Anadolu Üniversitesi Bilim ve Teknoloji Dergisi A- Uygulamalı Bilimler ve Mühendislik
Anadolu University Journal of Science and Technology A- Applied Sciences and Engineering

2017 - Volume: 18 Number: 1
Page: 139 - 145
DOI: 10.18038/aubtda.300421
Received: 04 October 2016 Revised: 10 January 2017 Accepted: 10 January 2017

SYNTHESIS AND CHARACTERIZATION OF THE T_d-TYPE CLATHRATES: M(2,2-DIMETHYL-1,3-DIAMINOPROPANE)M'$(CN)_4.2C_6H_6$ (M= Mn or Cd, M'= Cd, Hg or Zn)

Türkay AYTEKİN AYDIN *

[1] Department of Physics, Science Faculty, Anadolu University, 26470, Eskişehir, Turkey

ABSTRACT

Mn(DMPDA)M$(CN)_4.2C_6H_6$ (M = Cd, Hg or Zn; DMPDA = 2,2-dimethyl-1,3-diaminopropane) and Cd(DMPDA)M$(CN)_4.C_6H_6$ (M= Cd or Hg) Hofmann-T_d-type clathrates were synthesized and characterized by vibrational spectroscopy. Infrared spectra of Mn(DMPDA)M$(CN)_4.2C_6H_6$ (M = Cd, Hg or Zn; DMPDA = 2,2-dimethyl-1,3-diaminopropane), the vibrational spectra of Cd(DMPDA)M$(CN)_4.C_6H_6$ (M= Cd or Hg) were reported. All the vibrational modes of coordinated DMPDA were characterised. The spectral features suggested that these compounds were similar in structure to the Hofmann-T_d-type clathrates.

Key words: Benzene, 2,2-Dimethyl-1,3-diaminopropane, Hofmann-T_d-type clathrates, Vibrational spectra

1. INTRODUCTION

Bidendate bridging ligand such as 2,2-Dimethyl-1,3-diaminopropane are determined as the smallest building block that allows to construct a more complicated construction with inorganic compounds often a superstructure or the so-called supramolecular structure [1, 2]. The superstructure exhibits new structural, physical and chemical properties that are excellent to the superstructure and have allowed to utilize the target identification and synthetic methodology as parts of crystallography [3, 4]. The structure of the Hofmann-T_d-type clathrates, $Cd(NH_3)_2M'(CN)_4.2C_6H_6$ (M´ = Cd or Hg) has already been determined [5]. Such a host framework, the M´ atom is tetrahedrally coordinated to the carbon atoms of the four cyanide ions. The octahedral Cd atom is surrounded by six nitrogen atoms; two from the NH_3 ligands, the other four from cyanide groups. Three-dimensional host structures are obtained by built of the CN linkages among the tetrahedral tetracyanometallate, $M'(CN)_4$ (M´ = Cd or Hg) groups and the $Cd(NH_3)_2$ moieties The multidimensional cyanometal complex host provides two kinds of cavities of molecular scale (α and β) in which organic guest molecules are included. The cavity α is isostructural to those in the Hofmann-type hosts with the shape of a rectangular box; the cavity β is the shape of a biprismatic [5-7].

In this study, five new compounds M(DMPDA)M′$(CN)_4.C_6H_6$ (M = Mn or Cd, M′ = Cd, Hg or Zn; C_6H_6 = benzene (bz)) were prepared in the powder form. In the present investigation, the infrared spectra of Mn(2,2-Dimethyl-1,3-diaminopropane)M$(CN)_4.C_6H_6$ (abbr. Mn-DMPDA-M; M= Cd, Hg or Zn) and vibrational spectra of the Cd(DMPDA)M$(CN)_4.C_6H_6$ (M= Cd or Hg; abbr. Cd-DMPDA-M) compounds were reported. The spectral data of the clathrates are structurally correlated with those of the corresponding Hofmann-T_d-type clathrates of known structures [5-8].

