Vibrational Spectroscopic Studies on the Dicycloheptylaminecobalt(II) Tetracyanonickellate(II) Host–Aromatic Guest Systems

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Abstract

Co(cycloheptylamine)$_2$Ni(CN)$_4$ host complex has been prepared in powder form and its vibrational spectra are investigated. The vibrational assignment of the cycloheptylamine in various phases (gas, solution, liquid and complex) are facilitated by means of DFT calculations performed on the free ligand molecule. The spectral data suggest that the prepared complex is similar in structure to the Hofmann-dma-type hosts. The sorption processes of some aromatic guests (benzene, toluene, *o*-, *m*-, *p*-xylene, 1,2-, 1,3-dichlorobenzene, 1,4-dichlorobenzene, 1,4-dibromobenzene and naphthalene) in this host complex have also been examined at room temperature by gravimetric and spectroscopic measurements. The desorption of the benzene guest against time has been measured. The structure of the Co(cycloheptylamine)$_2$Ni(CN)$_4$ host changes on inclusion of the guest molecule and recovers after liberation.

Introduction

The Hofmann-type clathrate compounds are designated with a general formula M(II)L$_2$M′(II)(CN)$_4$·nG (abbr. M-L-M′-nG) where, M is Mn, Fe, Co, Ni, Cu, Zn or Cd; M′ is 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]. The host framework (Figure 1) consists of two-dimensional polymeric layers composed of ML$_2$ cations and M′(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 6N atoms, four from the CN groups and the other two are from two ligand molecules. The ligand molecules lie above and below the layers. The layers and the ligands as blocking units provide empty spaces of varying shapes and dimensions, in which guest molecules may be imprisoned.

The host structure described above is not unique for the given chemical formula. A number of studies have suggested that similar compositions never support similar structures for the cyanometallate inclusion and complex systems [1–2]. Among them, dimethylamine (dma) [2] gives a number of inclusion compounds with a selectivity very different from the Hofmann-type

hosts mentioned above. The host Cd(dma)$_2$Ni(CN)$_4$ can include, beside benzene, toluene, xylenes, naphthalene, chlorobenzene, bromobenzene, dichlorobenzene, and *o*-, *p*- and *m*-toluidine, which have never been found enclathrated into Hofmann-type and the analogous hosts. Some of these inclusion compounds show X-ray diffraction patterns characteristic of the intercalate structures of these guests between the layered metal complex sheets. The expanded spacing (in the range of 9.2–9.5 Å for toluene, chlorobenzene, bromobenzene, *p*-xylene and naphthalene) has been interpreted in terms of the guest molecules arranged between sheets covered with hydrophobic methyl groups which may form a tunnel-like cavity between the sheets.

We recently commenced exploring the inclusion behaviours of the Hofmann-dma-type host compounds [2] with a series of cycloalkylamines and a variety of aromatic guest molecules [3–5] different in size and shape from the guests enclathrated in the Hofmann-type hosts [1, 2]. In our previous papers, infrared and gravimetric spectroscopic studies on the ML2Ni(CN)$_4$-Guest (L = cyclopentylamine (CPA) or cyclohexylamine (CHA), Guest = benzene, toluene, *o*-, *m*-, *p*-xylene, 1,2-, 1,3-, 1,4-dichlorobenzene, 1,4-dibromobenzene and naphthalene) systems were described [3–5].

Now we have prepared a new Hofmann-dma-type host complex, Co(cycloheptylamine)$_2$Ni(CN)$_4$ (abbr.

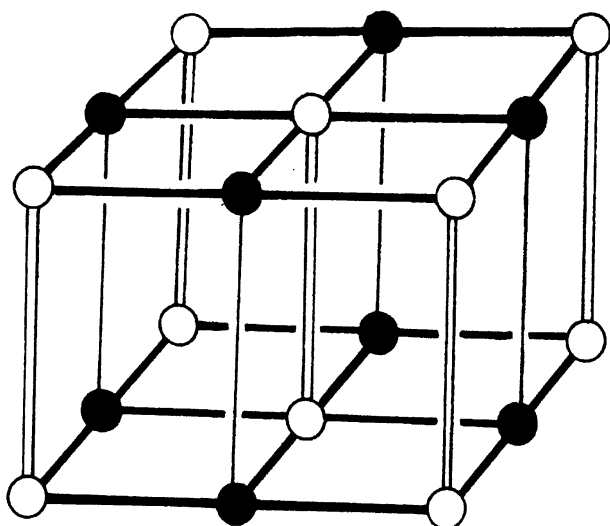* Author for correspondence. E-mail: kantarci@gazi.edu.tr

Figure 1. The model for the Hofmann-dma-type host structure (open circle: 6-coordinate M, solid circle: square planar Ni, open column: an ambient ligand, thick line: CN bridge and thin line: edge of cavity).

Co-cha-Ni), in powder form. In this study, the structure of this complex was elucidated on the basis of spectral data presented here. For the purpose of comparison, the infrared spectra of the gaseous and liquid cycloheptylamine and the Raman spectra of liquid cha have been purchased from Aldrich Library [7], and the infrared spectral data for the solution of cha in an inert solvent (nujol or fluorolube) has also been presented. The assignment of the fundamental vibrational bands observed in the infrared and Raman spectra of cha (cycloheptylamine) were facilitated by the DFT (density functional theory) calculations (A comprehensive study of the geometrical and vibrational properties for cha using experimental, *ab initio* and DFT methods is reported in a paper in preparation.). In addition, vibrational spectroscopic and gravimetric measurements of the sorption processes of the aromatic guests (benzene, toluene, *o*-, *m*-, *p*-xylene, 1,2-, 1,3-, 1,4-dichlorobenzene, 1,4-dibromo-benzene and naphthalene) in the vapour phase have also been examined at room temperature. The loss of benzene from the host complex against time has been measured.

Experimental

All chemicals used were reagent grade (Merck) and used without further purification. Co-cha-Ni host complex was prepared similar to the preparation method of Kantarcı and Bülbül [3] by adding 3 mM of cha in solution in ethanol (ca. 20 ml) into 1 mM of $Co(H_2O)_2Ni(CN)_4 \cdot 4H_2O$ complex which was prepared by the procedure of Mathey and Mazieres [6]. The precipitate was filtered, washed with ethanol and ether, successively, and dried in air to constant weight. The

complex $Co(cha)_2Ni(CN)_4$ was obtained in quantitative yield. The freshly prepared complex was analysed for C, H and N with the following results (found %/calculated %): C = 48.63/48.24, H = 6.37/6.74, N = 18.83/18.75.

The clathrate compounds were prepared by leaving the host complex in the saturated guest vapour as described below.

