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Infrared and Raman spectroscopic study of the Hofmann-type clathrates M(1,7-diaminoheptane)Ni(CN)$_4$·G (M = Ni or Co; G = chlorobenzene, *m*-xylene or naphthalene)

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Abstract

Two new Hofmann-diaminoheptane-type clathrates of the form M(1,7-diaminoheptane) Ni(CN)$_4$·G (M = Ni or Co; G = chlorobenzene, *m*-xylene or naphthalene) have been prepared in powder form. Their spectral data were compared with those of the corresponding host. Their structure consists of corrugated polymeric layers of $\{M–Ni(CN)_4\}_\infty$ with the 1,7-diaminoheptane molecules bound directly to the metal (M). © 1997 Elsevier Science B.V.

Keywords: Hofmann-type clathrates; Infrared spectroscopy; Raman spectroscopy

1. Introduction

Recently, Hofmann-α,ω-diaminoalkane-type hosts have been developed from the Hofmann-type host lattice $Cd(NH_3)_2Ni(CN)_4$ by replacing the pair of ammine ligands by the α,ω-diaminoalkane ligands behaving ambidently, with the aim of enlarging the range of guest molecules which can be accommodated in the host lattices [1–5]. In this work we report the infrared spectra of M(dahp)Ni(CN)$_4$·G (M = Ni or Co; dahp = 1,7-diaminoheptane; G = chlorobenzene, *m*-xylene or naphthalene) (abbreviated to M–Ni–G) compounds and the Raman spectra of Ni(dahp)-Ni(CN)$_4$·G compounds for the first time. We also report the infrared spectra of Cd(dahp)Ni(CN)$_4$·G compounds for comparison. The Raman spectra of the compound with M = Co could not to be obtained by using the 488 or 515 nm laser line. We have given in detail the infrared wavenumbers of the dahp molecule relative to its density and to the presence of the different transition metals.

2. Experimental

The compounds M(dahp)Ni(CN)$_4$·G (M = Ni, Co or Cd; G = chlorobenzene, *m*-xylene or naphthalene) were prepared by adding slightly more than 1 mmol of 1,7-diaminoheptane to 1 mmol of $K_2Ni(CN)_4$ and 1 mmol of MCl_2 solution in water saturated with the guest molecule. Infrared spectra of the compounds as mulls in Nujol and as KBr discs were recorded in the range 4000 to 400 cm^{-1} on a MATTSON 1000 FTIR spectrometer. The Raman spectra were recorded on a Jobin-Yvon U1000 spectrometer using the 514.5

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Table 1
The vibrational wavenumbers (cm^{-1}) of 1,7-diaminoheptane (dahp) in the M–Ni–G compounds

Assignment[a]	Liquid dahp[b]	Co–Ni–G G = Chlorobenzene	Ni–Ni–G G = Chlorobenzene	Cd–Ni–G G = Chlorobenzene	Co–Ni–G G = *m*-Xylene
ν (NH_2)	3367s	3365s	3363s	3338s	3366s
ν (NH_2)	3288s	3292m	3300m	3293m	3297m
ν (CH_2)	2927vs	2920vs	2924vs	2926vs	2922vs
ν (CH_2)	2854vs	2852vs	2852vs	2856vs	2854vs
δ (NH_2)	1598s	1583m	1585m	1583m	1585m
δ (CH_2)	1464s	1464m	1464m	1468m	1474m,sh
δ (CH_2)	1439w	1439vw	1439vw	–	1437m
ρ_w (CH_2)	1390w	1394vw	1394vw	1398vw	1396vw
ρ_w (CH_2)	1371w	1369vw	1369vw	1378vw	1367vw
ρ_t (CH_2)	1356vw	1354vw	1353vw	1352vw	–
ρ_t (NH_2)	1308vw	1308vw	1306vw	1306vw	–
ν (CN)	1093w	–	1093vw	1101vw	1082vw
ν (CN)	1072m	–	–	1072vw	1076vw
ρ_w (NH_2)	1016vw	993m	1001m	982m	997m
ρ_r (CH_2)	954s,sh	957m	960m	958m	956w
ρ_r (CH_2)	840m,br	865w	868w	860w	870w
ρ_r (CH_2)	725w	729w	727w	725w	725w