2. METHODS AND MATERIALS

All chemicals used were purchased from Sigma-Aldrich Co. and used without further purification. The clathrates Mn-DMPDA-M-bz (M= Cd, Hg or Zn) were synthesized as follow:

---

*Corresponding Author: maytekin@anadolu.edu.tr

1 mmol of DMPDA, 1 mmol of $K_2M(CN)_4$ (M= Cd, Hg or Zn) solution in water and 1 mmol of $MnCl_2$ solution in water saturated with benzene were vigorously stirred for three days at room temperature. The obtained powder was filtered, washed with water, ethanol and ether, successively, and kept in a desiccator containing saturated benzene vapour. The clathrate compounds Cd-DMPDA-Cd-bz and Cd-DMPDA-Hg-bz were prepared similar to the previous references [9-11]. The elemental analyses of freshly prepared compounds were analysed for C, H and N by a LECO CHNS-932 analyzer with the following results (found % / calculated %):

$Cd(C_5H_{14}N_2)Cd(CN)_4.2C_6H_6$: C=42.73/42.95, H=4.35/4.46, N=14.11/14.31
$Cd(C_5H_{14}N_2)Hg(CN)_4.2C_6H_6$: C=35.78/37.34, H=3.47/3.88, N=12.29/12.44
$Mn(C_5H_{14}N_2)Zn(CN)_4.2C_6H_6$: C=51.77/52.24, H=5.03/5.43, N=17.13/17.41
$Mn(C_5H_{14}N_2)Cd(CN)_4.2C_6H_6$: C=47.43/47.61, H=4.67/4.95, N=15.49/15.86
$Mn(C_5H_{14}N_2)Hg(CN)_4.2C_6H_6$: C=40.33/40.81, H=4.07/4.24, N=13.39/13.60

The data of elemental analyses were agreement with the proposed formula and indicate that the number of guest molecules in the compounds is 2. Infrared spectra (4000-400 cm^{-1}) between KBr windows as Nujol mulls of the compounds were recorded via a Bruker IFS 66 v/s Fourier-transform infrared (FT-IR) spectrometer with 2 cm^{-1} resolution in vacuum. The spectrometer was calibrated using polystyrene and indene. For the Raman spectra, the measurements were recorded at room temperature using a Bruker Senterra Dispersive Raman microscope spectrometer at 532 nm excitation from a 3B diode laser having 9-18 cm^{-1} resolution between 3700 and 60 cm^{-1} spectral region.

3. RESULTS AND DISCUSSION

The analysis of vibrational spectra of the studied compounds showed that each spectra was similar to each other and had similar structural features (Figure 1). The vibrations may be divided into three groups and as the 2,2-Dimethyl-1,3-diaminopropane ligand, $M'(CN)_4$ groups and guest molecule benzene.

The assignments and vibrational wavenumbers of the observed bands of the $M'(CN)_4$ groups, 2,2-Dimethyl-1,3-diaminopropane in the M-DMPDA-M′-bz (M = Mn or Cd; M′= Cd, Hg or Zn) clathrates and the guest molecule benzene are summarized in Tables 1-3, respectively, together with corresponding spectral data for comparison. These results, likewise elemental analyses, indicate that the number of the guest molecules in the compounds is two. A similar number of the guest molecules has been reported for some T_d-type clathrates [10-12].

2,2-Dimethyl-1,3-diaminopropane vibrations:

DMPDA is a small molecule that has a primary amine group and a tertiary amine group connected by an ethylenediamine unit. Because of the low symmetry for the molecule, the assignments of the spectral bands were made in terms of characteristic group frequencies. The vibrational analysis of the fundamental vibrations of the DMPDA observed in the spectra of the compounds under study were made according to the literature data [5, 13-16]. In order to assign and interpret the bands attributable to the DMPDA ligand in the clathrate compounds, we refer to the spectral data for the isolated DMPDA molecule. The observed wavenumbers, intensities and assignments of the principal spectral bands are tabulated in Table 1. The vibrational data for DMPDA in the clathrate compounds would be expected to be consistent with all the vibrational features of a coordinated ligand. The N–H and N–C stretching frequencies should decrease while the C–H and C–C frequencies should increase. It may be explained as consecutive inductive effects, in other words, on coordination N–H and C–C bonds appear to become weaker and C–H and C–C bonds become stronger [5, 10, 13]. But our case, this expectation is not fully realized and a non-systematic frequency alteration has been observed for the N-H stretching vibrations (Table 1). This has also been observed in similar benzene clathrates [8-10].

