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Investigation of host–guest interactions in the Hofmann-dabn-type clathrates: M(1,4-diaminobutane)Ni(CN)$_4$·1.5G (M = Co or Ni, G = benzene derivatives)

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Abstract

Infrared spectra of M(1,4-diaminobutane)Ni(CN)$_4$·1.5G (M = Co or Ni; G = chlorobenzene, *m*-xylene, or *p*-xylene) are reported. The spectral data suggest that the compounds are similar in host structure to that of Hofmann-type clathrates M(1,4-diaminobutane)Ni(CN)$_4$·1.5C$_6$H$_6$ (M = Mn, Fe, Co, Ni or Cd). © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Hofmann-type clathrates; Tetracyanonickelate; 1,4-diaminobutane; Infrared spectra; Benzene derivatives

1. Introduction

Hofmann-α,ω-diaminoalkane-type hosts have been developed from the Hofmann-type host lattice, Cd(NH$_3$)$_2$Ni(CN)$_4$, by replacing the pair of ammine ligands by the bifunctional α,ω-diaminoalkane ligands, with the aim of enlarging the range of guest molecules which can be accommodated in the host lattices [1–5].

In our previous papers [6–8], the infrared (IR) spectra of the Hofmann-diam-type clathrates showed that their host structures consist of corrugated polymeric layers of {M–Ni(CN)$_4$}$_\infty$ with the diam molecules bound to the metal (M), similar to the host framework of Hofmann-type clathrates [6–10].

In this work, we report IR spectra of newly prepared M(1,4-diaminobutane)Ni(CN)$_4$·1.5G (M = Co or Ni; G = chlorobenzene, *m*-xylene, *p*-xylene) (abbr. M–Ni–G or, M–Ni–Cl, M–Ni–*m*Xy, M–Ni–*p*Xy, respectively) compounds. The IR spectral features of the M–Ni–G compounds are correlated with those of Hofmann-type M(1,4-diaminobutane)-Ni(CN)$_4$·1.5C$_6$H$_6$ (M = Mn, Fe, Co, Ni or Cd) clathrates [6].

2. Experimental

The compound(s) M–Ni–G was (were) prepared as follows: K$_2$Ni(CN)$_4$ (1 mmol) and MCl$_2$ (1 mmol) in solution were mixed with water saturated with the G guest molecule followed by the addition of 1,4-diaminobutane (slightly more than 1 mmol). IR spectra of the compounds as mulls in Nujol and KBr discs were recorded in the range of 4000–400 cm^{-1} on MATTSON 1000 FTIR spectrometer. The freshly

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Table 1
The vibrational wave numbers (cm^{-1}) of 1,4-diaminobutane (dabn) in the M–Ni–G compounds (v = very, s = strong, m = medium, w = weak, br = broad)

Assignment[a]	Liquid dabn[a]	Co–Ni–Bz [a,b]	Ni–Ni–Bz [a,c]	Co–Ni–Cl	Ni–Ni–Cl	Co–Ni–*m*Xy	Ni–Ni–*m*Xy	Co–Ni–*p*Xy	Ni–Ni–*p*Xy
$\nu(NH_2)$	3346s	3354s	3356s	3356s	3357s	3349s	3351s	3352s	3354s
$\nu(NH_2)$	3280s	3291s	3294s	3294s	3295s	3291s	3293s	3294s	3294s
$\nu(CH_2)$	—	2953s	2950s	2953m	2954m	2952m	2954m	2953m	2957m
$\nu(CH_2)$	2926vs	2914s	2912m	2921m	2923m	2918m	2918m	2919m	2920m
$\nu(CH_2)$	—	2887s	2879m	2887m	2889m	2886m	2887m	2882m	2882m
$\nu(CH_2)$	2853vs	2854s	2830s	2852m	2853m	2855m	2855m	2856m	2858m
$\delta(NH_2)$	1606s	1591m	1587w	1591s	1593s	1588s	1588s	1590s	1590s
$\delta(NH_2)$	1497s	1462m	1460m	1462m	1462m	1467m	1467w	1469w	1469w
$\rho_w(CH_2)$	1390w	1378vw	1377w	1384vw	1385vw	1378vw	1378vw	1379vw	1379vw
$\rho_w(CH_2)$	1353vw	1364vw	1366vw	1368vw	1368vw	1363vw	1364vw	1363vw	1362vw
$\rho_t(CH_2)$	1309vw	—	1315vw	1315vw	1316vw	1312vw	1312vw	1310vw	1310vw
$\delta_t(NH_2)$	1145vw	1167vw	1170w	1169vw	1170vw	1171vw	1171vw	1173vw	1180vw
$\nu(CN)$	1070m	—	1068vw	1068w	1069w	1068w	1068w	1068w	1068w
$\nu(CN)$	—	1055mw	1057m	1055m	1055m	1055w	1053m	1057m	1057m
$\rho_w(NH_2)$	954w	1002mw	1010m	1001s	1007s	1019m	1021m	1020w	1021vw
$\rho_w(NH_2)$	—	944vw	945vw	941vw	944vw	936vw	937vw	923vw	923vw
$\rho_r(CH_2) + \rho_w(NH_2)$	878m,br	910vw	910vw	909vw	912vw	918vw	919vw	—	—
$\rho_r(CH_2)$	863m,br	—	—	—	—	—	—	852vw	852vw
$\rho_r(CH_2)$	738w	743vw	742vw	740vvw	740w	741w	741vw	741vw	741vw

