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Vibrational Spectroscopic Investigation of the Hofmann-type Clathrates: M(piperidine)$_2$Ni(CN)$_4$.G (M=Co, Ni or Cu; G = benzene derivatives)

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Abstract

Infrared spectra of M(piperidine)$_2$Ni(CN)$_4$.0.5G (M=Co, Ni or Cu; G= chlorobenzene, 1,2-dichlorobenzene or 1,3-dichlorobenzene; M=Co or Ni; G=1,4-dichlorobenzene) compounds are reported. The piperidine molecules in the host permit the inclusion of bulky guest molecules. The spectral features suggest that the compounds are similar in structure to the Hofmann-type clathrates.

Introduction

Piperidine is an important versatile industrial molecule which is used as a chemical intermediate in the rubber industry, as a corrosion inhibitor, as a solvent, and in the synthesis of optical brighteners, pharmaceutical products, crop protection agents, and dyes. The solubility of this amine in water and its widespread applications contribute to the release of chemicals in the environment where it can be transformed into N-nitroso compounds [1]. The molecular structure of piperidine is shown in Figure 1.

Detailed studies have been published on the vibrational spectra of Hofmann-type clathrates with the general formula M(NH$_3$)$_2$M$'$(CN)$_4$.2G, where M is a metal in six-coordination with two NH$_3$ molecules and four nitrogen atoms of the CN ligands; M$'$ is a metal in four-coordination with four carbon atoms of CN, and G represents the guest molecule [2, 3]. Based on this structure, several metal complex clathrates, have been developed by replacing the ammonia molecules by other N-donor ligands (L) [4].

We have prepared eleven new dipiperidine metal(II) tetracyanonickelate clathrates, M(piperidine)$_2$Ni(CN)$_4$.0.5G (M=Co, Ni or Cu; G = chlorobenzene, 1,2-dichlorobenzene or 1,3-dichlorobenzene; M=Co or Ni; G = 1,4-dichlorobenzene). The hypothetical structure of Hofmann-type (host) compounds M(piperidine)$_2$Ni(CN)$_4$ is given in Figure 2. The aim of this study is to give further examples of Hofmann-type clathrates.

Experimental

The M(piperidine)$_2$Ni(CN)$_4$.0.5G (M=Co, Ni or Cu; G = chlorobenzene, 1,2-dichlorobenzene or 1,3-dichlorobenzene; M=Co or Ni; G = 1,4-dichlorobenzene) clathrates were prepared by adding slightly more than two millimoles of piperidine and one millimole of K$_2$Ni(CN)$_4$ solution in water to one millimole of MCl$_2$ solution in water, saturated with the guest molecules. The precipitate was filtered, washed with water and ether, and kept in a desiccator containing molecular sieves and saturated guest vapour. Attempts to prepare the Cu/1,4-dichlorobenzene clathrate were unsuccessful.

The freshly prepared compounds were analysed for C, H and N by a Leco CHNS-932 analyser (Table 1).

The infrared spectra of the compounds were recorded in the range 4000 to 400 cm^{-1} on a Mattson 1000 FTIR spectrometer which was calibrated using a polystyrene film and indene solution. The samples were prepared as mulls in nujol and as KBr discs.

Results and discussion

The infrared spectra of the compounds M(piperidine)$_2$-Ni(CN)$_4$.0.5G (M=Co, Ni or Cu; G = chlorobenzene, 1,2-dichlorobenzene or 1,3-dichlorobenzene; M=Co or Ni; G = 1,4-dichlorobenzene) are very similar, but the copper compound shows different spectral features. The similarities between the IR spectral features of the compounds suggest that the eight clathrates have the same structure. The IR spectra of Co(piperidine)$_2$Ni(CN)$_4$.0.5G (G = chlorobenzene) and Cu(piperidine)$_2$Ni(CN)$_4$.0.5G (G = chlorobenzene) are given in Figures 3 and 4 respectively. The assignments are divided into three groups arising from the Ni(CN)$_4$ units, from the piperidine and from the guest molecule moieties, respectively. The infrared wavenumbers of the bands in the spectra of these species are tabulated in Tables 2–9, respectively, together with some relevant spectral data for comparison.

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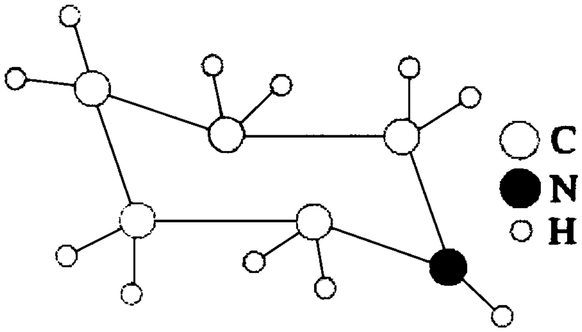

Figure 1. The molecular structure of piperidine.