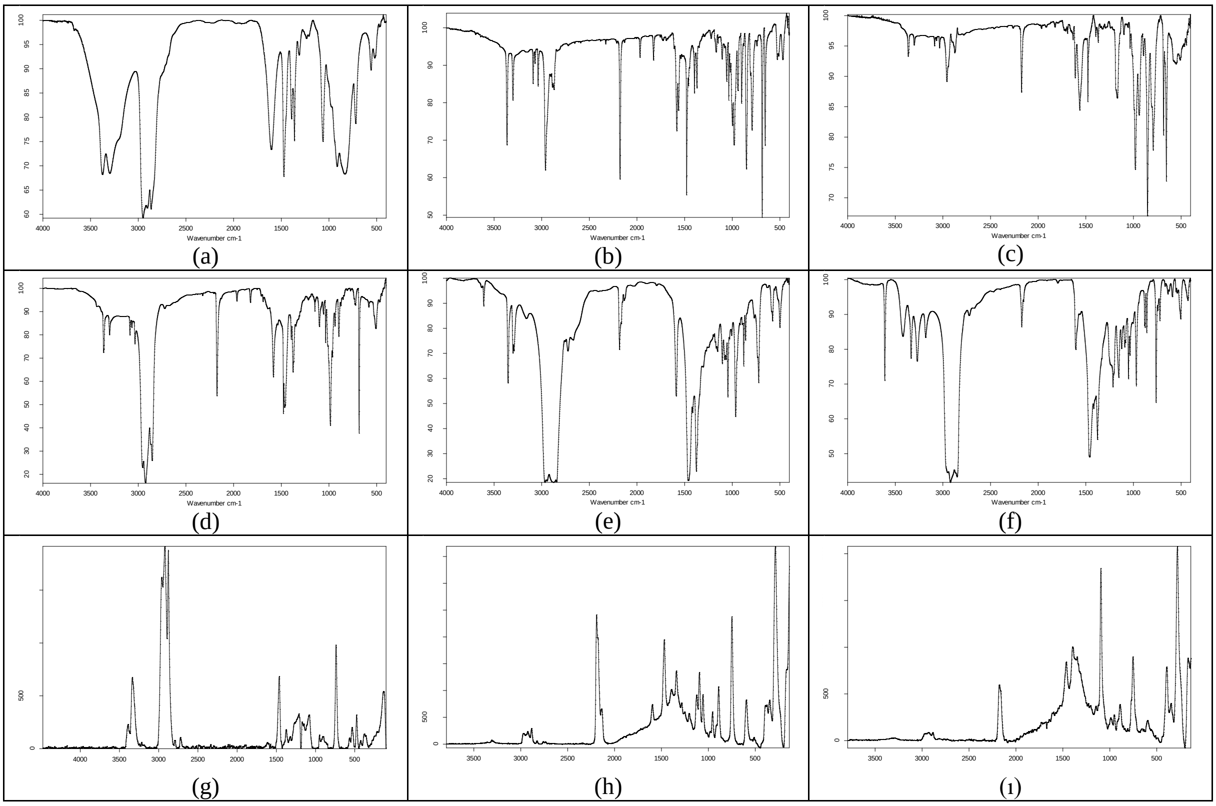

Figure 1. Infrared spectra of the ligand and clathrates in nujol: (a) DMPDA, (b) Mn-DMPDA-Zn-bz, (c) Mn-DMPDA-Cd-bz, (d) Mn-DMPDA-Hg-bz, (e) Cd-DMPDA-Cd-bz, (f) Cd-DMPDA-Hg-bz; Raman spectra of the (g) DMPDA, (h) Cd-DMPDA-Cd-bz, (ı) Cd-DMPDA-Hg-bz