Infrared spectra of the compounds were recorded in the range 4000–400 cm^{-1} on a Mattson 1000 FT-IR spectrometer which was calibrated using an indene/camphor/cyclohexane standard solution. The samples were prepared as mulls in nujol (or fluorolube) in a CsI cell. The Raman spectra of the samples (liquid cha and complex) were excited using the 514.5 nm line of Spectra-Physics Model 2016-4S argon ion laser and recorded on a Jobin-Yvon U1000 spectrometer, which was calibrated against the plasma emission lines. Owing to the high intensity fluorescence (with 488 or 514.5 nm line) we could only detect the strongest band of $Ni(CN)_4$ unit (v_1) $A_1 = 2160$ cm^{-1} in the host complex. Normal mode frequencies of free cha have been calculated at B3LYP/6-31G(2d,2p) level by using package Gaussian 03 [8]. Potential energy distributions of the normal modes have been calculated using REDONG program [9, 10].

Results and discussion

It will be convenient to divide the vibrations of compounds into three; arising from the $Ni(CN)_4$ (Table 1) unit, from the ligand (Table 2) and from the guest species (Tables 4–11). The assignment of the spectral bands due to the $Ni(CN)_4$ and the guest moities are straightforward, since these bands are persistent and picked out with ease [3–5, 8–21]. For the purposes of comparison and discussion, Figure 2 shows the most important infrared bands of cycloheptylamine, $Ni(CN)_4$ unit, and benzene and naphthalene moieties in different chemical states (solution, host complex and clathrate).

Before dealing with the inclusion and liberation of the guest species in the host complex, it is appropriate to elucidate the host structure on the basis of available spectral data. The assignment and the wavenumbers of the fundamental vibrations arising from the $Ni(CN)_4$ and cha moieties in the complexes are given in Table 1 and Table 2, respectively.

Ni(CN)₄ group vibrations

The fact that in the host framework of the Hofmann-type clathrates [1–6, 11–15, 18–22] and Hofmann-type host complexes [3–6, 11–13, 16, 17], the metal atom in $Ni(CN)_4$ is square planar and surrounded by the carbon ends of the CN ions suggests that the host framework of the complex studied also has square planar $Ni(CN)_4$

Table 1. The infrared wavenumbers (cm⁻¹) of the Ni(CN)4 unit in the hosts, clathrates and related compounds

Assignment[a,b]	Na2Ni(CN)4[a]	CO-CHA-Ni[c,d]	Co-cha-Ni-2G, G = benzene	Co-cha-Ni-2G, G = toluene	Co-cha-Ni-2G, G = o-xylene	Co-cha-Ni-1.8G, G = m-xylene	Co-cha-Ni-1.4G, G = p-xylene	Co-cha-Ni-2G, G = 1,2-dichloro benzene	Co-cha-Ni-2G, G = 1,3-dichloro benzene	Co-cha-Ni-2G, G = naphthalene
γ1, γ(CN), A1		2160								
γ8, γ(CN), Eu	2132vs, 2128vs	2153vs	2160s	2160vs	2160vs	2160s	2160vs	2158s	2161s	2157s,sh, 2162vs
Hot band	–	2126w	2122w	2124w	2124w	2122w	2122w	2127w	2125w	2124w,sh
γ13(CN)	2087w	2112w	–	–	–	–	–	–	–	–
γ9, γ(NiC), Eu	543w	–	–	–	–	–	–	–	–	–
γ12, π(NiCN), A2u	488w	–	–	–	–	–	–	–	–	–
γ10, δ(NiCN), Eu	427vs	432vs	435s	435s	435s	434m	435s	434s	435s	435vs

[a] Taken from Ref. [21].
[b] γ13(CN), Eu; γ9, γ(NiC), Eu; γ12, π(NiCN), Eu; γ12, π(NiCN), A2u bands of Ni(CN)4 units in our compounds could not be observed.
[c] CHA = cyclohexylamine.
[d] Taken from Ref. [3].
Abbr.: v = very, s = strong, m = medium, w = weak, sh = shoulder.

units. In order to assign the bands attributable to the Ni(CN)4 ion in the spectra, we refer to the work of McCullough *et al.* who presented vibrational data for the salt Na2Ni(CN)4 in the solid state [23]. In this salt Ni(CN)4 anion is not coordinated to Na cation; therefore, it can be treated as an isolated unit with D4h symmetry and thus used as a reference to comment on vibrational changes when Co–NC bonding takes place. The spectral data for Ni(CN)4 groups in the host compounds are given in Table 1, together with spectral data of Ni(CN)4 in Na2Ni(CN)4 salt and clathrates. The assigned wavenumber of the Ni(CN)4 units of the complex appear to be much higher than those for isolated Ni(CN)4 ion. Such frequency shifts have been observed for Hofmann-type host frameworks [3–6, 11–23] and are attributed to the mechanical coupling of the internal modes of Ni(CN)4 with the M–NC vibrations. It follows that the N-termini of the Ni(CN)4 group are bound to a Co atom in the host compound investigated.

Cycloheptylamine vibrations

Up to the time of writing, there have been no reports for the vibrational spectroscopic studies of the cha molecule in literature. The assignment and the wavenumbers of the fundamental vibrations arising from the cha moities in various phases are tabulated in Table 2. The most striking spectral feature in the observed infrared or Raman spectrum of cha (Table 2) is that the number of fundamental bands are much lower than the expected number of 63. This is due to that the vibrations in a particular type (e.g., antisymm. str., symm. str., bending, wagging, etc.). fuse together into one broadband. For this reason, each observed fundamental modes is correlated with the calculated one which has the highest infrared intensity among the modes of its own type. The assignments are based on the potential energy distribution and the animations of the harmonic vibrations of the cha molecule based on DFT calculations. The purposed assignments (Table 2) are in agreement with the calculated results (Unpublished conformational and optimisation studies which are in preparation for submission have shown that the isolated cha should be exist with a *gauche* orientation of the –NH2 group.). As seen from Table 2, however, this sort of calculation over estimates the force constants, and hence, the calculated frequencies are higher then the experimental ones. The usually applied correction factor of ca. 0.96 [25] does not allow us to reproduce precisely the experimental frequencies (the scaled frequencies (cm⁻¹) are given in Table 2). This is due to the fact that the vibrational frequencies are derived from the harmonic approximation. Large amplitude (floppy) vibrational modes often exhibit significant anharmonicity that may increase errors in computed wavenumbers. In addition to anharmonicity, generally

Table 2. Assignment and the vibrational wavenumbers (cm^{-1}) for cha in host, clathrates and related compounds