[a] Taken from Ref. [6].
[b] Co(1,4-diaminobutane)$Ni(CN)_4 \cdot 1.5\ C_6H_6$.
[c] Ni(1,4-diaminobutane)$Ni(CN)_4 \cdot 1.5\ C_6H_6$.

Table 2
The vibrational wave numbers (cm^{-1}) of cyanide group for the M–Ni–G compounds (M = Co or Ni; G = chlorobenzene, *m*-xylene, or *p*-xylene) (v = very, s = strong, m = medium, w = weak)

Assignment[a]	$N_{a2}Ni(CN)_4$[a]	Co–Ni–Bz[b,c]	Ni–Ni–Bz[b,d]	Co–Ni–Cl	Ni–Ni–Cl	Co–Ni–*m*Xy	Ni–Ni–*m*Xy	Co–Ni–*p*Xy	Ni–Ni–*p*Xy
ν_8 (CN), E_u	2132	2164vs	2169vs	2164vs	2169vs	2161vs	2166vs	2161vs	2166vs
	2128	—	—	—	—	—	—	—	—
Hot band?	—	2127vw	2129vw	2124vw	2127vw	2123vw	2126vw	2124vw	2127vw
ν_9 (NiC), E_u	543	554s	579s	554s	579s	552s	575s	550s	573s
π (NiC), A_{2u}	448	453vw	457vw	453vw	456vw	456vw	458vw	457vw	457vw
δ (NiCN), E_u	433	437s	440s	437s	440s	435s	439s	435s	440s
	421	—	—	420vw	420vw	419vw	420vw	419vw	419vw

[a] Taken from Ref. [11].
[b] Taken from Ref. [6].
[c] Co(1,4-diaminobutane)$Ni(CN)_4 \cdot 1.5C_6H_6$.
[d] Ni(1,4-diaminobutane)$Ni(CN)_4 \cdot 1.5C_6H_6$.

Table 3
The vibrational wave numbers (cm^{-1}) of chlorobenzene in the M–Ni–Cl (M = Co or Ni) compounds (v = very, s = strong, m = medium, w = weak, sh = shoulder)

Assignment[a]	Liquid chlorobenzene[b]	Co–Ni–G[b,c]	Ni–Ni–G[b,d]	Co–Ni–Cl	Ni–Ni–Cl
ν(CH), A_1	3087w,sh	—	3087vw	3086vw	3086vw
ν(CH), B_2	3072s	3078vw	3070vw	—	—
ν(CH), A_1	3060w,sh	—	—	3064vw	3064vw
ν(CH), A_1	3030w,sh	—	3032vw	—	—
ν(CH), B_1	3006w	—	—	—	—
ν(CC), B_2	1586s	1580w,sh	—	1580m	1580m
ν(CC), A_1	1571w,sh	1560vw	1562w,sh	1559vw	1559vw
ν(CC), A_1	1479vs	1479w	1477w	1474m	1477m
ν(CC), B_2	1447s	1444vw	1444vw	1443m	1443m
β(CH), A_1	1123w	—	—	—	—
β(CH), B_2	1084s	1081w	1082w	1080w	1080w
β(CH), B_2	1069vw	—	—	—	—
β(CH), A_1	1023m	1021w	1022vw	1018vw	1018vw
γ(CH), B_1	1003vw	1002vw,sh	—	—	—
γ(CH), B_1	902vw	907vw	—	—	—
γ(CH), B_1	741vs	749s	748s	749s	749s
δ(ring), B_1	702s	701m	702m	701s	701s
δ(ring), B_2	687s	688m	685m	688m	688m
δ(ring), B_1	471m	470w	469w	472vw	473vw

