spectra of Ni-danon-M-2G (M = Cd or Hg) clathrates are compatible with each other. This indicates that the compounds have similar spectral features. Infrared spectra of the compounds are given in Figure 1. The spectral analysis of each compound has been performed by taking into account danon ligand molecule, $M(CN)_4$ group and 1,3CIBz guest molecule individually.

3.1. Danon vibrations

Danon has been used as ligand molecule in the M-danon-Ni-G (M = Ni or Cd; G = Benzene, Naphthalene, Anthracene or Phenanthrene) Hofmann type and Ni-danon-M-2G (M = Cd or Hg; G = Benzene, 1,2-dichlorobenzene or 1,4-dichlorobenzene) Hofmann- T_d -type clathrates [4, 6]. The assignments and wavenumbers for danon in the infrared spectra of the clathrates under study are given in Table 1 together with the wavenumbers of danon in CCl_4 solution [6, 7]. The NH_2 stretching frequencies of danon in the compounds are found to be lower than those of danon in CCl_4 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 have been reported for the Hofmann- T_d -type clathrates [3, 4, 8].

Another spectral feature is that the asymmetric and symmetric stretching vibrations of the NH_2 groups appear as two single sharp bands, hence, no splitting for these bands. This implies that the ligand molecule in the compounds behaves as a bridge (bidentate coordination). From the present spectral data, it is not possible to give an account of the conformation of danon in the compounds [4].

3.2. $M(CN)_4$ (M = Cd or Hg) vibrations

Assignments of the bands for $M(CN)_4$ (M = Cd or Hg) ions in the spectra of the present compounds have been carried out by means of the vibrational data of the $K_2M(CN)_4$ (M = Cd or Hg) salts in the solid phase reported by Jones [9] who assigned the vibrational data on the basis of T_d -symmetry.