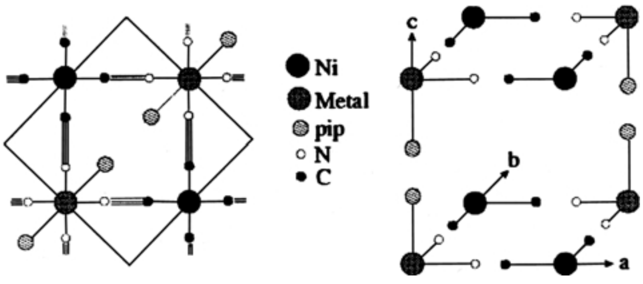

Figure 2. The hypothetical structure of Hofmann-type compounds M((piperidine)$_2$Ni(CN)$_4$.

Ni(CN)$_4$ group vibrations

The assigned wavenumbers for Ni(CN)$_4$ groups in our compounds are given in Tables 2 and 3, together with the vibrational wavenumbers of Na$_2$Ni(CN)$_4$ [5]. The wavenumbers of the ν(CN) and δ(NiCN) modes are found to be similar to those of Hofmann-type complexes [3, 4, 6–9], indicating that the $|$M–Ni(CN)$_4|_\infty$ layers have been preserved. The observation of one IR active (E$_u$) ν(CN) and one IR active δ(NiCN) modes of Ni(CN)$_4$ showed that the nickel atoms have a local D$_{4h}$ symmetry in the Co or Ni clathrates. The ν(CN) frequencies depend on the metal and this reflects the strength of the metal nitrogen bond (M–N).

Table 1. Analytical data for compounds prepared (L = piperidine)

Compound	C% Found/Calculated	H% Found/Calculated	N% Found/Calculated
Co (L)$_2$Ni(CN)$_4$.0.5G G = chlorobenzene	45.50/45.54	5.43/5.50	18.81/18.74
Co(L)$_2$Ni(CN)$_4$.0.5G G = 1,2-dichlorobenzene	43.26/43.38	5.33/5.25	17.94/17.86
Co(L)$_2$Ni(CN)$_4$.0.5G G=1,3-dichlorobenzene	43.57/43.38	5.36/5.25	17.88/17.86
Co(L)$_2$Ni(CN)$_4$.0.5G G = 1,4-dichlorobenzene	43.48/43.38	5.38/5.25	17.70/17.86
Ni(L)$_2$Ni(CN)$_4$.0.5G G = chlorobenzene	45.78/45.57	5.60/5.51	18.73/18.75
Ni(L)$_2$Ni(CN)$_4$.0.5G G = 1,2-dichlorobenzene	43.58/43.38	5.44/5.25	17.55/17.86
Ni(L)$_2$Ni(CN)$_4$.0.5G G = 1,3-dichlorobenzene	43.34/43.38	5.72/5.25	18.01/17.86
Ni(L)$_2$Ni(CN)$_4$.0.5G G = 1,4-dichlorobenzene	43.66/43.38	5.56/5.25	17.89/17.86
Cu(L)$_2$Ni(CN)$_4$.0.5G G = chlorobenzene	44.95/45.08	5.39/5.45	18.17/18.55
Cu(L)$_2$Ni(CN)$_4$.0.5G G = 1,2-dichlorobenzene	43.26/43.38	5.41/5.25	17.63/17.86
Cu(L)$_2$Ni(CN)$_4$.0.5G G = 1,3-dichlorobenzene	43.45/43.38	5.22/5.25	17.75/17.86

In the Cu(piperidine)$_2$Ni(CN)$_4$.0.5G (G = chlorobenzene, 1,2-dichlorobenzene or 1,3-dichlorobenzene) clathrates, two strong bands are observed in the (E$_u$) ν(CN) and (E$_u$) δ(NiCN) regions of the infrared spectra; the observation of two strong bands in these regions is related directly to a change of symmetry and removal of degeneracy. This is the well known Jahn–Teller effect and has been observed previously in metal pyridine and 8-hydroxyquinoline tetracyanonickelate complexes [8, 9].

Vibrations of piperidine

The vibrational modes of piperidine have been given by several workers [10–15]. The first detailed vibrational assignment for piperidine was made by Titova *et al.* [10], where they reported the calculated and experimental frequencies and the forms of the normal vibrations for the axial and the equatorial conformations of piperidine. Vedal et al. [15] have reported the IR spectra of piperidine as vapour, liquid and as amorphous and crystalline solids at −180 °C between 4000 and 200 cm^{-1}. They have also reported the Raman spectrum of N-deuterated piperidine in the liquid state.