[a] Taken From Ref. [12].
[b] Taken From Ref. [7].
[c] Co(1,8-diaminooctane)$Ni(CN)_4$·chlorobenzene
[d] Ni(1,8-diaminooctane)$Ni(CN)_4$·chlorobenzene.

prepared compounds were analyzed for C, H and N and the following results (found %/calculated %) were obtained:

$Co(C_4H_{12}N_2)Ni(CN)_4 \cdot 1.5C_6H_5Cl$
C = 42.10/42.65, H = 3.95/4.11, N = 17.71/17.55;
$Ni(C_4H_{12}N_2)Ni(CN)_4 \cdot 1.5C_6H_5Cl$
C = 42.63/42.67, H = 4.02/4.11, N = 17.88/17.56;
$Co(C_4H_{12}N_2)Ni(CN)_4 \cdot 1.5p\text{-}C_8H_{10}$
C = 51.20/51.21, H = 5.73/5.80, N = 18.12/17.91;
$Ni(C_4H_{12}N_2)Ni(CN)_4 \cdot 1.5p\text{-}C_8H_{10}$
C = 50.08/51.23, H = 5.65/5.80, N = 18.22/17.92;
$Co(C_4H_{12}N_2)Ni(CN)_4 \cdot 1.5m\text{-}C_8H_{10}$
C = 50.98/51.21, H = 5.51/5.80, N = 18.03/17.91;
$Ni(C_4H_{12}N_2)Ni(CN)_4 \cdot 1.5m\text{-}C_8H_{10}$
C = 51.11/51.23, H = 4.90/5.80, N = 18.10/17.92.

These analytical results are poor for the samples obtainable in powder form because of partial decomposition. Such instabilities have been reported for clathrates having low boiling guest molecules [9].

3. Results and discussion

The IR spectra of the compounds M–Ni–G (M = Co or Ni, G = chlorobenzene, *m*-xylene, or *p*-xylene) are very similar, suggesting that they also have similar structural features and the degrees of the interactions of the guest molecules, 1,4-diaminobutane (dabn) ligand and the $Ni(CN)_4$ species with their surroundings are almost the same for each compound. Thus, it may be most convenient to divide the vibrations into three groups arising from the dabn ligands, from the $Ni(CN)_4$ units and from the guest moieties, respectively. The vibrational wave numbers of the bands in the spectra of these species are recorded in Tables 1–5, respectively, together with some relevant spectral data for comparison.

The bands observed in the range 3349–3291 cm^{-1} (Table 1) assigned to the NH_2 symmetric and asymmetric stretching frequencies which are lower than the corresponding values of the free dabn molecule are characteristic of coordinated $-NH_2$ groups. The absence of splitting of these bands indicate that ligands are bonded in a bidentate manner.

Table 4
The vibrational wave numbers (cm^{-1}) of *m*-xylene in the M–Ni–*m*Xy (M = Co or Ni) compounds (v = very, s = strong, m = medium, w = weak, sh = shoulder)

Assignment[a]	*m*-Xylene[a]	Co–Ni–G[b,c]	Ni–Ni–G[b,d]	Co–Ni–*m*Xy	Ni–Ni–*m*Xy
ν(CH), B_2	3052	—	—	—	—
ν(CH), A_1	3032	—	—	3024vw	3019vw
ν(CC), B_2	1613	1619w	1620vw	1623vw	1621vw
ν(CC), A_1	1595	1596vw	1600w,sh	1606w	1606w
ν(CC), B_2	1492	1495vw	1496w,sh	1487w	1487w
ν(CC), A_1	1460	1460vw	1464m	1459w	1460w
β(CH), B_2	1303	1306vw	1309vw	1308vw	1309vw
α(CCC), B_2	1264	1276vw	1277vw	1287vw	1286vw
X-sens, A_1	1252	1250vw	1250vw	—	—
β(CH), B_2	1167	1168vw	—	1160vw	1161vw
X-sens, B_2	1154	1153vw	1155vw	1137w	1138w
β(CH), A_1	1094	1090vw	1093vw	1093vw	1098vw
γ(CH), B_1	968	960vw	966vw	—	—
X-sens, B_2	905	—	—	906vw	906vw
γ(CH), B_1	876	—	—	—	—
γ(CH), B_1	768	769vw	771vw	769w	769w
X-sens, A_1	724	—	—	—	—
π(CC), B_1	690	696w	684vw	696w	696w
X-sens, A_1	537	—	—	—	—
X-sens, B_2	515	521vw	522vw	517vw	515vw
π(CC), B_1	433	—	—	—	—
X-sens, B_2	404	—	—	—	—

[a] Taken From Ref. [13].
[b] Taken From Ref. [8].
[c] Co(1,7-diaminoheptane)$Ni(CN)_4$·*m*-xylene.
[d] Ni(1,7-diaminoheptane)$Ni(CN)_4$·*m*-xylene.