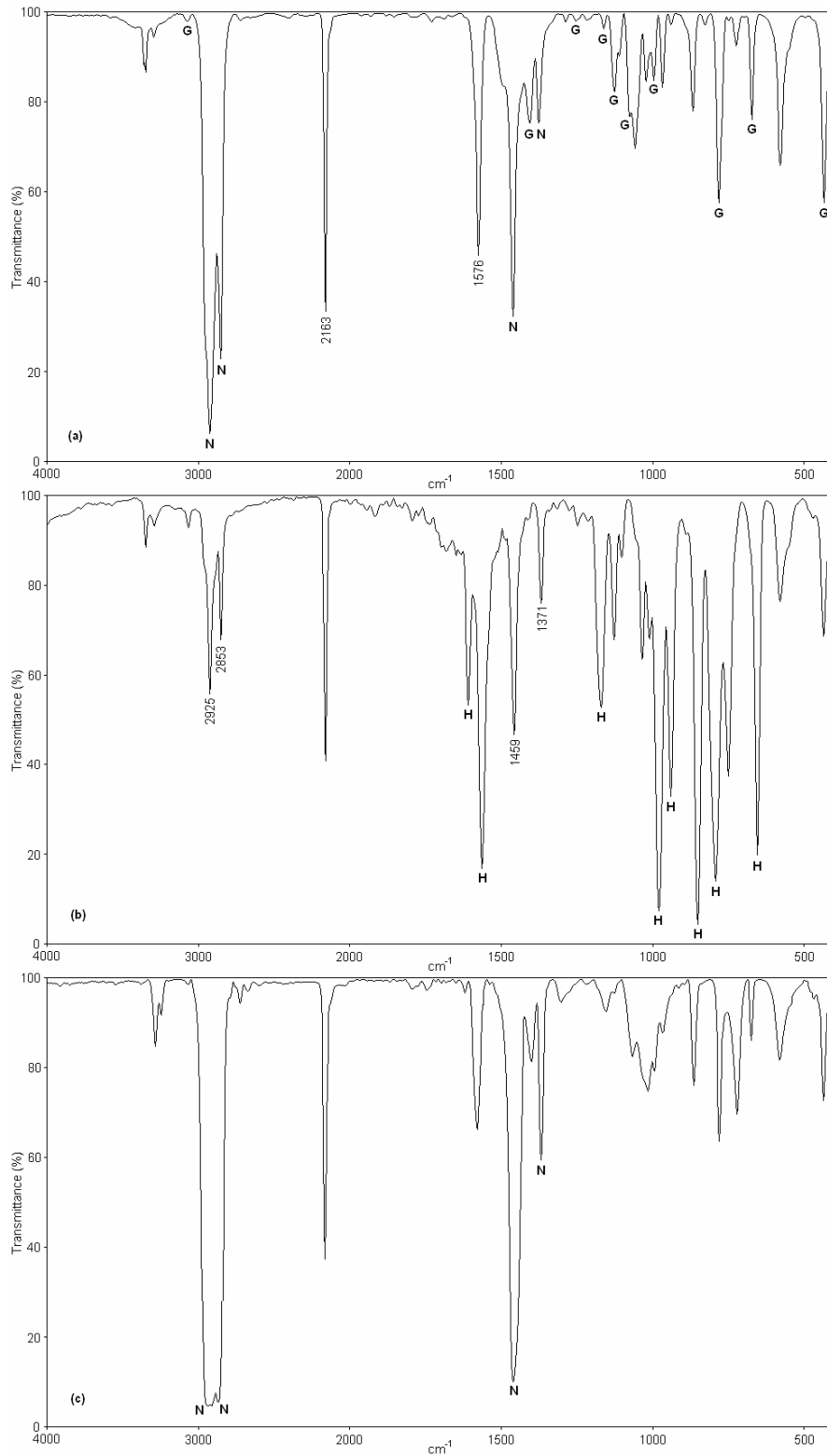


Figure 1. The FT-IR spectra of the Ni-danon-M-2G (M = Hg (a, b) or Cd (c)) clathrates in nujol (a, c), in hexachloro-1,3-butadiene (b). N, H and G: Bands of nujol, hexachloro-1,3-butadiene and 1,3CIBz, respectively.

Table 1. The vibrational wavenumbers (cm⁻¹) of danon in the Ni-danon-M-2G (M=Cd or Hg) clathrates.

Assignment ^a	Danon in CCl ₄ ^b	Ni-danon-Cd-2G	Ni-danon-Hg-2G
v _a (NH ₂)	3361 vs	3286 vs	3349 vs
v _s (NH ₂)	3325 vs	3247 s	3297 s
v _a (CH ₂)	2926 vs	2923 vs ^c	2925 vs ^c
v _s (CH ₂)	2856 vs	2851 vs ^c	2853 vs ^c
δ(NH ₂)	1581 vs	1579 vs	1576 vs
δ(CH ₂)	1489 vs	1460 vs ^c	1459 vs ^c
ρ _w (CH ₂)	-	1375 m ^c	1371 s ^c
ρ _t (CH ₂)	1313 m	1304 m	-
ρ _t (NH ₂)	1225 w	1221 w	1219 w
v(CN)	1097 vw	-	1110 vw
v(CN)	1070 w	1068 m	1060 m
ρ _w (NH ₂)	-	1017 m	1023 m
ρ _r (CH ₂)	931 m	967 m	968 s
ρ _r (CH ₂)	877 m	865 s	868 s
ρ _t (CH ₂)	721 m	722 vs	725 s
δ(skeletal)	576 m	581 s	580 s

^{a, b} Taken from Ref. [7] and [6]. ^c In hexachloro-1,3-butadiene. vs: very strong, s: strong, m: medium, w: weak.