It is known that the piperidine rings exist in chair forms as indicated by electron diffraction and NMR results for cyclohexanes and piperazines [16]. The detailed ring geometry was also given [17]. A large number of studies concerning the conformations of piperidine is reported, including IR, NMR and microwave spectroscopic techniques as well as dipole measurements, and these works have been reviewed by Jones *et al.* [18]. In spite of the very conflicting results of these studies, Katritzky and co-workers have established a slight preference for the equatorial conformer of piperidine in the vapour phase and in non-interacting solvents [19].

The assignments and the wavenumbers of the vibrational bands of piperidine observed in the IR spectra of the M(piperidine)$_2$Ni(CN)$_4$.0.5G clathrates are listed in Tables 4 and 5, together with our vibrational data on liquid piperidine. Since the piperidine molecule has only C$_s$ symmetry, all 45 molecular vibrations are both IR and Raman active. Infrared spectral data for piperidine in the compounds studied are consistent with all the characteristics of a coordinated ligand [6–9], that is, several modes (except NH) of piperidine have upward shifts in wavenumber in comparison with those of liquid piperidine. Similar shifts are observed in the pyridine, 8-hydroxyquinoline and 3-chloro-4-methylaniline complexes and explained by coupling of the internal vibrations of the ligand with the M–N(ligand) stretching frequency [8, 9, 20]. The ν(NH) bands in the clathrates are shifted towards lower wavenumbers of about 10 cm^{-1} using as reference the value of 3280 cm^{-1} for ν(NH) for liquid piperidine.

It is known that the NH vibrational modes of piperidine and piperazine are much affected by complex formation [14]. For example the NH stretching band moves to lower

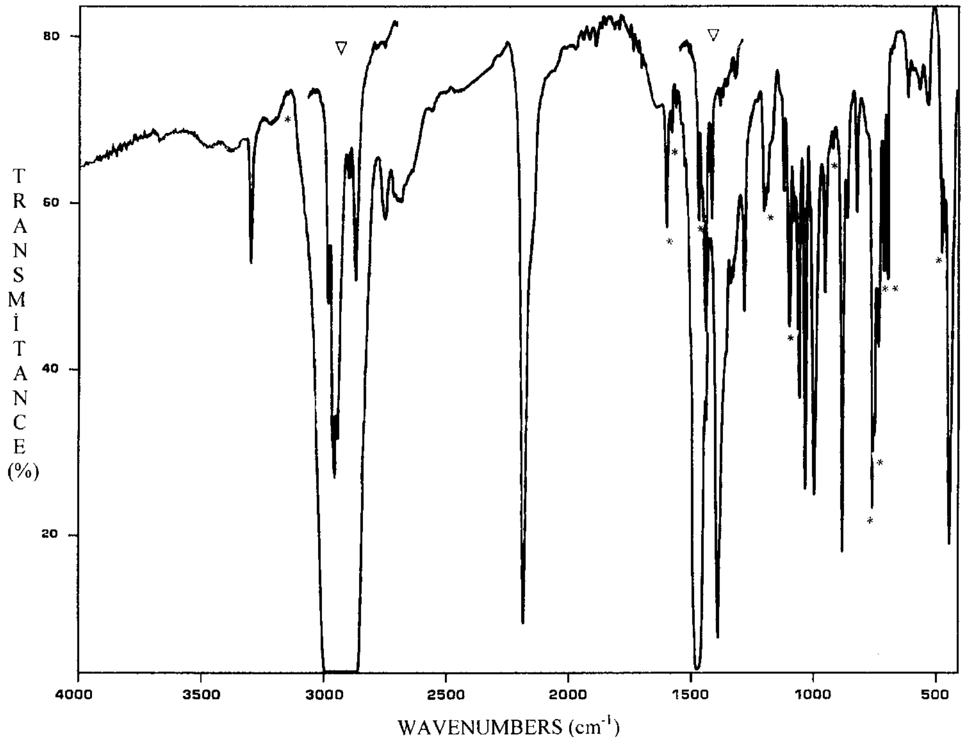

Figure 3. The infrared spectrum of the Co(piperidine)$_2$Ni(CN)$_4$0.5 chlorobenzene clathrate in nujol mull (∇ in KBr). Chlorobenzene bands marked *.