Approximate description	Cha			DFT	cha in nujol or fluorolube	Co-cha-Ni	Co-cha-Ni-2G G = benzene
	IR (gas)	IR (liq.)	R (liq.)				
NH$_2$ antisymm. str.	3388w	3356m	3370w	3408	3362m, 3356m	3350w	3336w
NH$_2$ symm. str.	3338w	3280m	3313m	3333	3285m	3288w	3281m
CH$_2$ antisymm. str.	2932vvs	2923vvs	2933vs	2917	2928vvs	2923vs	2923vs
CH$_2$ symm. str.	2914m,sh	2902m,sh	2906m,sh	2906	2906m,sh	2909m,sh	no
CH str.	2863vs	2855vs	2853vs	2889	2858vs	2852vs	2854s
HNH def.	1618m	1600m	1615w	1593	1620s	1581s	1581s
HCH def.	1461m	1459m	1465m,sh	1440	1583m	1560w,sh	1560w
HCH def.	1446m,sh	1446m,sh	1444vvs	1434	1462s	1457s	1458m
HCC def.	1371m	1370vbr	1359w	1374	obsc.	obsc.	obsc.
HCN def./HCC def.	1317m	1332m, 1312m	1320w	1332	1311m	1305m	1307m
HCC def./HNC def.	1265m	1278m, 1250w	1283vs	1243	1278m	1263w,sh	1256w
HCC def.	1206w	1206m, 1183w	1209w	1194	1205w	1206w	1206w
HCC def./C–C str./HCC def.	1111w	1122w	1122w	1152	1112w	1122w	1120w
C–C str./HCH def.	1060w	1063m, 1048m	1063m, 1056m	1067, 1041	1064m	1069m	1046m,sh
C–N str./HCC def.	1012w	1019w	1007s	1028	1018w	1005m	1009m
C–C str./HCC def.	950w,sh	948w,sh	948w	979	947m	949m,sh	946w
C–N str./HCC def.	895w,sh	926w,sh	897w	915	892s,sh	890m	890w
HCC def./C–N str.	865w,sh	900vw,sh	850w	845	866sh	864m	864w
HNC/HCC def.	833m,sh	848m	792w	834	841s	832m	832w
C–C str.	790m	792m	759m	790	802m	803w	809w
C–N str./HCC def.	750m,sh	755m	723vvs	755	obsc.	obsc.	obsc.
NCC def./CCC def.	545m	550m	552m	480	549w	546m	545m
NCC def./CCC def.	462w,sh	465w	448m	430	470w	452w,sh	454w,sh

def. = deformation, v = very, s = strong, m = medium, w = weak, br = broad, no = not observed, obsc. = obscured.

there might be coupling between vibrational modes which is not accounted for in the computational model.

On going from gas phase through solution to neat liquid, N–H stretching wavenumbers of the ligand molecule decreases due to the N...H hydrogen bonding.

The N–H stretching frequencies of the ligand molecule in the complex compound are found to be ca. 40 cm^{-1} lower than those in gas phase (Table 2). These downward frequency shifts may be explained as weakening of the N–H bonds resulting from the electron draining from the N atom on account of its coordination to the metal atom (Co). A metal dependent downward frequency shift is also observed for the NH$_2$ scissoring mode (Table 2). Similar shifts have been observed in metal-coordinated aniline compounds [14, 15, 23] and cycloalkylamine metal(II) tetracyanometallate(II) host compounds [3–5].

Gravimetric results and spectral changes upon enclathration

When the host complex is subjected to the guest vapour in equilibrium with its liquid phase in a desiccator at ambient conditions, the guest molecules are sorbed by the host at a rate depending on the vapour pressure of the guest. The amount of the sorbed guest molecules was determined gravimetrically by leaving the host complexes in the saturated guest vapour to constant weight. *n*, the number of guest molecules per molecular formula of the host complex and their sorbing duration (the times required to attain constant weight) are given in Table 3. (It should be noted that when these preparations are attempted in solution in ethanol host complexes with much lower number of guest molecules than those in Table 3 are obtained.). The most notable in Table 3 is that the number of some enclathrated guest molecules appear

Table 2. Continued

Co-cha-Ni-2G, G = toluene	Co-cha-Ni-2G, G = o-xylene	Co-cha-Ni-1.8G, G = m-xylene	Co-cha-Ni-1.4G, G = p-xylene	Co-cha-Ni-2G, G = 1,2-dichloro benzene	Co-cha-Ni-2G, G = 1,3-dichloro benzene	Co-cha-Ni-G, G = naphthalene
3346w	3340w	3339m	3342m	3342sh, 3336m	3344m	3342m
3283w	3280w	3281m	3281w	3282m	3285w	3282m
2923vs	2921vs	2922vs	2923vs	2924s	2923m	2922vs
no	no	no	no	no	no	no
2855s	2855s	2855s	2855s	2857m, 2854m	2854m	2854s
1580m	1581s	1581s	1580s	1576s	1577s	1580s
1560w	1562w,sh	1559m	1559m	1559m	1560m	1560m
1458m	1459s	1459m	1459m	1456s	1461s	1458m
obsc.	obsc.	obsc.	obsc.	obsc.	obsc.	obsc.
1307w	1305m	1306w	1308w	1304w	1306w	1304w
1255w	1254w	1253w	1254w	1259w,sh	1254w	1253w
1206w	1206w	1206w	1206w	1206w	1206w	1206m,sh
1121w	1119w	1120w	1120m	1128s	1124m	1128m
1043m,sh	1050m,sh	1045m,sh	1044m,sh	–	1043m,sh	1045m,sh
1006m	1008m	1008m	1007m	1009m	1008m	1009m
947w	946m	947w	946w	947m	947w	948m
892w	891w	889w	891w	891w	890w	889w
864w	864w	866w,sh	864w	864w	866m	865w
832w	823w	832w	832w	832w	831w	833w
808w	807w	807w	–	808w	–	809w
obsc.	obsc.	obsc.	obsc.	obsc.	obsc.	obsc.
545w	547m	546m	547m	545m	546m	546m
454w	454w,sh	455w,sh	455m,sh	455m	453m,sh	455m

to be more than the formal maximum number of 2 found in the Hofmann-type clathrates prepared previously [1].