Assignment[a]	Ni–Ni–G G = *m*-Xylene	Cd–Ni–G G = *m*-Xylene	Co–Ni–G G = Naphthalene	Ni–Ni–G G = Naphthalene	Cd–Ni–G G = Naphthalene
ν (NH_2)	3365s	3338s	3357s	3357s	3338s
ν (NH_2)	3305m	3292m	3289s	3298s	3282s
ν (CH_2)	2920vs	2926vs	2926vs	2924vs	2926vs
ν (CH_2)	2852vs	2856vs	2854vs	2854vs	2856vs
δ (NH_2)	1583m	1585m	1587s	1587s	1583s
δ (CH_2)	1475w,sh	1472w,sh	1468m	1466m	1470m
δ (CH_2)	1439w	1439w	1439w	1440w	1437w
ρ_w (CH_2)	1394vw	1392vw	–	–	–
ρ_w (CH_2)	1367vw	1378vw	–	–	1377vw
ρ_t (CH_2)	1354vw	1355vw	1363vw	1365vw	1354vw
ρ_t (NH_2)	–	1317vw	–	–	–
ν (CN)	1089vw	1099vw	–	–	–
ν (CN)	1078vw	–	1078vw	1078w	1076vw
ρ_w (NH_2)	1001m	982m	1008m	1008m	1007m
ρ_r (CH_2)	955w	957w	995w	997w	968w
ρ_r (CH_2)	871w	860w	865vw	862vw	862vw
ρ_r (CH_2)	725w	725vw	725w	727w	727w

[a] Taken from [6].
[b] The solution in CCl_4.
v = very, s = strong, m = medium, w = weak, br = broad, sh = shoulder.

or 488 nm line of a Spectra-Physics Model 2016-Ar^+ ion laser. The freshly prepared compounds were analyzed for C, H and N by a LECO CHNS-932 analyzer. The results are as follows (% found/% calculated):

$Ni(C_7H_{18}N_2)Ni(CN)_4{\cdot}C_6H_5Cl$: C = 42.83/43.97, H = 4.70/4.99, N = 17.83/18.10;

$Co(C_7H_{18}N_2)Ni(CN)_4{\cdot}C_6H_5Cl$: C = 43.04/43.95, H = 4.54/4.99, N = 18.55/19.09;

$Ni(C_7H_{18}N_2)Ni(CN)_4{\cdot}C_8H_{10}$: C = 49.12/49.84, H = 5.91/6.16, N = 18.03/18.35;

$Co(C_7H_{18}N_2)Ni(CN)_4{\cdot}C_8H_{10}$: C = 49.07/49.81, H = 5.54/6.16, N = 18.44/18.34;

$Ni(C_7H_{18}N_2)Ni(CN)_4{\cdot}C_{10}H_8$: C = 52.04/52.56, H = 5.54/5.46, N = 17.10/17.51;

$Co(C_7H_{18}N_2)Ni(CN)_4{\cdot}C_{10}H_8$: C = 52.52/52.54, H = 5.65/5.46, N = 16.98/17.50.

3. Results and discussion

The infrared spectra of the compounds M–Ni–G (M = Ni, Co or Cd) are very similar. The similarities between the infrared and Raman spectral features of the compounds suggest that they also have similar structural features and the degrees of interaction of the guest molecules, dahp ligand and $Ni(CN)_4$ species with their surroundings are almost the same for each compound. It may be most convenient to divide the vibrations into three groups arising from the dahp ligands, from the $Ni(CN)_4$ units and from the guest moieties, respectively. The vibrational wavenumbers of the bands in the spectra of these species are given in Tables 1–5, respectively, together with some relevant spectral data for comparison.

To the best of our knowledge no complete vibrational assignment has been reported for the free dahp molecule. The assignments and the wavenumbers of the vibrational bands of the dahp molecule observed in the spectra of the compounds under study are given in Table 1 together with the spectral data for the dahp molecule in the liquid phase and in solution in CCl_4 on which the assignments are based. Some vibration bands of dahp show shifts up or down when compared to the same vibrations in the pure ligand. These shifts can be explained by the consecutive inductive effect [12]. Similar observations were also reported for ethylenediamine [13] and trimethylenediamine [12] clathrates. The NH_2 stretching frequencies which are lower than the corresponding values of the free dahp molecule (in Table 1) show that the ligand molecules are bound directly to the metal M (M = Co, Ni or Cd). Based on the present spectral data it is not possible to

Table 2
The vibrational wavenumbers (cm^{-1}) of the cyanide group for the M–Ni–G compounds[a]