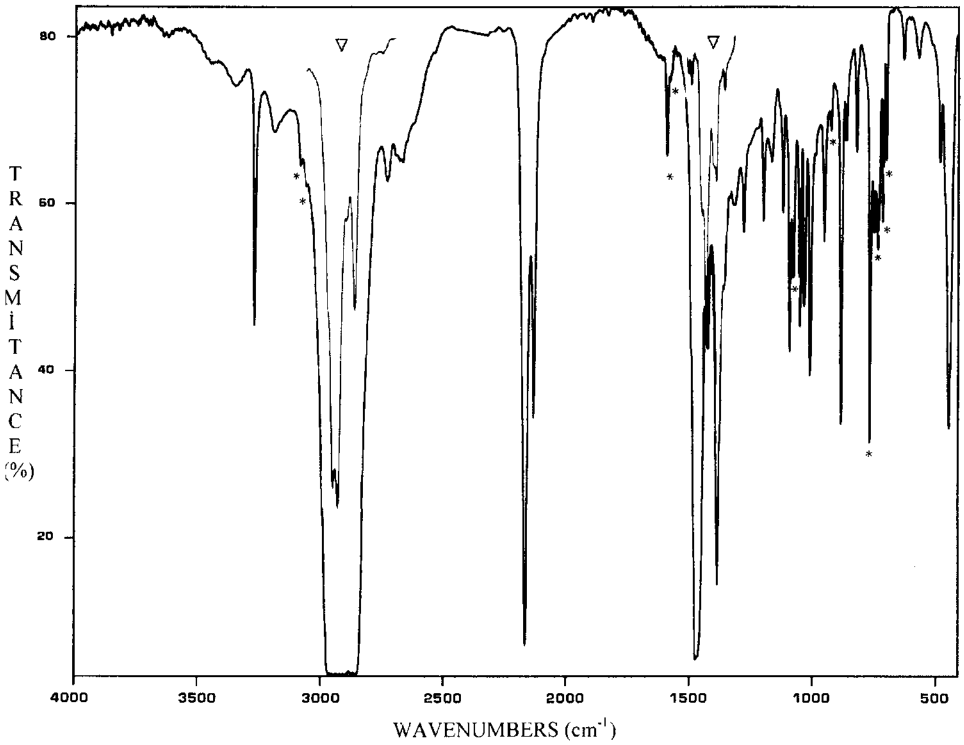

Figure 4. The infrared spectrum of the Co(piperidine)$_2$Ni(CN)$_4$0.5 chlorobenzene clathrate in nujol mull (∇ in KBr). Chlorobenzene bands marked *.

Table 2. The vibrational wavenumbers (cm^{-1}) of the Ni(CN)$_4$ group for the CoL$_2$Ni(CN)$_4$ 0.5G (L = piperidine; G = chlorobenzene, 1,2-dichlorobenzene, 1,3-dichlorobenzene, 1,4-dichlorobenzene) clathrates

Assignment*	Na$_2$Ni(CN)$_4$*	Co cl-bn	Co 1,2 cl-bn	Co 1,3cl-bn	Co 1,4cl-bn
ν_8(CN), E_u	2132	2165 vs	2161 vs	2163 vs	2159 vs
ν_8(CN), E_u	–	2127 vw, sh	2128 vw, sh	2129 vw, sh	2130 vw, sh
ν_9(NiC), E_u	543	598 w	597 w	600 w	597 w
π(NiC), A_{2u}	448	466 w	466 vw	468 w	463 w
δ(NiCN), E_u	433	437 vs	437 vs	437 vs	434 vs

vs: very strong, s: strong, m = medium, w: weak, vw: very weak, and sh: shoulder; cl-bn = chlorobenzene, 1,2cl-bn = 1,2-dichlorobenzene, 1,3cl-bn =1 ,3-dichlorobenzene and 1,4cl-bn = 1,4-dichlorobenzene.
*Taken from Ref. [5].

Table 3. The vibrational wavenumbers (cm^{-1}) of the Ni(CN)$_4$ group for the ML$_2$Ni(CN)$_4$ 0.5G (L = piperidine; M=Ni or Cu; G = chlorobenzene, 1,2-dichlorobenzene, 1,3-dichlorobenzene; M=Ni ; G = 1,4-dichlorobenzene) clathrates

Assignment*	Na$_2$Ni(CN)$_4$*	Ni cl-bn	Ni 1,2cl-bn	Ni 1,3cl-bn	Ni 1,4cl-bn	Cu cl-bn	Cu 1,2cl-bn	Cu 1,3cl-bn
ν_8(CN), E_u	2132	2169 vs	2170 vs	2168 vs	2166 vs	2160 vs	2163 vs	2159 vs
						2125s	2130 s	2128 s
ν_8(CN), E_u	—	2129 vw, sh	2127 vw, sh	2129 vw, sh	2130 vw, sh	2114 w	2114 w	2113 w
ν_9(NiC), E_u	543	604 w	602 w	605 w	602 w	617 w	600 w	597 w
π(NiC), A_{2u}	448	468 w	468 w	470 w	457 w	454 w	468 w	468 vw
δ(NiCN), E_u	433	440 vs	440 vs	438 vs	439 vs	435 vs	437 vs	434 vs

vs: very strong, s: strong, m = medium, w: weak, vw: very weak, and sh: shoulder; cl-bn = chlorobenzene, 1,2cl-bn = 1,2-dichlorobenzene, 1,3cl-bn = 1,3-dichlorobenzene and 1,4cl-bn = 1,4-dichlorobenzene.
*Taken from Ref. [5].