Table 3. n, the number of the guest molecules, included in the Co-cha-Ni host and the duration of the inclusion (the time required to attain constant weight)

Guest	n	Duration (approx.)
Benzene	3.32	24 h
Toluene	2.77	7 days
o-Xylene	2.34	6 days
m-Xylene	1.81	15 days
p-Xylene	1.42	15 days
1,2-Dichlorobenzene	2.10	15 days
1,3-Dichlorobenzene	2.29	15 days
1,4-Dichlorobenzene	0.00	30 days
1,4-Dibromobenzene	0.04	30 days
Naphthalene	0.97	30 days

When these clathrates are left in open air, the number of guest molecules, n, decreases rapidly down to 1, and then, continues to decrease at a slower rate. This liberation process for benzene in Co-cha-Ni is illustrated in Figure 3, which plot the decrease of n against time. The discontinuity at $n = 1$ on the plot suggest that the clathrate formed for $n \leq 1$ is more stable than those of $n > 1$. Similar observations have been made for benzene in Cd-cha-Ni and toluene in M-L2-Ni (M = Co or Cd, L = CPA [4] or CHA [3]) hosts. One possible interpretation for this may be due to flexible ligand, resulting in stable conformations of the alkyl ring. Another possible suggestion might be that the decomposition part of the curve for $n > 1$ is due to adsorbed guest molecules, and the part for $n \leq 1$ is due to enchlatrated guest molecules. This view may be discounted because of that if this were the case then the two sets of guest bands would be observed, one from the guest and the other from the surface adsorbed species.

At this point the structure of the clathrate compounds may be questioned: Are the guests simply

Table 4. The vibrational wavenumbers (cm^{-1}) of benzene in the Co-cha-Ni-2Bz clathrate

Assignment[a]	Liquid benzene[a]	Co-CHA-Ni-Bz[b]	Co-cha-Ni-2Bz
$\gamma_8 + \gamma_{19}$	3075	3063w	3066w
γ_{20}, E_{1u}	3073	3088m	3086m
γ_{13}, B_{1u}	3062	3033m	3032m
γ_2, A_{1g}	3059	no	no
γ_7, E_{2g}	3046	no	no
$\gamma_5 + \gamma_5 + E_{14}$	1955	1970w	1968w
γ_8, E_{2g}	1596	no	no
$\gamma_{10} + \gamma_{17}$	1815	1824w	1822w
γ_{19}, E_{1u}	1479	1477s	1478s
γ_{14}, E_{2u}	1309	1303vw	1307w
γ_9, E_{2g}	1178	no	no
γ_{15} B_{2u}	1149	no	no
γ_{18}, E_{2u}	1036	1035m	1035s
γ_1, A_{1g}	992	no	no
γ_5, B_{2g}	989	no	no
γ_{17}, E_{2u}	996	968s	984s
γ_{10}, E_{1u}	849	no	no
γ_{11}, A_{2u}	670	688s, 684, 678	684s, 677s
γ_6, E_{2g}	606	no	no

[a]Taken from Ref. [25].
[b]Taken Ref. [3].
Abbr.: v = very, s = strong, m = medium, w = weak, no = not observed.

Table 5. The infrared wavenumbers (cm^{-1}) of toluene in the Co-cha-Ni-2To clathrate

Assignment[a]	Toluene (liquid)[a]	Co-CHA-Ni-2To[b]	Co-cha-Ni-2To
$\gamma(CH)$, A_1	3085	3087w	3083w
$\gamma(CH)$, A_1	3070	no	no
$\gamma(CH)$, A_1	3058	3056w	3054w
$\gamma(CH)$, B_2	3037	3032vw,sh	no
$\gamma(CH)$, B_2	3028	3023w	3023w
$\gamma(CH_3)$, B_1	2979	2975w,sh	2974w,sh
$\gamma(CH_3)$, B_2	2950	obsc.	obsc.
$\gamma(CH_3)$, A_1	2920	obsc.	obsc.
$\gamma(CC)$, A_1	1604	1604w	1601w
$\gamma(CC)$, B_2	1584	obsc.	obsc.
$\gamma(CC)$, A_1	1493	1496m	1494m
$\delta(CH_3)$, B_2	1455	obsc.	obsc.
$\delta(CH_3)$, A_1	1378	obsc.	obsc.
$\gamma(CC)$, B_2	1331	no	no
$\beta(CH)$, B_2	1313	no	no
$\gamma(C\text{-}CH_3)$ X-sens., A_1	1208	obsc.	obsc.
$\beta(CH)$, A_1	1176	1180w	1176w,sh
$\beta(CH)$, B_2	1153	1159w	1167w
$\beta(CH)$, B_2	1080	1080w	1080w
$\gamma(CH_3)$ B_1	1040	1043m	1031m
$\beta(CH)$, A_1	1028	obsc.	obsc.
Ring, A_1	1002	no	no
$\gamma(CH)$, B_1	983	no	990
$\gamma(CH)$, B_1	893	obsc.	obsc.
$\alpha(CCC)$ X-sens., A_1	784	obsc.	obsc.
$\gamma(CH)$, B_1	734	734vs, 728vs	736, 728m
$\phi(CC)$, B_2	690	699s, 694s	695m
–		no	no
$\alpha(CCC)$, B_2	620	no	618vw
$\beta(CCC)$ X-sens., A_1	524	no	no
$\phi(CCC)$ X-sens., B_1	467	obsc.	obsc.

[a]Taken from Ref. [27].
[b]Taken from Ref. [3].
Abbr.: v = very, s = strong, m = medium, w = weak, no = not observed, obsc. = obscured by ligand.

adsorbed on the surface or enclathrated in the host framework? In this context, we report two observations which may throw some light on the issue: (i) Several Hofmann-type host complexes ($M(L_2Ni(CN)_4$ (M = Co, Ni or Cd))) with different ligand molecules (NH_3, alkyldiamines ($H_2N(CH_2)_nNH_2$ (n = 2,3,4,5,6)), pyridine, pyrazine and 4,4′-bipyridine) were subjected to benzene vapour in equilibrium with its liquid phase in a desiccator at ambient conditions for a fortnight. Gravimetric measurements did not, however, indicate any increase in the weights of the host compounds. (ii) The clathrate of naphthalene in a filter has been washed several times with ether. But the measurements did not show any notable decrease in the weights.

Nevertheless, it should be emphasized that based on the present observations, one cannot be absolutely conclusive about the clathrate composition. Therefore, a comprehensive decomposition studies are required (i.e., constant rate thermal analysis). In addition, another requirement may be an X-ray diffraction study for exploring the expansion of spacing. But these sort of studies are beyond the scope of our research activities.