Table 1. The vibrational vawenumbers (cm^{-1}) of DMPDA in the M-DMPDA-M′-Bz (M = Mn or Cd; M′= Cd, Hg or Zn) clathrates

Assignment [a]	DMPDA		Cd-DMPDA-Cd-bz		Cd-DMPDA-Hg-bz		Mn-DMPDA-Zn-bz	Mn-DMPDA-Cd-bz	Mn-DMPDA-Hg-bz
	IR[b]	Raman[b]	IR	Raman	IR	Raman	IR	IR	IR
ν(NH)	3377 vs	3390 w	3353 m	-	3334 m	-	3364 s	3365 w	3364 w
ν(NH)	3300 vs	3337 w	3302 w	-	3270 m	-	3303 m	3302 w	3302 w
ν(CH)	2951 vs	2962 w	2964 w	2974 w	2961 w	2978 w	2962 vs	2959 w	2959 m
ν(CH)	2964 vs	2922 vs	2927 w	2927 w	-	2933 w	-	2943 vw	2944 w
ν(CH)	2867 vs	2877 s	2754 vw	2886 w	2877 w	2895 w	2888 w	2877 w	2877 w
ν(CH)	-	2790 w	2876 w	-	-	-	2871 w	-	
ν(CH)	-	2724vw	2721 vw	-	2724 vw	-	2723 vw	-	
sci(NH)	1605 s	1615 vw	1611 w	1597 w	1605 w	1616 vw	1611 vw	1611 m	1611 w
sci(CH)	-	-	1589 m	-	-	1597 w	1582 m	-	1583 vw
sci(CH)	-	-	1564 s	-	1561 vw	-	1563 w	1564 s	1564 m
sci(CH)	1474 vs	1463 m	1479 w	1470 m	-	-	1479 vs	1478 m	1478 s
sci(CH)	-	-	1469 vw	-	1461 vs	1464 w	1460 vw	-	-
wag(CH)	1392 m	-	1416 vw	-	1417 vw	-	1397 w	1396 w	1396 w
wag(CH)	1363 s	1375 w	1372 vw	1394 vw	1378 s	1376 vw	1370 w	1377 w	1370 w
wag(CH)	1313 w	1324 vw	-	1342 m	-	1352 vw	1350 vw	1350 vw	1348 vw
tw(CH)	1269 w	1267 vw	1274 vw	1284 vw	-	1267 vw	1294 vw	1299 vw	1299 vvw
tw(CH)	1237 w	-	1220 vw	-	-	-	1223 vw	-	-
tw(CH)	1212 w	1212 w	-	1205 w	1215 m	1208 vw	-	1216 vw	1217 vw
ρ(CH)	-	1170 w	1170 m	-	-	1187 w	1169 w	1170 m	1170 w
wag(CH)	-	1150 w	-	-	1154 m	-	1150 vw	-	1149 vw
ν(CN)	1063 s	1081 m	1065 vw	1096 m	1052 m	1094 w	1058 w	1058 vw	1058 w
ν(CC)	974 vw	-	982 vs	980 vw	970 m	1004 vs	981 s	983 vs	984 vs
ρ(CH)	915 s	880 vw	880 w	891 m	883 m	897 vw	902 m	896 w	897 w
wag(CH)	838 vs	850 vvw	853 vs	-	860 m	845 w	852 s	853 vs	853 vs
bend(NH)	720 s	739 s	737 w	749 s	762 s	767 w	742 vw	732 vw	730 vw
τ(CCN)	560 w	568 vw	577 w	596 m	592 w	619 w	588 vw	581 vw	582 vw
τ(CCCN)	522 w	477 vw	517 vw	514 vw	504 w	480 w	514 w	509 w	509 w

vs: very strong, s: strong, m: medium, w: weak, vw: very weak, -: not observed.