Table 4. The infrared wavenumbers (cm^{-1}) of piperidine molecules in CoL$_2$Ni(CN)$_4$ 0.5G (L = piperidine; G = chlorobenzene, 1,2-dichlorobenzene, 1,3-dichlorobenzene, 1,4-dichlorobenzene) clathrates

Assignment*	Liquid* piperidine	This study liquid piperidine	Co cl-bn	Co 1,2-cl-bn	Co 1,3-cl-bn	Co 1,4-cl-bn
A′	3341 s, br	3340 m, br	3349 w, br	3350 w, br	3350 w, br	3348 w, br
A′	3309 s, br	3280 s	3272 w	3273 w	3275 w	3278 w
						3255 w
A′	2931 vs, br	2931 vs	2964 m	2964 m	2965 m	2963 m
a′, a″	2850 vs	2851 vs	2940 vs	2945 vs	2940 vs	2943 sp
			2922 sp	2924 vs	2923 sp	2923 vs
A″/	2803 vs	2804 s	2882 w	2882 w	2881 w	2883 w
A′	2730 s	2734 s	2852 m	2854 m	2851 m	2853 m
A″	1468 s	1468 s	1465 w	1458 vs	1460 vs	1456 vs
A′	1444 s, sh	1443 vs	1450 vs	1450 vs	1450 s	1452 vs
A′	1386 m	1385 w	1422 m	1422 m	1422 m	1422 m
A′	1365 m	1365 w	1384 w	1384 vw	1385 w	1390 w
A′	1346 m, sh	1345 w	1374 w	1371 w	1374 w	1375 w
A″	1332 s	1332 s	1343 vw	1344 vw	1342 vw	1346 vw
A″	1318 s	1317 vs	1322 w	1323 w	1323 w	1321 vw
A″	1258 m	1258 s	1266 w	1264 w	1265 w	1263 w
A″	1191 m	1191 s	1187 m	1188 m	1189 w	1186 m
A′	1164 m	1151 s	1175 w	1177 w	1179 w 1170 w	1175 w
A″	1146 s	1135 s	1154 w	1158 w	1164 w	1155 vw
A″	1115 vs	1115 vs	1108 m	1109 m	1108 w	1108 m
A″	1052 s	1051 s	1089 m	1089 w	1089 w	1090 s
A′	1035 s	1035 s	1045 s	1045 m	1045 m	1047 m
A′	1006 m	1007 m	1021 s	1021 s	1021 s	1020 s
A″	964 m	963 w	985 vs	983 s	983 s	974 s
–	938 m	938 m	936 m	939 m	940 m	936 m
–	917 w, br	917 w	918 vw	918 vw	918 vw	919 vw
A′	859 s	860 vs	872 vs	871 vs	870 vs	873 vs
A′	822 m	823 m	845 m	848 m	849m	845m
A″	810 m, sh	795 vs, sh	812 w	811 w	812 m	812 m
A′	743 vs	744 vs	740 s	739 s	–	–
A′	546 s	547 s	598 vw	597 vw	597 vw	597 vw
A′	432 m	432 m	455 m	456 m	458 m	455 m
A′	404 w	404 m	–	401 w	403 w	402 w

vs:very strong, s: strong, m = medium, w: weak, vw: very weak, and sh: shoulder; cl-bn = chlorobenzene, 1,2cl-bn = 1,2-dichlorobenzene, 1,3cl-bn = 1,3-dichlorobenzene 1,4cl-bn=1,4-dichlorobenzene.
*Taken from Ref. [15]

Table 5. The infrared wavenumbers (cm^{-1}) of piperidine molecules in $ML_2Ni(CN)_4$ 0.5G (L = piperidine; M=Ni or Cu; G = chlorobenzene, 1,2-dichlorobenzene, 1,3-dichlorobenzene; M=Ni; G = 1,4-dichlorobenzene;) clathrates

