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Vibrational Spectroscopy 24 (2000) 249–255

VIBRATIONAL SPECTROSCOPY

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Infrared spectroscopic study of the Hofmann-dadn-type clathrates: M(1,10-diaminodecane)$Ni(CN)_4 \cdot 1{,}5G$ (M = Co, Ni or Cd; G = chlorobenzene, 1,2-, 1,3- or 1,4-dichlorobenzene)

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Received 28 January 2000; received in revised form 19 May 2000; accepted 5 June 2000

Abstract

Infrared (IR) spectra of M(1,10-diaminodecane)$Ni(CN)_4 \cdot 1{,}5G$ (M = Co, Ni or Cd; G = chlorobenzene, 1,2-, 1,3- or 1,4-dichlorobenzene) clathrate compounds are reported. The spectral data suggest that these compounds are similar in structure to those of the Hofmann-diam-type clathrates. The host structure of these clathrates consists of planar infinite polymeric sheets, $[M\text{-}Ni(CN)_4]_\infty$, formed from $Ni(CN)_4$ anions coordinated to bridging M(1,10-diaminodecane)$_2$ cations. The Ni atoms are surrounded by four C atoms of CN groups in a square-planar environment. The M atoms are bound to four nitrogen atoms of the CN ions. The octahedral configuration of the M atom is completed by coordination of two ligand molecules. The sheets are stacked on top of another by bridging ligand molecules, in a way that every consecutive layer is superimposed. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Inclusion compounds; Tetracyanonickelate; 1,10-Diaminodecane; Infrared spectra; Benzene derivatives

1. Introduction

A series of three-dimensional host lattices, Cd(α,ω-diaminoalkane)$Ni(CN)_4$, have been developed from the two-dimensional Hofmann-type host lattice, $Cd(NH_3)_2Ni(CN)_4$, by replacing the two ammonia molecules with a bidentate ligand molecule with a long CH_2– chain [1–3]. Their strategy was to enlarge the range of guest molecules with different size and shape which can be accommodated in the host lattice. The α,ω-diaminoalkane ligand bridging the cadmium atoms in adjacent two-dimensional $[Cd\text{-}Ni(CN)_4]_\infty$ sheets give a three-dimensional host structure, and allow the inclusion of bulkier guest molecules [4,5].

In our previous work [6], we reported that the infrared (IR) spectral results suggest that the structure of M(1,10-diaminodecane)$Ni(CN)_4 \cdot 1{,}5C_6H_6$ (M = Mn, Co, Ni, Cu, Zn or Cd) compounds are similar to those found in Hofmann-diam-type clathrates [4,5]. The structure provides an α-type cavity (rectangular box) for the guest molecules [2–4].

In the present work, 12 new clathrates M(dadn)$Ni(CN)_4 \cdot 1{,}5G$ (M = Co, Ni or Cd; dadn = 1,10-diaminodecane; G = chlorobenzene, 1,2-dichlorobenzene, 1,3-dichlorobenzene or 1,4-dichlorobenzene) (abbr. M-Ni-1,5G or M-Ni-ClBz, M-Ni-1,2ClBz, M-Ni-1,3ClBz and M-Ni-1,4ClBz), have

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PII: S0924-2031(00)00095-3

been prepared and their IR spectra are reported for the first time.

2. Experimental

The clathrates were prepared according to the study reported previously [6]. The clathrates $M(dadn)Ni(CN)_4 \cdot 1{,}5G$ (M = Co, Ni or Cd; G = chlorobenzene, 1,2-dichlorobenzene, 1,3-dichlorobenzene or 1,4-dichlorobenzene) were prepared by adding slightly more than 1 mmol of 1,10-diaminodecane in ethanol to a solution containing 1 mmol of $K_2Ni(CN)_4$, 1 mmol of MCl_2, 20 ml of water and 20 ml of ethanol, saturated with the guest molecules. The precipitate was filtered, washed with water, acetone and ether, successively, and stored in a desiccator containing guest vapour. IR spectra of the clathrate compounds were recorded in the range 4000–400 cm^{-1} on a MATTSON 1000 FTIR spectrometer which was calibrated using an indene/camphor/cyclohexane standard solution. The samples were prepared as mulls (without grinding the finely powdered compounds) in nujol and poly-(chlortrifluorethylene)-oil between CsI windows and as KBr discs.

3. Results and discussion

The IR spectrum of the Cd-Ni-1.5 1,3-ClBz clathrate is given in Fig. 1 as a representative. The IR spectral features of the host moieties of the M-Ni-1,5G (M = Co, Ni or Cd; G = chlorobenzene, 1,2-dichlorobenzene, 1,3-dichlorobenzene or 1,4-dichlorobenzene) compounds are found to be similar to each other, suggesting that they have similar structural features also. These in turn suggest that the degrees of the interactions of the dadn ligand, $Ni(CN)_4$ species and the guest molecules with their surroundings are almost the same for each compound and the symmetry restrictions of the compounds with different crystal symmetry possibilities are not effective. It will be most favourable to divide the vibrations into three groups arising from the dadn ligands, from the $Ni(CN)_4$ units and from the guest moieties.