Assignment[b]	$Na_2Ni(CN)_4$[b]	Cd–Ni–Bz[c,d]	Co–Ni–G G = Chlorobenzene	Ni–Ni–G G = Chlorobenzene	Cd–Ni–G G = Chlorobenzene	Co–Ni–G G = *m*-Xylene
ν_1 (CN), A_{1g}	–	–	–	(2185s)	–	–
ν_4 (CN), B_{1g}	–	–	–	(2173m)	–	–
ν_8 (CN), E_u	2132	2156vs	2160vs	2166vs	2139vs	2164vs
	2128	–	–	–	–	
ν_9 (NiC), E_u	543	554m,br	567m	580m	551m	565m
ν_9 (NiC), E_u	–	–	555w	553w	536w	555w
π(NiC), A_{2u}	448	446vw	457vw	457vw	447vw	460vw
δ(NiCN), E_u	433	425vs	436vs	439s	422s	445s

Assignment[b]	Ni–Ni–G G = *m*-Xylene	Cd–Ni–G G = *m*-Xylene	Co–Ni–G G = Naphthalene	Ni–Ni–G G = Naphthalene	Cd–Ni–G G = Naphthalene
ν_1 (CN), A_{1g}	(2186s)	–	–	(2186s)	–
ν_4 (CN), B_{1g}	(2177m)	–	–	(2175m)	–
ν_8 (CN), E_u	2165vs	2140vs	2160vs	2166vs	2146vs
	–	–	–	–	–
ν_9 (NiC), E_u	565m	542m	557m	578m	538m
ν_9 (NiC), E_u	555w	–	–	–	–
π (NiC), A_{2u}	457vw	–	455vw	457vw	–
δ (NiCN), E_u	440s	422s	438s	440s	422s

[a] Raman bands in parentheses.
[b] Taken from [7].
[c] $Cd(NH_3)_2Ni(CN)_4{\cdot}2C_6H_6$.
[d] Taken from [8].
v = very, s = strong, m = medium, w = weak, br = broad.

Table 3
The vibrational wavenumbers (cm^{-1}) of chlorobenzene in the M–Ni–G compounds (M = Co, Ni or Cd; G = chlorobenzene)

Assignment[a]	Liquidchlorobenzene	Co–Ni–G	Ni–Ni–G	Cd–Ni–G
ν (CH), A_1	3087w,sh	3091vw	3088vw	3080vw
ν (CH), B_2	3072s	–	–	3076vw
ν (CH), A_1	3060w,sh	–	–	–
ν (CH), A_1	3030w,sh	–	3026vw	3028vw
ν (CH), B_1	3006w	3005vw	–	–
ν (CC), B_2	1586s	1586vw,sh	–	–
ν (CC), A_1	1571w,sh	1560vw	1560vw	1568vw
ν (CC), A_1	1479vs	1477vw	1477w	1477m
ν (CC), B_2	1447s	1443vw	1444vw	1444vw
β (CH), A_1	1123w	–	1119vw	–
β (CH), B_2	1084s	1082w	1078w	1080w
β (CH), B_2	1069vw	1072vw	–	1068vw
β (CH), A_1	1023m	1024w	1029w	1022w
γ (CH), B_1	1003vw	–	–	999vw
γ (CH), B_1	902vw	–	–	908vw
γ (CH), B_1	741vs	750m	750m	750m
δ (ring), B_1	702s	701vw	702vw	702vw
δ (ring), B_2	687s	690m	688m	688m
δ (ring), B_1	471m	469vw	469vw	470vw

[a] Taken from [9].
v = very, s = strong, m = medium, w = weak, br = broad, sh = shoulder.

Table 4
The vibrational wavenumbers (cm^{-1}) of *m*-xylene in the M–Ni–G compounds (M = Co, Ni or Cd; G = *m*-xylene)

Assignment[a]	*m*-Xylene[a]	Co–Ni–G	Ni–Ni–G	Cd–Ni–G
ν (CH), B_2	3052	–	–	–
ν (CH), A_1	3032	–	–	–
ν (CC), B_2	1613	1619w	1620vw	1619vw
ν (CC), A_1	1595	1596vw	1600w,sh	1598w,sh
ν (CC), B_2	1492	1495vw	1496w,sh	1494w
ν (CC), A_1	1460	1460w	1464m	1468m
β (CH), B_2	1303	1306vw	1309vw	1306vw
α (CCC), B_2	1264	1276vw	1277vw	–
X-sens, A_1	1252	1250vw	1250vw	–
β (CH), B_2	1167	1168vw	–	1161vw
X-sens, B_2	1154	1153vw	1155vw	1153vw
β (CH), A_1	1094	1090vw	1093vw	–
γ (CH), B_1	968	960vw	966vw	–
X-sens, B_2	905	–	–	910vw
γ (CH), B_1	876	–	–	–
γ (CH), B_1	768	769vw	771vw	775w
X-sens, A_1	724	–	–	–
π (CC), B_1	690	696w	684w	688w
X-sens, A_1	537	–	–	–
X-sens, B_2	515	521vw	522vw	–
π (CC), B_1	433	–	–	–
X-sens, B_2	404	–	–	–

[a] Taken from [10].
v = very, s = strong, m = medium, w = weak, br = broad, sh = shoulder.