As for the spectral changes upon enclathration the notable features arising from the host and the guest moieties are as follows: Of the host moieties, $Ni(CN)_4$ unit does not exhibit significant spectral changes upon sorption, except in clathrates with naphthalene guest (Table 1). These results suggest that the polymeric structure of $[Co-Ni(CN)_4]_\infty$ is generally preserved upon enclathration. In the case of clathrates with bulky

naphthalene molecule, U_8 (E_u) vibration appears (at 2162 and 2157 cm^{-1}) as a twin bands of almost similar intensity (Table 1). Such twin bands have also been observed for $M(cyclohexylamine)_2Ni(CN)_4$ (M = Co or Cd) hosts upon inclusion of the aromatic guest molecules [3]; and conceivably suggested that the primary ligand $Ni(CN)_4$ behaves as a bidentate ligand as $NC-Ni(CN)_2-CN$ in the host framework (Such a $NC-Ni(CN)_2-CN$ unit has also been found in some clathrates of the chemical formula given for the Hofmann-type clathrates [1].). This view is discounted for our case due to the fact that the frequency value of 2157 cm^{-1} is too high for the presence of terminal cyano groups. Howsoever, conceivable suggestion may be that the primary ligand $Ni(CN)_4$ behaves as a

Table 6. The infrared wavenumbers (cm^{-1}) of o-xylene in the Co-cha-Ni-2G clathrate

Assignment[a]	o-Xylene[a] (liquid)	Co-CHA-Ni-1.5G, G = o-xylene[b]	Co-cha-Ni-G, G = o-xylene
1, γ(CH), A$_1$	3080	no	no
21, γ(CH), B$_2$	3080	no	no
2, γ(CH), A$_1$	3064	3064w	3064w
22, γ(CH), B$_2$	3048	3045w	3046w
3, γ(CC), A$_1$	1608	1606w	1601w
23, γ(CC), B$_2$	no	no	no
4, γ(CC), A$_1$	1494	1490w	1496m
24, γ(CC), B$_2$	1468	1466m	1459m
5, Kekule, A$_1$	1292	1285w	1293m
25, β(CH), B$_2$	1290	1291w	1290w
6, X-sens., A$_1$	1222	no	no
26, X-sens., B$_2$	1185	1188vw	no
7, β(CH), A$_1$	1155	obsc.	obsc.
27, β(CH), B$_2$	1121	1119m	1119m
8, β(CH), A$_1$	1052	1052m,sh	1050m,sh
17, γ(CH), B$_1$	930	no	no
12, γ(CH), A$_2$	(970)	no	no
13, γ(CH), A$_2$	860	no	no
28, X-sens., B$_2$	826	no	no
18, γ(CH), B$_1$	741	743vs, 755vs	741vs/751s
9, X-sens., A$_1$	733	no	no
14, ϕ(CC), A$_2$	[702]	no	no
10, X-sens., A$_1$	(581)	no	no
15, ϕ(CC), A$_2$	505	no	no
29, X-sens., B$_2$	505	no	no
19, ϕ(CC), B$_1$	435	435m,sh	435vs
30, X-sens., B$_2$	406	nm	no
20, X-sens., B$_1$	325	nm	no
11, X-sens., A$_1$	255	nm	no
16, X-sens., A$_2$	180	nm	no
γ_{as}(CH$_3$)	2968, 2950	2971w, 2947w	no
γ_{s}(CH$_3$)	2933	2933w	no
2 γ_{as}(CH$_3$)	2882	no	no
2 δ_{s}(CH$_3$)	2732	2733w	2731w
2 δ_{as}(CH$_3$)	1454, 1445, 1384	no	1459, 1447, 1383m
δ_{s}(CH$_3$)	1374	1386m	1375s
CH$_3$ rock	1020, 984, 940	obsc.	obsc.

[a]Taken from Ref. [28].
[b]Taken from Ref. [3].
Abbr.: v = very, s = strong, m = medium, w = weak, no = not observed, obsc. = obscured by ligand.

Table 7. The infrared wavenumbers (cm^{-1}) of m-xylene in the Co-cha-Ni-2G clathrate

Assignment[a]	m-Xylene[a] (liquid)	Co-CHA-Ni-2G, G = m-xylene[b]	Co-cha-Ni-2G, G = m-xylene
γ(CH), B$_2$	3052	–	–
γ(CH), A$_1$	3032	3029m	3039w
γ(CC), B$_2$	1613	1615m	1614m
γ(CC), A$_1$	1595	1608w,sh	1608w,sh
γ(CC), B$_2$	1492	1487w	1489m,sh
γ(CC), A$_1$	1460	obsc.	obsc.
β(CH), B$_2$	1303	1378m	–
α(CCC) B$_2$	1264	obsc.	obsc.
X-sens., A$_1$	1252	obsc.	obsc.
β(CH), B$_2$	1167	obsc.	obsc.
X-sens., B$_2$	1154	no	1158w,sh
β(CH), A$_1$	1094	1097w	1094w
γ(CH), B$_1$	968	no	no
X-sens., B$_2$	905	906vw	905w
γ(CH), B$_1$	876	obsc.	obsc.
γ(CH), B$_1$	768	769vs	767vs
X-sens., A$_1$	724	obsc.	obsc.
π(CC), B$_1$	690	691s	691vs
X-sens., A$_1$	537	no	no
X-sens., B$_2$	515	obsc.	obsc.
π(CC), B$_1$	433	obsc.	obsc.
X-sens., B$_2$	404	obsc.	obsc.

[a]Taken from Ref. [29].
[b]Taken from Ref. [3].
Abbr.: v = very, s = strong, m = medium, w = weak, no = not observed, obsc. = obscured by ligand.

Table 8. The infrared wavenumbers (cm^{-1}) of p-xylene in the clathrate

Assignment[a]	p-Xylene[b] (liquid)	CO-CHA-Ni-5.G[b], G = 2p-xylene	Co-cha-Ni-1.5G, G = 2p-xylene
γ(CH), B$_{1u}$	3044	3051w	3045m,sh
γ(CH), B$_{2u}$	3017	3020w	3018m,sh
γ(CH$_3$), B$_{2u}$	2975, 2947	obsc.	obsc.
γ(CH$_3$), B$_{3u}$	2923	obsc.	obsc.
γ(CC), B$_{1u}$	1529	1517s	1516vs
δ(CH$_3$), B$_{3u}$	1458, 1452	obsc.	obsc.
γ(CC), B$_{3u}$	1421	no	no
δ(CH$_3$), B$_{2u}$	1379	obsc.	obsc.
α(CCC), B$_{2u}$	1324	no	no
X-sens., B$_{2u}$	1220	no	1220w
β (CH), B$_{2u}$	1120	1118m	1120m
γ(CH$_3$), B$_{2u}$	1041	1040w,sh	1033w
β (CH), B$_{1u}$	1023	obsc.	obsc.
γ(CH), B$_{3u}$	795	796vs	794vs, 799m,sh
X-sens., B$_{1u}$	725	obsc.	obsc.
ϕ(CC), B$_{3u}$	483	obsc.	obsc.

[a]Taken from Ref. [30].
[b]Taken from Ref. [3].
Abbr.: v = very, s = strong, m = medium, w = weak, no = not observed, obsc. = obscured by ligand.

partial bidentate ligand which is an intermediate between the tetradendate ligand Ni(CN)$_4$ and the bidentate ligand NC–Ni(CN)$_2$–CN (i.e., the strength of the two M–NCNi bonds that are trans each other are weaker than the other two bonds). It should be noted that this suggestion is tentative and possibly speculative but it is consistent with the present spectral data.