Liquid* Piperidine	This study Liquid piperidine	Ni cl-bn	Ni 1,2-cl-bn	Ni 1,3-cl-bn	Ni 1,4-cl-bn	Cu cl-bn	Cu 1,2-cl-bn	Cu 1,3-cl-bn
3341 s,br	3340 m, br	3347 w, br	3348 w, br	3343 w, br	3346 w, br	3343 w, br	3345 w	3342 w, br
3309 s, br	3280 s	3273 w	3275 w	3269 w	3276 w	3269 m	3273 w	3275 w
2931 vs, br	2931 vs	2964 m	2965 m	2972 m	2967 m	2978 m	2964 m	2965 m
2850 vs	2851 vs	2945 vs	2940 vs	2940 vs	2942 vs	2941 vs	2945 vs	2940 vs
		2924 vs	2923 sp	2923 sp	2923 sp	2927 vs	2924 vs	2923 sp
2803 vs	2804 s	2882 w	2881 w	2889 w	2882 w	2885 w	2882 w	2881 w
2730 s	2734 s	2854 m	2851 m	2858 m	2853 m	2858 m	2854 m	2851 m
1468 s	1468 s	1458 vs	1460 vs	1460 vs	1463 m	1465 vs	1458 vs	1460 vs
1444 s, sh	1443 vs	1450 vs	1450 s	1450 s	1450 vs	1452 vs	1450 vs	1450 s
1386 m	1385	1422 m	1422 m	1422 m	1422 s	1408 m	1422 m	1422 m
1365 m	1365 w	1384 vw	1385 w	1385 w	1390 w	1384 vw	1384 vw	1385 w
1346 m, sh	1345 w	1371 w	1374 w	1375 w	1373 w	1374w	1371 w	1374 w
1332 s	1332 s	1344 vw	1342 vw	1342 vw	1341 vw	1344 vw	1344 vw	1342 vw
1318 s	1317 vs	1323 w	1323 w	1323 w	1323 w	1323 w	1323 w	1323 w
1258 m	1258 s	1264 w	1265 w	1268 w	1263 w	1269 w	1264 w	1265 w
1191 m	1191 s	1188 m	1189 w	1189 w	1188 w	1190 m	1188 m	1189 w
1164 m	1151 s	1177 w	1179 w	1179 w	1177 w	1180 vw	1177 w	1179 w
			1170 w	1170 w				1170 w
1146 s	1135 s	1158 w	1164 w	1164 w	1155 w	1157 w	1158 w	1164 w
1115 vs	1115 vs	1109 m	1108 w	1108 w	1108 m	1110 m	1109 m	1108 w
1052 s	1051 s	1089 w	1089 w	1083 w	–	1082 m	1089 w	1089 w
1035 s	1035 s	1045 m	1045 m	1042 m	1046 m	1045 m	1045 m	1045 m
1006 m	1007 m	1021 s	1021 s	1025 s	1020 s	1021 s	1021 s	1021 s
964 m	963 w	983 s	983 s	983 s	983 s	983 s	983 s	983 s
938 m	938 m	939 m	940 m	940 m	938 m	939 m	939 m	945 m
917 w, br	917 w	918 vw	918 vw	918 vw	918 vw	918 vw	918 vw	918 vw
859 s	860 vs	871 vs	870 vs	870 vs	873 vs	871 vs	871 vs	876 vs
822 m	823 m	848 m	849 m	849 m	848 m	848 m	848 m	856 m
810 m, sh	795 vs, sh	811 w	812 m	812 m	811 m	811 w	811 w	812 m
743 vs	744 vs	740 s	737s	–	–	739 w	737 s	–
546 s	547 s	597 vw	597 vw	597 vw	602 vw	597 vw	597 vw	597 vw
432 m	432 m	456 m	458 m	458 m	457 m	456 m	456 m	454 m
404 w	404 m	401 w	403 w	403 w	415 w	401 w	401 w	403 w

vs: very strong, s: strong, m = medium, w: weak, vw: very weak, and sh: shoulder; cl-bn = chlorobenzene, 1,2cl-bn = 1,2-dichlorobenzene, 1,3cl-bn = 1,3-dichlorobenzene, 1,4cl-bn = 1,4-dichlorobenzene.
*Taken from Ref. [15].

Table 6. The vibrational wavenumbers (cm^{-1}) of chlorobenzene in the $ML_2Ni(CN)_4$ 0.5G (M=Co, Ni or Cu; G = chlorobenzene; L = piperidine) clathrates