[a] Taken from ref.[13-16]. [b] Assigned in this study by the obtained IR and Raman spectra of 2,2-dimethyl-1,3-diaminopropane along with the assignments of related molecules

Table 2. The vibrational wavenumbers (cm^{-1}) of the M′(CN)$_4$ (M′= Cd, Hg or Zn)group for the M-DMPDA-M′-Bz (M = Mn or Cd; M′= Cd, Hg or Zn) clathrates*

Assignment[a]	$K_2Cd(CN)_4$[a]	$K_2Hg(CN)_4$[a]	$K_2Zn(CN)_4$[a]	Cd-DMPDA-Cd-Bz	Cd-DMPDA-Hg-Bz	Mn-Zn-DMPDA-Bz	Mn-DMPDA-Cd-Bz	Mn-DMPDA-Hg-Bz
ν_1(CN)	(2149)	(2149)	(2157)	(2165 vw)	(2154 vw)	-	-	-
ν_5(CN)	2145	2146	2152	2183 m	2173 m	2178 vs	2174 m	2174 s
Hot band				2136 vw	-	2132 vw	2130 vvw	2130 vvw
ν_2(MC)	(324)	(335)	(342)	(320 vw)	(323 vw)	-	-	-
ν_6[ν(MC)+δ(NCM)]	316	330	359	357 vs	372 vs	393 vs	375 vs	377 vs
ν_7[ν(MC)+δ(NCM)]	250	235	315	269 m	268 m	268 w	270 m	270 m

*Raman bands are in parentheses. vs: very strong, s: strong, m: medium, w: weak, vw: very weak, -: not observed.

[a] Taken from Ref.[17].

Table 3. The vibrational wavenumbers (cm^{-1}) of benzene in the M-DMPDA-M′-Bz clathrates*

Assignment[a]	Liquid Benzene[a]	Cd-DMPDA-Cd-Bz	Cd-DMPDA-Hg-Bz	Mn- DMPDA-Zn-Bz	Mn- DMPDA-Cd-Bz	Mn- DMPDA-Hg-Bz
$\nu_8+\nu_{19}$	3075	3075 w	3074 w	3090 m	3088 w	3088 w
ν_{20}, E_{1u}	3073	3090 m	3091 m	3071 w	3069 m	3068 w
ν_{13}, B_{1u}	3062	3033 m	3033 m	3038 m	3036 w	3036 w
ν_2, A_{1g}	(3059)	(3074 m)	(3074 m)	-	-	-
$\nu_5+\nu_{17}$, E_{1u}	1955	1972 w	1974 w	1969 w	1967 vw	1966 w
ν_8, E_{2g}	(1596)	(1584 m)	(1585 m)	-	-	-
ν_{19}, E_{1u}	1479	1479 s	1477 s	1479 vs	1478 m	1478 s
ν_{14}, B_{2u}	1309	1306 vw	1306 vw	1310 vw	1309 vw	1309 vw
ν_9, E_{2g}	(1178)	1170 m	1170 m	1169 w	1170 m	1170 m
ν_{15}, B_{2u}	1149	-	-	1150 vw	-	1149 w
ν_{18}, E_{1u}	1036	1046 m	1046 m	1037 m	1036 w	1036 m
ν_1, A_{1g}	(992)	(993 m)	(993 m)	-	-	-
ν_{10}, E_{1g}	(849)	(843 w)	(843 w)	-	-	-
ν_{11}, A_{2u}	670	655 vs	655 vs	685 vs	686 s	684 vs
ν_6, E_{2g}	(606)	(608 w)	(609 w)	-	-	-

*Raman bands are in parentheses. vs: very strong, s: strong, m: medium, w: weak, vw: very weak and -: not observed.

[a]Taken from Ref. [19]. Raman bands from Ref.[20].