As to the spectral changes in the guest molecules, the most outstanding features are as follows: The CH

Table 9. The infrared wavenumbers (cm^{-1}) of 1,2-dichlorobenzene in the Co-cha-Ni-2G clathrate

Assignment[a]	1,2-Dichloro benzene[a] in CCl$_4$ or CS$_2$	Cd-CHA-Ni-2G[b], G = 1,2-dichloro benzene	Co-cha-Ni-2G, G = 1,2-dichloro benzene
1, γ(CH), A$_1$	3072	3072w	–
21, γ(CH), B$_2$	3072		3067w
2, γ(CH), A$_1$	no		no
22, γ(CH), B$_2$	no		no
3, γ(CC), A$_1$	1576	obsc.	obsc.
23, γ(CH), B$_2$	1576		
4, γ(CH), A$_1$	1458		1456s
24, γ(CH), B$_2$	1438	1436m	1435m
5, Kekule, A$_1$	1276		1274w
25, β(CH), B$_2$	1252	no	1251m
6, X-sens., A$_1$	1155	obsc.	1157w
26, X-sens., B$_2$	1130	1125s	no
7, β(CH), A$_1$	1130	1125s	1128vs
27, β(CH), B$_2$	1038	1036vs	1036vs
8, β(CH)A$_1$	no		no
12, γ(CH), A$_2$	975	obsc.	obsc.
17, γ(CH), B$_1$	940	949w	947w
13, γ(CH), A$_2$	850	obsc.	obsc.
18, γ(CH) B$_1$	748	748vs	738s, 748vs, 758s
28, X-sens., B$_2$	740	762vs	764s
14, ϕ(CC) A$_2$	no		no
9, X-sens., A$_1$	660	659s	659s
10, X-sens., A$_1$	480	obsc.	485w
15, ϕ(CC)A$_2$	no	no	no
19, ϕ(CC) B$_1$	435	no	no
29, X-sens., B$_2$	427	no	no
30, X-sens., B$_2$	336		no
20, X-sens., B$_1$	239	nm	nm
11, X-sens., A$_1$	202	nm	nm
16, X-sens., A$_2$	152	nm	nm
γ_s(CH$_3$)	2977, 2950		no
γ_s(CH$_3$)	2922	no	no
	2856	no	no
2δ_{as}(CH^3)	2742	no	
2δ_s (CH$_3$)	1458, 1439	1456s	1456s
δ_{as} (CH$_3$)	1382	1382w	1382w
δ_s (CH$_3$)	no	no	no
(CH$_3$) rock	1042, 988	no	no

[a]Taken from Ref. [28].
[b]Taken from Ref. [3].
Abbr.: v = very, s = strong, w = weak, no = not observed, nm = not measured, obsc. = obscured by ligand.

out-of-plane vibrational bands for some guests are found to be shifted to higher frequencies from that of the guests not enclathrated (Table 4). Similar upward frequency shifts were observed for benzene in Hofmann-type clathrates and explained as being due to the presence of a weak hydrogen bond between π electrons located above and below the plane of benzene ring and the ammonia molecules of the host lattice [12, 13, 27]. Similar shifts have also been found for other members of the Hofmann-type clathrates [3–5, 14, 15, 17, 20–22]. Therefore, we may reasonably suggest that the frequency shifts in our compounds are due to the π electron donation from the guests to the hydrogen

atoms of the NH$_2$ group of the ligand molecule which has a more electrophilic character caused by coordination to Co.

Another outstanding feature of the CH out-of-plane vibration in benzene is that it appears as a triplet for M(en)M′(CN)$_4$·2C$_6$H$_6$(M = Mn or Cd, M′ = Cd or Hg) [18]; a doublet for Co(cycloheptylamine)$_2$Ni(CN)$_4$· 2C$_6$H$_6$, Co(cyclooctylamine)$_2$Ni(CN)$_4$·2C$_6$H$_6$ and Co(cyclohexylamine)$_2$Ni(CN)$_4$ [3, 5] and for Cd(pyr-azine)M(CN)$_4$ · C$_6$H$_6$(M = Cd or Hg) [19], M(NH$_3$)$_2$ M′(CN)$_4$·2C$_6$H$_6$ (M = Mn or Cd, M′ = Cd or Hg) [20] and M(tn)Zn(CN)$_4$·2C$_6$H$_6$?(M = Mn or Zn) [21]; a singlet for M(NH$_3$)$_2$Ni(CN)$_4$·2C$_6$H$_6$(M = Mn, Fe,

Table 10. The infrared wavenumbers (cm^{-1}) of 1,3-dichlorobenzene in the clathrate

Assignment	1,3-dichlorobenzene[a] (liquid)	1,3-dichlorobenzene[b] in CCl$_4$ or CS$_2$	Cd-CHA-Ni-2G[c] G = 1,3-dichlorobenzene	Co-cha-Ni-2G G = 1,3-dichlorobenzene
A$_1$, γ_1, γ(CH)	3071	3071	3069w	3065w
γ_2, γ(CH)			no	no
γ_3, γ(CH)			no	no
γ_4, γ(CC)	1577	1580	1578vs	obsc.
γ_5, γ(CC)	1412	1412	1413	1413m
γ_6, X-sens.	1124	1127	1124m	1124m
γ_7, β(CH)	1073		1072m	1072m
γ_8 ring	997	1000	999s	990m
γ_9 X-sense.	663	663	663	663w
γ_{10}X-sens.	398	399	no	no
γ_{11}X-sens.	198	198	no	no
A$_2$, γ_{12} γ(CH)	892	896	890m	890w
γ_{13}, ϕ(CC)	532		529	no
γ_{14}X-sens.,				
B$_1$, γ_{15}, γ(CH)	964	966	967m	970w
γ_{16}, γ(CH)	867	869	867m	866m
γ_{17}, γ(CH)	773	775	774s	774s
γ_{18}, ϕ(CC)	672	674	674s	674s
γ_{19}, ϕ(CC)	433	428	no	no
γ_{20}X-sens.,	175		nm	nm
B$_2$, γ_{21}, γ(CH)	3095	3095	3092w	no
γ_{22}, γ(CC)	1577	1580	1580vs	obsc.
γ_{23} γ(CC)	1462	1464	1462vs	1460vs
γ_{24}, β(CH)	1289	1330	1341w,sh	1341w,sh
γ_{25}, Kekule	1258	1258	1255w	1254w
γ_{26}, β(CH)	1161	1161	1162w	1162w
γ_{27}, X-sens.	1080	1079	1081m	1078m
γ_{28}, X-sens.	784	784	783vs	782s
γ_{29}, X-sens.				
γ_{30}, X-sens.	365	364	nm	nm

[a]Taken from Ref. [29].
[b]Taken from Ref. [31].
[c]Taken from Ref. [3].
Abbr.: v = very, s = strong, w = weak, no = not observed, nm = not measured.