Assignment[a,b]	Gas chlorobenzene[a,b]	Liquid chlorobenzene[a]	Co chlorobenzene	Ni chlorobenzene	Cu chlorobenzene
ν_{20b} ν(CH), B_2	3096	–	3090 vw	3090 vw	3093 vw
ν_{20a} ν(CH), A_1	3082	3085 s	3079 vw	3077 vw	3079 vw
ν_{7b} ν(CH), B_2	3067	3070 vs	3069 vw	3069 vw	3069 vw
ν_2 ν(CH), A_1	3054	3059 s	3050 vw	3052 vw	3050 vw
ν_{13} ν(CH), A_1	3031	3027 m	3019 vw	3020 vw	3022 vw
ν_{8b} ν(CC), B_2	1598	1591 m, sh	1581 m	1581 m	1582 m
ν_{8a} ν(CC), A_1	1586	1584 vs	1569 vw	1577 vw	1579 vw
ν_{19a} ν(CC), A_1	1483	1477 vs	1476 vs	1476 vs	1470 vs
ν_{19b} ν(CC), B_2	1448	1445 vs	–	1445 m, sh	1444 vw
ν_{14} ν(CC), B_2	1326	1325 m	1309 vw	1309 vw	1313 w
ν_3 δ_t(CH), B_2	1271	1273 m	–	–	–
ν_{9a} δ_t(CH), A_1	1153	1157 m	1125 w	1125 w	–
ν_{7a} X-sens., A_1	1092	1083 vs	1084m	1082 s	1082 m
ν_{15} δ_t(CH), B_2	1068	1068 s	1066 vw	1066 vw	1066 vw
ν_{18a} δ_t(CH), A1	1025	1022 vs	–	–	–
ν_1 ring stretch	1003	1002 s	1001 vw	1001vw	–
ν_5 γ(CH), B_1	981	983 vw	–	–	–
ν_{17a} γ(CH), A_2	961	965 vw	–	–	–
ν_{17b} γ(CH), B_1	902	903 s	907 vw	907 vw	907 vw
ν_{10a} γ(CH), A_2	831	830 w	835 vw	835 vw	835 vw
ν_{10} γ(CH), B_1	741	745 vs	749 vs	750 vs	756 vs
ν_{12} X-sens., A_1	706	702 s	701 m	701 m	703 s
ν_4 γ(CC), B_1	685	685 vs	687 m	687 m	689 m
ν_{6b} Ring	615	614 w	–	–	–
ν_{16b} X-sens., B_1	467	468 vs	467 w	468 w	472 m
ν_{6a} X-sens., A_1	417	418 m	–	–	–

vs: very strong, s: strong, m = medium, w: weak, vw: very weak, and sh: shoulder.
[a] Taken From Ref. [21]. [b] Taken From Ref [22].

Table 7. The vibrational wavenumbers (cm^{-1}) of 1,2-dichlorobenzene in the $ML_2Ni(CN)_4$ 0.5G (M=Co, Ni or Cu; G = 1,2-dichlorobenzene; L = piperidine) clathrates

Assignment[a]	1,2-dichlorobenzene CCl_4 and CS_2 solution[a]	Liquid 1,2-dichlorobenzene[b]	Co 1,2-Cl-Bz	Ni 1,2-Cl-Bz	Cu 1,2-Cl-Bz
ν(CH), A_1	3072	3072	3067 vw	3062 w	3058 vw
ν(CC), A_1	1576	1576	1574 vs	1573 vs	1587 vs
ν(CC), A_1	1458	1458	–	–	–
ν(CC), B_2	1438	1438	1434 m	1436 s	1435 m
ν(CC), A_1	1276	–	1274 w	1272 w	1273 w
β(CH), B_2	1252	1252	1252 w	1251 w	1252 w
X-sens, A_1	1159	1155	–	–	–
X-sens, B_2	1129	1130	1128 vs	1128 s	1124 m
β(CH), B_2	1038	1038	1037 s	1036 vs	1036 s
γ(CH), A_2	975	975	972 w, sh	973 w, sh	969 w, sh
γ(CH), B_1	940	940	–	–	–
γ(CH), A_2	850	850	–	–	–
γ(CH), B_1	748	748	748 vs	760 vs	759 vs
X-sens, A_1	660	660	660s	660 s	659 s
X-sens, A_1	480	480	486 vw	485 vw	484 vw
ϕ(CC), B_1	435	435	–	–	425 s
X-sens, B_2	427	427	–	419 vw	411 vw

vs: very strong, s: strong, m = medium, w: weak, vw: very weak, and sh: shoulder.
[a] Taken From Ref. [25].
[b] Taken From Ref. [23]. 1,2-Cl-Bz=1,2-dichlorobenzene.