As expected, two bands were observed in the N-H stretching region at 3377 and 3300 cm^{-1} in the clathrates. The absence of splitting of these sharp bands imply the bidentate coordination of the ligand DMPDA molecule in the clathrates. The NH_2 stretching frequencies of the 2,2-Dimethyl-1,3-diaminopropane molecules in the compounds are found to be higher than those of 2,2-Dimethyl-1,3-diaminopropane in solution (Table 1). These upward shifts may be explained as weakening of the N–H bonds resulting from the electron draining from the N atom in the –NH_2 unit because of its coordination to the Cd atom in the octahedral arrangement and the hydrogen bonding to the π electrons of the guest benzene ring. The NH_2 scissoring wavenumber of the 2,2-Dimethyl-1,3-diaminopropane in the compounds were found to be lower than those of 2,2-Dimethyl-1,3-diaminopropane molecule in solution (Table1). Such frequency shifts have also been observed for similar T_d-type clathrates [8-11]. From observations on these spectral data, the determination of the conformation of the 2,2-Dimethyl-1,3-diaminopropane molecule in the clathrates is not possible. The similar bands were observed in Raman spectra of the $Cd(DMPDA)M(CN)_4.C_6H_6$ (M= Cd or Hg) clathrates.

Tetrahedral M′(CN)$_4$ (M′= Cd, Hg or Zn) group vibrations:

The bands assigned to M′(CN)$_4$ (M'= Cd, Hg or Zn) ions in the spectra of the compounds under study showed the features similar to that of $K_2M(CN)_4$ (M= Cd, Hg or Zn) salts in the solid phase [17]. The resulting wavenumbers, intensities and assignments of the M′(CN)$_4$ groups in the compounds are summarized in Table 2, together with the vibrational wavenumbers of the $K_2M(CN)_4$ (M= Cd, Hg or Zn) salts [17]. The wavenumbers assigned to $M'(CN)_4$ groups in the compounds under study appear to be much higher than those of isolated $M(CN)_4$ groups in $K_2M(CN)_4$ (M= Cd, Hg or Zn) (Table 2). Such frequency shifts have also been observed for similar T_d-type clathrates [5-12, 18] and are attributed to the mechanical coupling of the internal modes of $M'(CN)_4$ (M= Cd, Hg or Zn) with the metal vibrations.

Benzene vibrations:

The wavenumbers, intensities and assignments of the vibrational bands of the benzene molecule observed in the vibrational spectra of the M-DMPDA-M′-bz (M = Mn or Cd; M′= Cd, Hg or Zn) clathrates were tabulated in Table 3; together with some relevant spectral data of benzene molecule in the liquid phase for comparison [19, 20].

In the spectra of studied clathrates, the CH out-of-plane mode (A_{2u}) for the benzene molecule appears to be shifted to higher frequency (Table 3) from that of liquid benzene. The same was pointed for Hofmann-T_d-type [6, 8-12, 18, 19] and Hofmann-type clathrates [21, 22]; and the important splitting may be clarified by the differences in the strength of the hydrogen bonding the π electrons located above and below the plane of the benzene ring and the ammonia molecules of the host framework. Thus, it may be reasonably suggested that the frequency shifts in studied clathrate compounds were caused by the π electron donation from the benzene molecule to the hydrogen atoms of the DMPDA of a more electrophilic character caused by the coordination.

Another notable feature of the out-of-plane mode is that it appears as a very intense single band in the infrared spectra of the studied clathrate compounds (Table 3). In the case of clathrates with a single band, because of the larger cavities due to the ligands, the interactions of the guest molecule with its surroundings are expected not to be effective for splitting [10]. A similar single band was observed for Hofmann-type clathrates $M(H_2N(CH_2)_9NH_2)Ni(CN)_4{\cdot}G$ (M = Cd or Ni; G = Benzene) [23]. This vibrational mode splits into a doublet in $Cd(cba)_2M'(CN)_4.2G$ (M′= Cd or Hg; cba = cyclobutylamine; G = benzene) [11] and into a triplet in $Cd(en)M'(CN)_4.2C_6H_6$ (M′ = Cd or Hg) [18]. In the case of clathrates with triplet or doublet features, splitting are due to the strong host-guest interactions (i. e. crystal field effects) [10, 11].