Table 11. The infrared wavenumbers (cm^{-1}) of naphthalene in the clathrate

Assignment[a]	Naphthalene[a] (in CCl$_4$ or CS$_2$)	Cd-CHA-Ni-2G[b], G = naphthalene	Co-cha-Ni-G, G = naphthalene
41 CH str., B$_{3u}$	3072vs	3065w	3065s
29 CH str., B$_{2u}$	3014s	3012vw,sh	no
42 CH str., B$_{3u}$	2976s	no	no
30 CH str., B$_{2u}$	2947m	no	no
43 CC str., B$_{3u}$	1680m	no	1684w
31 CC str., B$_{2u}$	1595s	1596m,sh	1595m,sh
44 CC str., B$_{3u}$	1510m	1507m	1509m
32 CC str., B$_{2u}$	1387vs	1390m	1388m
33 CH bend, B$_{2u}$	1268vs	1269s	1269m
45 CH bend, B$_{3u}$	1211s	1213m	1210m
34 CH bend, B$_{2u}$	1139s	1130m	1128m
46 CH bend, B$_{3u}$	1012s	1010m,sh	1009s
22 CH bend, B$_{1u}$	957s	no	963m
47 skeletal breat., B$_{3u}$	876m	880	880w
23 CH bend, B$_{1u}$	782vs	786vvs	786vvs
35 skeletal distor., B$_{2u}$	752s	754vw	no
48 skeletal distor., B$_{3u}$	618s	618m	618w
24 CC distor., B$_{1u}$	475s	480m	479s

[a]Taken from Ref. [31].
[b]Taken from Ref. [3].
Abbr.: v = very, s = strong, w = weak, no = not observed.

The noteworthy spectral features arising from the ligand molecule on guest inclusion are as these: On going from the host complex to the clathrates, the symmetric and antisymmetric stretching frequencies of NH$_2$ decrease (Table 2). This downward shift may be due to hydrogen bonding between the π electron of the guest ring and the ligand molecules, as has been suggested for the Hofmann-type benzene clathrates with amine and diamine ligands [3–5, 18–21].

Based on the present spectral data, it is not possible to determine the conformation of the ligand or the orientation of the guest molecules in the clathrates studied. As in the Hofmann-type and Hofmann-T$_d$-type benzene clathrates, the relative orientation of the N–H bonds of cycloalkylamine with respect to the axis of the π cloud of guest must be the one most favourable for hydrogen bonding [34].

It should be noted that experiments with a large number of aromatic guest molecules and host complexes with M = Mn, Fe, Cu, Ni, Zn or Cd, M′ = Ni, Pd or Pt and a series of cycloalkylamines (cyclopropylamine, cyclobutylamine, cyclopentylamine, cyclohexylamine, cycloheptylamine, cyclooctylamine, cyclododecylamine, cyclohexyldiamine, cycloheptyl cyanide, cycloheptanecarbonitrile, cyclohexanecarbonitrile, cyclohexyl isocyanide, cyclohexyl isothiocyanate and cyclohexyl mercaptan) are in progress.
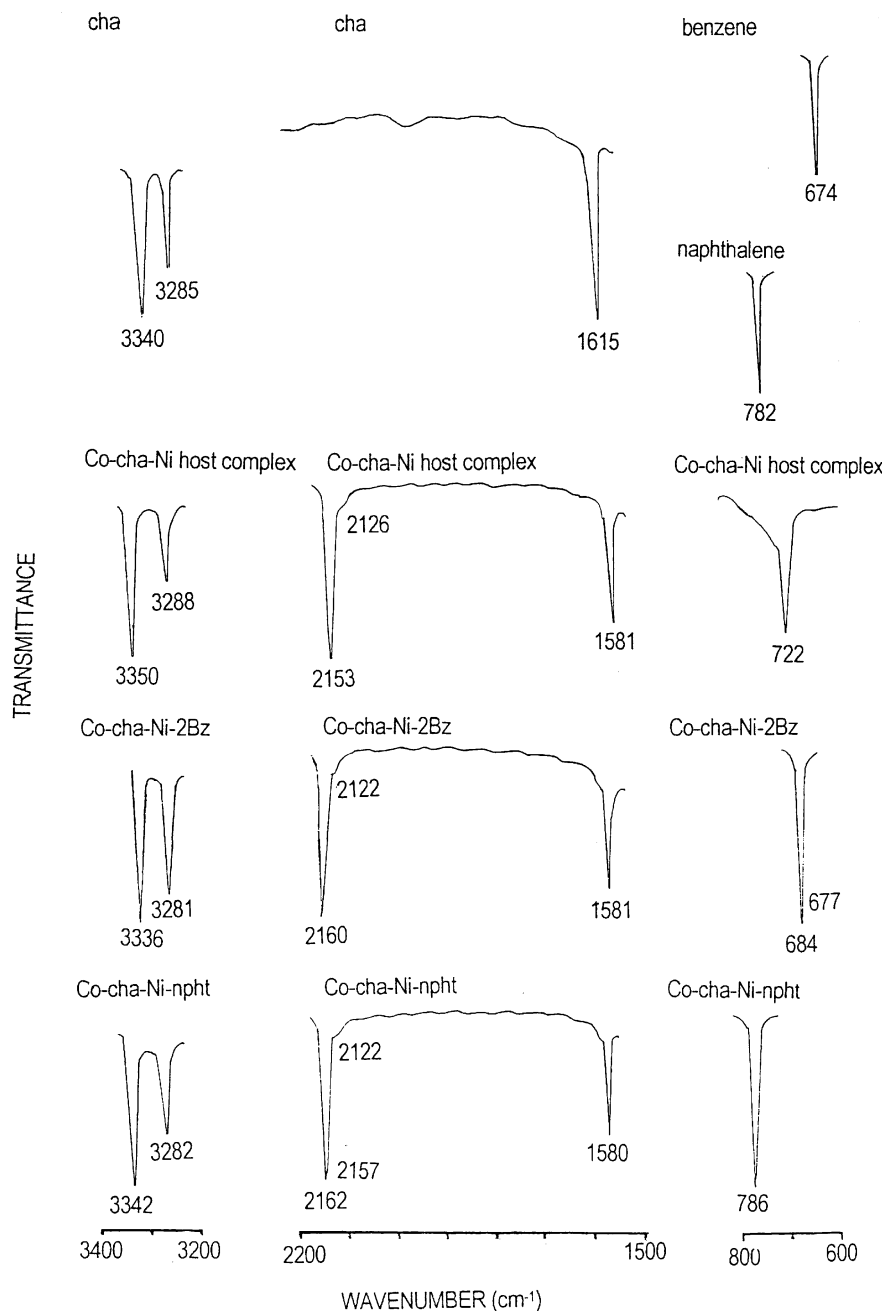
Ni, Cu, Zn or Cd) [12, 13], Cd(4,4′-bipyridyl) M′(CN)$_4$·2C$_6$H$_6$ (M′ = Cd or Hg) [22] and Cd(cyclohexylaminee)$_2$Ni(CN)$_4$·2C$_6$H$_6$ [3]. In the case of doublet or triplet features the splittings have been ascribed to crystal field effects (strong host–guest interactions) [11–13, 18–22]. In the case of a single band, because of the larger cavities due to the ligands, the host–guest interactions are expected not to be effective for splitting [3, 11, 13, 22]. Splitting has also been observed for toluene (Table 6) and *o*-xylene (Table 7). The band positions of benzene and toluene are found as being not dependent on the value of n (n ≤ 2 or n ≤ 2).