Table 8. The vibrational wavenumbers (cm^{-1}) of 1,3-dichlorobenzene in $ML_2Ni(CN)_4$ 0.5G (M=Co, Ni or Cu; G = 1,3-dichlorobenzene; L = piperidine) clathrates

Assignment[a]	1,3-dichlorobenzene CCl_4 and CS_2 solution[a]	Liquid 1,3-dichlorobenzene[b]	Co 1,3-Cl-Bz	Ni 1,3-Cl-Bz	Cu 1,3-Cl-Bz
ν(CH), B_2	3095	–	3071 vw	3084 vw	3084 w
ν(CH), A_1	3074	3071	3068 w	3067 w	3060 w
ν(CC), A_1	1580	1580	1577 vs	1577 vs	1577 vs
ν(CC), B_2	1464	1464	–	–	–
ν(CC), A_1	1412	1412	1413 m	1413 m	1405 m
β(CH), B_2	1330	–	–	–	–
β(CH), B_2	1258	1258	1255 w	1255 w	1255 w
X-sens, B_2	1161	1161	1164m	1162 m	1162 m
X-sens, A_1	1127	1127	1124 m	1124 m	1122 m
β(CH), B_2	1079	1079	–	–	–
β(CH), A_1	1000	–	1005 w	1005 s	1003 s
γ(CH), B_1	966	966	–	–	996 m, sh
γ(CH), A_2	896	896	891 w	893 w	894 w
γ(CH), B_1	869	–	–	–	–
X-sens, B_2	784	784	783 vs	782 vs	–
γ(CH), B_1	775	775	773 s	774 s	781 vs
γ(CH), B_1	674	–	676 s	675 s	675 m
X-sens, A_1	663	663	662 w	664 w	668 w
X-sens, A_1	428	428	425 w	–	425 s

vs: very strong, s: strong, m: medium, w: weak, vw: very weak, and sh: shoulder.
[a]Taken From Ref. [25].
[b]Taken From Ref. [24]. 1,3-Cl-Bz: 1,3-dichlorobenzene.

frequency on complex formation which has been explained as a weakening of the N–H bond resulting from the electron drainage from the nitrogen atom on account of its coordination to the metal atom [20].

Vibrations of guest molecules

The assignments and the wavenumbers of the bands arising from the guest molecules observed in the IR spectra of $M(piperidine)_2Ni(CN)_4.0.5G$ (M=Co, Ni or Cu; G = chlorobenzene, 1,2-dichlorobenzene or 1,3-dichlorobenzene; M=Co or Ni G = 1,4-dichlorobenzene) compounds are given in Tables 6–9, respectively, together with the wavenumbers of the liquid guest molecule on which the assignments are based. The assignment of the guest molecule wavenumbers in the IR spectra of the clathrate compounds were based on the studies of Bist *et al.* [21], Jain and Bist [22], Green [23, 24] and Scherer *et al.* [25], respectively.

Our assignment of the guest molecule bands in the IR spectra of clathrates agrees with that of the literature [21–25]. The infrared spectral data of the compounds under study suggest that the guest molecules retain the free molecule symmetry.

The most notable spectral feature which merits comment is the following : the CH out-of-plane vibrational bands of the guest molecules are found to be shifted to higher frequencies (Tables 6–9) than those of the guest molecules in solutions. Similar positive frequency shifts were observed for Hofmann-type clathrates [4] and explained by the presence of a weak hydrogen bond between π-electrons located above and below the plane of the benzene ring and the ligand molecules of the host lattice. Some excellent theoretical discussions on the host-guest interactions in the Hofmann clathrates $Ni(NH_3)_2Ni(CN)_4.2G$ (G = benzene, pyrrole, aniline) were given by Ruiz *et al.* [26–27]. Therefore, we may reasonably suggest that the frequency shifts in our clathrates are due to the π-electron donation from the benzene ring

Table 9. The vibrational wavenumbers (cm^{-1}) of 1,4-dichlorobenzene in the $ML_2Ni(CN)_4$ 0.5G (M=Co or Ni; G = 1,4-dichlorobenzene; L = piperidine) clathrates

Assignment^a	1,4-dichloro-benzene^b	Co 1,4-dichloro-benzene	Ni 1,4-dichloro-benzene
ν(CH), B_{2u}	3087	3087 vw	3088 vw
ν(CH), B_1u	3078	3071 vw	3073 vw
ν(CC), B_{1u}	1477	1476 s	1475 s
ν(CC), B_2u	1394	1395 m	1392 m
α((CCC), B_{2u}	1220	1222 vw	1223 vw
β(CH), B_{2u}	1107	1100 w, sh	1102 w, sh
X-sens., B_{1u}	1090	–	–
β(CH), B_{1u}	1015	1013 m, sh	1013 m, sh
γ(CH), A_u	951	963 m	957 m
γ(CH), B_{2g}	934	–	–
γ(CH), B_{3u}	819	818 m	818 s
X-sens., B_{2g}	–	669 w	669 vw
X-sens., B_{1u}	550	548 m	548 m
ϕ(CC), B_{3u}	485	484 m	487 m
ϕ(CC), A_u	405	–	–

vs: very strong, s: strong, m = medium, w: weak, vw: very weak, and sh: shoulder.
[a] Taken From Ref. [25].
[b] Taken From Ref. [24].

to the hydrogen atoms of the piperidine which has a more electrophilic character caused by the coordination.

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