The studies on these salts have shown that the K-CN distances are 2.9 Å in K₂Cd(CN)₄ [10], K₂Hg(CN)₄ [11] while the Cd-NC distances are 2.3 Å in the T_d-symmetry. Therefore, we have used them as references to account for the vibrational changes when the stiffer M-NC bonding takes place. The infrared and Raman wavenumbers for M(CN)₄ groups in our clathrates are given in Table 2 along with Jones's data. The assigned infrared and Raman wavenumbers for the M(CN)₄ group in the compounds studied appear to be much higher than those for the M(CN)₄ groups in K₂M(CN)₄ (Table 2, Figure 1). Such frequency shifts have been observed for other Hofmann-T_d type complexes [5, 12] and clathrates [3, 4, 8, 12] and have been explained that the shifts arise from the mechanical coupling of the internal modes of M(CN)₄ (M = Cd or Hg) with metals as both ends of the CN group are bonded to the transition metals. Accordingly the shifts observed in the compounds can be attributed to the mechanical coupling of the internal modes of M(CN)₄ with metal.

Table 2. The vibrational wavenumbers (cm⁻¹) of M(CN)₄ group in the Ni-danon-M-2G (M=Cd or Hg) clathrates.

Assignment ^a	K ₂ Cd(CN) ₄ ^a	K ₂ Hg(CN) ₄ ^a	Ni-danon-Cd-2G	Ni-danon-Hg-2G
v ₁ (CN)A ₁	(2149)	(2149)	(2171) vs	(2175) vs
v ₅ (CN)F ₂	2145	2146	2166 vs	2163 vs
v ₆ [v(MC)+δ(NCM)]F ₂	316	330	351 s	354 s
v ₇ [v(MC)+δ(NCM)]F ₂	250	235	264 m	268 m

^a Taken from Ref. [9]. The observed Raman data are given in parentheses. vs: very strong, s: strong, m: medium.

3.3. 1,3CIBz vibrations

The assignments and wavenumbers of the vibrational bands for 1,3CIBz of the clathrates are given in Table 3 along with the frequencies of 1,3CIBz in the gas phase [13] for comparison. It can be seen from Table 3 that the CH out-of-plane mode of the guest molecule in the clathrates is shifted to higher frequencies (994 cm⁻¹ for Ni-danon-Cd-2G and 996 cm⁻¹ for Ni-danon-Hg-2G) than that of free 1,3CIBz (966 cm⁻¹).

The frequency shifts are due to the π electron donation from the 1,3ClBz ring to the hydrogen atom of the NH₂ group of the ligand molecule. Similar positive frequency shifts have been reported for the Hofmann-T_d-type and Hofmann type clathrates with benzene and benzene derivatives guest molecules [3, 4, 6, 8, 12, 14]. 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-T_d-type clathrates [3, 4].

Table 3. The vibrational wavenumbers (cm⁻¹) of 1,3ClBz in the Ni-danon-M-2G (M=Cd or Hg) clathrates.

Assignment ^a	1,3ClBz ^a	Ni-danon-Cd-2G	Ni-danon-Hg-2G
v(CH), A ₁	3071	3068 w	3070 w
v(CC), A ₁	1580	1579 vs ^b	1576 vs ^b
v(CC), B ₂	1464	1460 vs ^{b, c}	1459 vs ^{b, c}
v(CC), A ₁	1412	1405 m	1406 m
β (CH), B ₂	1258	1254 vw, sh	1255 w
X-sens., B ₂	1161	1161 m	1162 w
X-sens., A ₁	1127	1127 w	1126 m
β (CH), B ₂	1079	-	1078 w
γ (CH), B ₁	966	994 m	996 m
X-sens, B ₂	784	782 vs	783 vs
X-sens., A ₁	663	673 s	674 s
X-sens., A ₁	428	437 vs	435 vs

^a Taken from Ref. [13]. ^b Obscured by the bands of danon. ^c In hexachloro-1,3-butadiene. vs: very strong, s: strong, m: medium, w: weak, sh: shoulder.

4. CONCLUSION

The similarities obtained for spectral features of the present compounds to the Hofmann-T_d-type structures, let us to conclude, that the compounds presented in this study are also new examples of the Hofmann-T_d type clathrates, in which the M atom is tetrahedrally coordinated to the carbon atoms of the four cyanide groups, while the Ni atom is octahedrally surrounded by six nitrogen atoms, two of which are from danon which have been coordinated as bidentate ligand and the rest are from cyanide groups. The cavities within this structure act as hosts for the 1,3ClBz guest molecules.

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