Figure 2. The important IR bands of cha, Ni(CN)$_4$, benzene and naphthalene species in different chemical states related to Co-cha-Ni-guest systems (all compounds are in nujol).
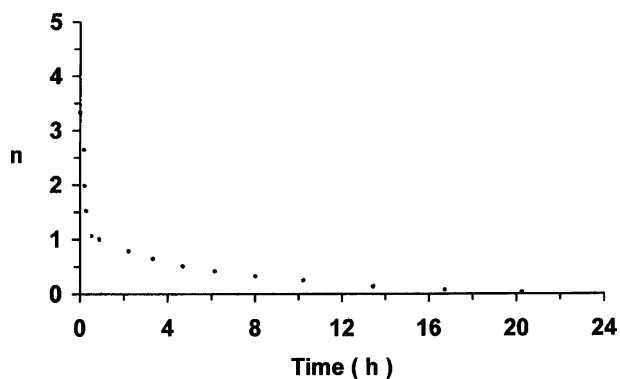

Figure 3. Decay of *n*, number of benzene molecules, against time for Co-cha-Ni-benzene system.

References

1. T. Iwamoto: *J. Incl. Phenom.* **24**, 61 (1996).
2. T. Iwamoto: The Hofmann-type and related inclusion compounds. In J.L. Atwood, J.E.D. Davies and D.D. Mae Nicol (eds.), *Inclusion Compounds* 1, Academic Press, pp. 29–57.
3. Z. Kantarc and M.M. Bülbül: *J. Incl. Phenom.* **40**, 105 (2001).
4. Z. Kantarc and C. Bayrak: *J. Incl. Phenom.* **45**, 129 (2003).
5. G. Kürkçüoglu, Z. Kantarcı, and M. Şenyel: *J. Incl. Phenom.* **45**, 129 (2003).
6. Y. Mathey and C. Mazieres: *Can. J. Chem.* **52**, 3637 (1974).
7. The Aldrich Library, Aldrich Chemical Company.
8. Gaussian 98 (Revision A.1x), M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, V.G. Zakrzewski, J.A. Montgomery, Jr., R.E. Stratmann, J.C. Burant, S. Dapprich, J.M. Millam, A.D. Daniels, K.N. Kudin, M.C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi,

R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G.A. Petersson, P.Y. Ayala, Q. Cui, K. Morokuma, P. Salvador, J.J. Dannenberg, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J. Cioslowski, J.V. Ortiz, A.G. Baboul, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, J.L. Andres, C. Gonzalez, M. Head-Gordon, E.S. Replogle and J.A. Pople: Gaussian, Inc., Pittsburgh PA, 2001.

9. QCPE, Program no: 628.
10. A. Allouche and J. Pourcin: *Spectrochim. Acta* **49A**, 571 (1993).
11. S. Akyüz, A.B. Dempster, R.L. Morehouse, and S. Susuki: *J.Mol. Struct.* **17**, 105 (1973).
12. J.E.D. Davies, A.B. Dempster, and S. Suzuki: *Spectrochim. Acta* **30A**, 1183 (1974).
13. S. Akyüz, A.B. Dempster, and R.L. Morehouse: *Spectrochim. Acta* **30A**, 1189 (1974).
14. S. Bayarı, Z. Kantarcı, and S. Akyüz: *J. Mol. Struct.* **351**, 19 (1995).
15. N. Karacan, Z. Kantarcı, and S. Akyüz: *Spectrochim. Acta* **A52**, 771 (1996).
16. S. Akyüz and J.E. Davies: *J. Mol. Struct.* **97**, 457 (1982).
17. S. Bayar, C. Bayrak, and Z. Kantarcı: *J. Incl. Phenom.* **38**, 23 (2000).
18. E. Kasap and Z. Kantarcı: *J. Incl. Phenom.* **23**, 1 (1995).
19. N. Ekici, Z. Kantarcı, and S. Akyüz: *J. Incl. Phenom.* **10**, 9 (1991).
20. E. Kasap and Z. Kantarcı: *J. Incl. Phenom.* **20**, 33 (1995).
21. Z. Kantarcı and C. Bayrak: *J. Incl. Phenom.* **30**, 59 (1998).
22. S. Bayar, Z. Kantarcı, and S. Akyüz: *J. Incl. Phenom.* **17**, 291 (1998).
23. R.L. McCullough, L.H. Jones, and G.A. Croaby: *Spectrochim. Acta* **16**, 929 (1960).
24. V.F. Kalasinsky and T.S. Little: *J. Raman Spectrosc.* **9**, 224 (1980).
25. A.P. Scott and L. Radom: *J. Phys. Chem.* 16502 (1996).
26. A. Thornton: *J. Coord. Chem.* **24**, 261 (1991) .
27. P.C. Painter and J.L. Koenig: *Spectrochim. Acta* **33A**, 1003 (1975).
28. A.P. Hitchcock and J.D. Laposa: *Mol. Spectrosc.* **54**, 223 (1975).
29. H.S. Green: *Spectrochim. J Acta* **26A**, 1913 (1970).
30. J.H.S. Green: *Spectrochim. Acta* **26A**, 1523 (1970).
31. J.H.S. Green: *Spectrochim. Acta* **26**, 1503 (1970).
32. J.R. Schever and J.C. Evans: *Spectrochim. Acta* **19**, 1739 (1963) .
33. E.R. Lippincott and E.J. O'Reilly: *J. Chem. Phys.* **23**, 238 (1955) .
34. E. Ruiz, J.J. Novoa, and S. Alvarez: *J. Phys. Chem.* **99**, 2296 (1995).