Owing to the vibrational spectroscopic results, it is not appropriate to decide the location of the guest benzene molecules in present clathrate compounds. A perfect single crystal analysis is expected to illuminate this suggestion. The present spectral data results are based upon the assumption that the host lattices of the clathrates are similar to those of the other T_d-type clathrates. Moreover, the observed results also indicate the inclusion ability of the host structure of the compounds for benzene guest molecules.

4. CONCLUSION

On the basis of this study, one can conclude that the compounds are mainly existed in Hofmann T_d-type clathrate form, in agreement with the conclusion which was obtained from vibrational spectroscopy studies. Detailed vibrational assignments of the compounds were ascribed to its structural vibrations. The assignments of fundamental frequencies were confirmed the other T_d-type clathrates. The analytical results were agreement with the vibrational spectra of the title compounds.

REFERENCES

[1] Zhang Q-L, Zhu B-X, Tao Z, Luo S-X, Lindoy LF, Wei G. Supramolecular design of coordination complexes of silver(I) and cadmium(II) with chiral bidentate bridging ligands. Polyhedron. 2014; 68: 40-45.

[2] House DA. Chloro complexes of cobalt(III) and chromium(III) with 2,2-dimethyl-1,3-diaminopropane. Synthesis, characterization, and acid hydrolysis kinetics. Inorganic Chemistry. 1986;25(10):1671-1674.

[3] Reddy DS, Craig DC, Desiraju GR. Supramolecular Synthons in Crystal Engineering. 4. Structure Simplification and Synthon Interchangeability in Some Organic Diamondoid Solids1. Journal of the American Chemical Society. 1996;118(17):4090-4093.

[4] Thalladi VR, Goud BS, Hoy VJ, Allen FH, Howard JAK, Desiraju GR. Supramolecular synthons in crystal engineering. Structure simplification, synthon robustness and supramolecular retrosynthesis. Chemical Communications. 1996(3):401-402.

[5] Yuge H, Iwamoto T. Crystal structures ofcatena-[diligatocadmium(II) tetra-μ-cyanocadmate(II)] host clathrates: Diamminecadmium(II) tetracyanocadmate(II)-benzene(1/2), diamminecadmium(II) tetracyanocadmate(II)-aniline(1/2), ethylenediaminecadmium(II) tetracyanocadmate(II)-aniline(1/2), and a novel type bis(aniline)cadmium(II) tetracyanocadmate(II)-aniline(2/1). Journal of inclusion phenomena and molecular recognition in chemistry. 1992; 14(3): 217-235.

[6] Kuroda R. A new type clathrate compound: The crystal structure of $Cd(NH_3)_2Hg(CN)_4.2C_6H_6$. Inorganic and Nuclear Chemistry Letters. 1973;9(1):13-18.

[7] Iwamoto T. Past, present and future of the clathrate inclusion compounds built of cyanometallate hosts. Journal of inclusion phenomena and molecular recognition in chemistry. 1996; 24(1): 61-132.

[8] Nishikiori S, Takahashi-Ebisudani Y, Iwamoto T. Novel series of clathrate compounds of the three-dimensional metal complex hosts (N-methyl-1,3-diaminopropane)cadmium(II) tetracyanonickelate(II), (N, N-Dimethyl-1,3-diaminopropane)cadmium(II) Tetracyanonickelate(II), and (2-Hydroxyethylmethylamine) cadmium(II) Tetracyanonickelate(II). Journal of inclusion phenomena and molecular recognition in chemistry. 1990; 9(2):101-112.

[9] Nishikiori S-i, Iwamoto T, Yoshino Y. Three-dimensional Metal Complex Structures with Ambident Propylene-diamine Ligands Serving as the Hosts of the Aromatic Guest Molecules. Hofmann-pn and pn-Td Type Clathrates. Bulletin of the Chemical Society of Japan. 1980; 53(8): 2236-2240.