The bands of the $Ni(CN)_4^{2-}$ ion in the compounds under study were assigned on the basis of the work of McCullough et al. who presented vibrational data for the ion $Ni(CN)_4^{2-}$ in $Na_2Ni(CN)_4$ [11]. If the unit cell has D_{4h} symmetry, only four fundamental vibrations are expected in the spectrum above 400 cm^{-1} [6–10]. Four fundamental bands are assigned in the IR spectra of the compounds (Table 2). The characteristic frequencies of the $Ni(CN)_4$ group are found to be similar to those of the Hofmann-type clathrates suggesting that coordination about the Ni atom is square planar and $\{M–Ni(CN)_4\}_\infty$ (M = Co or Ni) layers have been preserved.

The assignments and the wave numbers of the bands arising from the guest G molecule (G = chlorobenzene, *m*-xylene, or *p*-xylene) in the IR spectra of our compounds are given in Tables 3–5 respectively, together with the wave numbers of the free guest molecule on which the assignments are based. The assignment of the bands of guest molecules in the IR spectra of the clathrate compounds were based on the studies of Steele and Lippincott [12], and Green [13,14]. We assigned the chlorobenzene bands in the spectra of the clathrates by comparing with the assignment of the C_6H_5F molecule in the work of Steele and Lippincott [12]. Our spectra are found to be very similar in frequency and band pattern to the spectra given by Steele and Lippincott [12], and Green [13,14]. These comparisons show that D_{2h} and C_{2v} symmetries are preserved for chlorobenzene and *p*-xylene, and *m*-xylene molecules in clathrates, respectively.

The preceding discussion considered together leads us to the conclusion that the compounds studied are similar in structure to the Hofmann-dabn-type clathrates M(1,4-diaminobutane) $Ni(CN)_4$·$1.5C_6H_6$ (M = Mn, Fe, Co, Ni or Cd) [6]. The decrease in the number of G molecules from 2 in Hofmann-type [6,7,10] and

Table 5
The vibrational wave numbers (cm^{-1}) of *p*-xylene in the M–Ni–*p*Xy (M = Co or Ni) compounds (v = very, s = strong, m = medium, w = weak, sh = shoulder)

Assignment[a]	*p*-Xylene[a]	Co–Ni–G[b,c]	Ni–Ni–G[b,d]	Co–Ni–*p*Xy	Ni–Ni–*p*Xy
ν(CH), B_{1u}	3044	—	—	3039vw	3038vw
ν(CH), B_{2u}	3017	3018vw	3018vw	3012vw	3013vw
$\nu(CH_3)$, B_{2u}	2975	2985w	2989w	2992vw	2992vw
	2947	—	—	2941vw	2942vw
$\nu(CH_3)$, B_{3u}	2923	—	—	2923vw	2924vw
ν(CC), B_{1u}	1529	1516w	1516w	1515w	1515w
$\delta(CH_3)$, B_{3u}	1458	1475w,sh	1477w,sh	1458m	1458m
	1452	—	—	1448vw	1449vw
ν(CC), B_{2u}	1421	1435vw	1436vw	1437vw	1438vw
$\delta(CH_3)$, B_{1u}	1379	—	—	—	—
α(CCC), B_{2u}	1324	—	—	—	—
X-sens, B_{2u}	1220	—	—	1220vw	1220vw
β(CH), B_{2u}	1120	1119vw	1119vw	1121w	1121w
r(CH_3), B_{2u}	1041	1049m	1049m	—	—
β(CH), B_{1u}	1023	1022vw	1022vw	1020w	1020w
γCH), B_{3u}	795	796s	795s	806s	806s
X-sens, B_{1u}	725	729m	729m	—	—
ϕ(CC), B_{3u}	483	484w	484w	489w	489w

[a] Taken from Ref. [14].
[b] Taken from Ref. [7].
[c] Co(1,8-diaminooctane)$Ni(CN)_4$·*p*-xylene.
[d] Ni(1,8-diaminooctane)$Ni(CN)_4$·*p*-xylene.

Hofmann-T_d-type [15] clathrates to 1.5 in the compounds studied is due to the fact that one of the four cavity units is occupied by the dabn ligands, and the other three cavity units of the host are occupied by the guest molecules. Host–guest interactions in the clathrate structure are not effective because of the bulkiness of dabn ligand molecules.

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