Table 5
The vibrational wavenumbers (cm^{-1}) of naphthalene in the M–Ni–G compounds (M = Co, Ni or Cd; G = naphthalene)

Assignment[a]	Naphthalene[a]	Co–Ni–Bz	Ni–Ni–Bz	Cd–Ni–Bz
ν_{41}, B_{3u}	3072	3062w	3066w	3061w
?	–	3053vw	3051vw	3051vw
ν_{29}, B_{2u}	3014	3014vw	3016vw	3012vw
ν_{42}, B_{3u}	2976	2968w,sh	2966w,sh	2972w,sh
ν_{30}, B_{2u}	2947	2956w,sh	2952w,sh	2956w,sh
ν_{43}, B_{3u}	1680	–	–	–
ν_{31}, B_{2u}	1595	1595s,sh	1597s,sh	1597s,sh
ν_{44}, B_{3u}	1510	1508m	1508m	1506m
ν_{32}, B_{2u}	1387	1390w	1390w	1390w
ν_{33}, B_{2u}	1268	1267m	1267w	1269m
ν_{45}, B_{3u}	1211	1213w	1213w	1216w
ν_{34}, B_{2u}	1139	1128w	1128w	1132w
ν_{46}, B_{3u}	1012	1011vw	1010vw	1012vw
ν_{22}, B_{1u}	957	–	950vw	951vw
ν_{47}, B_{3u}	876	–	–	–
ν_{23}, B_{1u}	782	795vs	793vs	793vs
ν_{35}, B_{2u}	752	781s	783s	783s
ν_{48}, B_{3u}	618	619w	619w	619w
ν_{24}, B_{1u}	475	478s	478s	482s

[a] Taken from [11].
v = very, s = strong, m = medium, w = weak, br = broad, sh = shoulder.

give an account of the conformation of the dahp ligand in our compounds.

In assigning the bands attributable to the $Ni(CN)_4^{2-}$ ion in the spectra of our compounds we refer to the work of McCullough et al. [7] who presented vibrational data for the ion $Ni(CN)_4^{2-}$ in $Na_2Ni(CN)_4$. The ion $Ni(CN)_4^{2-}$ can be treated as an isolated unit and thus used as a reference to observe the effect on the vibrations when coordination to the metals M takes place. The vibrational data for $Ni(CN)_4$ groups in the compounds studied are given in Table 2 together with the vibrational wavenumbers of $Na_2Ni(CN)_4$. The wavenumbers of the infrared spectra of the $Ni(CN)_4$ group in the clathrate $Cd(NH_3)_2Ni(CN)_4{\cdot}2C_6H_6$ [8] are also listed for comparison in Table 2. The assigned wavenumbers for the $Ni(CN)_4$ group in the compounds studied appear to be much higher than those for isolated $Ni(CN)_4$ units (Table 2). Such frequency shifts were observed for other Hofmann-type clathrates [8] in which both ends of the CN group were coordinated and explained as the mechanical coupling of the internal modes of $Ni(CN)_4$ with the metal (Ni–NC) vibrations. The characteristic frequencies of the $Ni(CN)_4$ group are found to be similar to those of the Hofmann-type clathrates suggesting that coordination around the Ni atom is square, and that $\{M–Ni(CN)_4\}_\infty$ layers have been preserved.

The assignments and the wavenumbers of the bands arising from the guest molecules observed in the infrared spectra of M–Ni–G (M = Co, Ni and Cd; G = chlorobenzene, *m*-xylene, naphthalene) compounds together with those of the guest molecules in the liquid phase [9–11] are given in Tables 3–5.

Our band assignment of the guest molecules in the infrared spectrum for the clathrates studied agrees with that of the literature [9–11]. Because of the large dahp ligand, host–guest interactions in the clathrate structure are not effective, and the guest molecules also keep free molecule symmetry.

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