[10] Kantarci Z, Bayrak C, Kasap E. An Infrared and Raman Spectroscopic Study of pn-Td-Type dl% -Propylenediaminemetal(II) Tetracyanometallate(II) Benzene Clathrates: $M(dl\text{-}pn)M'(CN)_4.nC_6H_6$ (M = Mn, M' = Zn, Cd or Hg; M = Cd, M' = Cd or Hg; $1 \leq n \leq 1.5$). Journal of inclusion phenomena and macrocyclic chemistry. 1999; 33(3): 285-294.

[11] Aytekin MT, Şenyel M. Infrared spectra of Hoffmann-T_d -type benzene clathrates. Chemical Papers. 2008; 62(5): 472-479.

[12] Iwamoto T, Kiyoki M, Ohtsu Y, Takeshige-Kato Y. The Analogs of Hofmann Type Clathrate Formed between Diammine-or Diaminemetal(II) Tetracyanometallate(II) Host and Aromatic Guest Molecule. Bulletin of the Chemical Society of Japan. 1978; 51(2): 488-491.

[13] Giorgini MG, Pelletti MR, Paliani G, Cataliotti RS. Vibrational spectra and assignments of ethylene-diamine and its deuterated derivatives. Journal of Raman Spectroscopy. 1983; 14(1): 16-21.

[14] E. Boesch S, S. York S, Frech R, A. Wheeler R. An experimental and computational investigation of the structure and vibrations of dimethylethylenediamine, a model for poly(ethylenimine). PhysChemComm. 2001; 4(1): 1-10.

[15] S. York S, E. Boesch S, A. Wheeler R, Frech R. The effect of lithium triflate and lithium bromide on the vibrational frequencies of DMEDA. PhysChemComm. 2002; 5(16): 99-99.

[16] Moon D, Choi J-H. Synthesis, conformational structure and spectroscopic properties of trans-diazidobis(2,2-dimethyl-1,3-propanediamine)chromium(III) perchlorate. Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy. 2015; 138: 774-779.

[17] Jones LH. Vibrational spectrum and structure of metal cyanide complexes in the solid state—V. Spectrochimica Acta. 1961; 17(2): 188-200.

[18] Iwamoto T, Shriver DF. Benzene clathrates with a novel kind of metal complex host lattice. $Cd(en)Cd(CN)_4.2C_6H_6$ and $Cd(en)Hg(CN)_4.2C_6H_6$. Inorganic Chemistry. 1972;11(10):2570-2572.

[19] Painter PC, Koenig JL. Liquid phase vibrational spectra of 13C-isotopes of benzene. Spectrochimica Acta Part A: Molecular Spectroscopy. 1977; 33(11): 1003-1018.

[20] Wilson EB. The Normal Modes and Frequencies of Vibration of the Regular Plane Hexagon Model of the Benzene Molecule. Physical Review. 1934; 45(10): 706-14.

[21] Suzuki S, Orville-Thomas WJ, Sopková A, Skoršepa J. Infrared and raman studies on the Hofmann-type clathrates $Ni(NH_3)_2Pd(CN)_4.2C_6H_6$ and $Cd(NH_3)_2Ni(CN)_4.2C_4H_4S$. Journal of Molecular Structure. 1979; 54: 1-9.

[22] Davies JED, Dempster AB, Suzuki S. Clathrate and inclusion compounds—II (1). The Raman spectra of Hofmann-type benzene and benzene-D6 clathrates. Spectrochimica Acta Part A: Molecular Spectroscopy. 1974; 30(6): 1183-1192.

[23] Şenyel M, Aytekin MT, Kantarci Z. An Infrared Spectroscopic Study on the Hofmann-diam-type 1,9-Diaminononanemetal(II) Tetracyanonickelate(II)-Aromatic Guest Clathrates: $M(H_2N(CH_2)_9NH_2)Ni(CN)_4.G$(M = Cd or Ni; G = Benzene, Naphthalene, Anthracene or Phenanthrene. Journal of inclusion phenomena and macrocyclic chemistry. 2001; 39(1): 169-174.