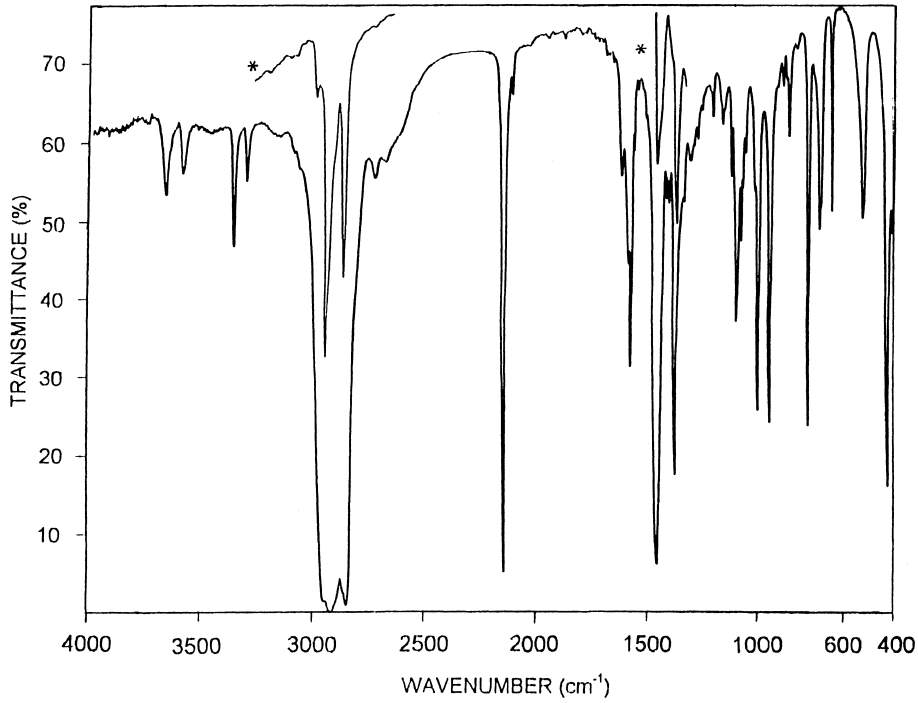

Fig. 1. The infrared spectrum of the Cd-Ni-3/2 1,3-ClBz clathrate in nujol (*: in poly-(chlortrifluorethylene)-oil).

Table 1
The vibrational wavenumbers (cm^{-1}) of 1,10-diaminodecane in the M-Ni-1,5G (M = Co, Ni or Cd; G = chlorobenzene, 1,2-dichlorobenzene, 1,3-dichlorobenzene, 1,4-dichlorobenzene)[a]

Assignment[b]	dadn in CCl_4[c]	Co-Ni-ClBz	Ni-Ni-ClBz	Cd-Ni-ClBz	Co-Ni-1, 2ClBz	Ni-Ni-1, 2ClBz	Cd-Ni-1, 2ClBz	Co-Ni-1, 3ClBz	Ni-Ni-1, 3ClBz	Cd-Ni-1, 3ClBz	Co-Ni-1, 4ClBz	Ni-Ni-1, 4ClBz	Cd-Ni-1, 4ClBz
$\nu_a(NH_2)$	3386s	3355s	3356s	3350s	3350s	3355s	3356s	3347s	3354s	3350s	3363s	3365s	3350s
$\nu_s(NH_2)$	3329s	3293m	3295m	3290m	3292m	3294m	3295m	3289m	3296m	3292m	3287m	3290m	3297m
$\nu_a(CH_2)$	2927vs	2921vs	2923vs	2919vs	2926vs	2923vs	2922vs	2925vs	2923vs	2925vs	2923vs	2923vs	2923vs
$\nu_s(CH_2)$	2854vs	2850vs	2850vs	2850vs	2854vs	2852vs	2852vs	2852vs	2852vs	2852vs	2851vs	2851vs	2851vs
$\delta(NH_2)$	1610s	1583s	1584s	1583vs	1587m	1587vs	1586s	1586s	1587m	1587m	1583m	1583m	1586m
$\delta(CH_2)$	1468s	1468s	1468s	1470s	1463s	1465s	1465s	1470s	1470s	1470s	1467s	1469s	1470s
$\delta(CH_2)$	1441m,sh	1445w	1445w	1445w	1436w	1435w	1436w	1438w	1438w	1438w	1437w	1437w	1437w
$\rho_w(CH_2)$	1389m	1383vw	1383vw	1381vw	1375vw	1375vw	1379vw	1366w	1366vw	1363vw	1366w	1364w	1366w
$\rho_w(CH_2)$	1363vw	1357vw	1357vw	1355vw	1355vw	1355vw	1355vw	1352vw	1354vw	1354vw	1354vw	1354vw	1354vw
$\rho_t(CH_2)$	1319w	1336vw	1338vw	1338vw	1342vw	1340vw	1338vw	1342vw	1343vw	1334w,sh	1339vw	1339vw	1339vw
$\rho_t(NH_2)$	1302w	1305w	1304w	1306w	1306w	1306m	1304w	1305vw	1307vw	1306vw	1304w	1305w	1305vw
ν(CN)	1092w,sh	1102m	1120m	1101s	1106m	1126s	1120m	1123w	1109m	1122s	1088m	1090w	1096m,sh
ν(CN)	1057s	1059m	1052m	1057m,sh	1050m	1052m	1052m	1061m	1055m	1058m	1055m	1058m	1046m
$\rho_w(NH_2)$	1016vw	1019w,sh	1020w	1020w	1019m	1019w	1020w	1019m	1018w,sh	1014w	1038m	1039m	1047m
$\rho_r(CH_2)$	962vw	1000s	1005m	1001s	1006m	1007m	1005m	1004s	1006s	1001s	996m	1005m	1001m
$\rho_r(CH_2)$	820m,br	n.o.	n.o.	n.o.	846vw	846vw	848vw	828vw	828vw	828vw	824vw	824vw	824vw
$\rho_r(CH_2)$	721w	739w	733w	736wm	725w	724w	730w	736vw	730vw	730vw	738vw	738vw	738vw
δ(skeletal)	n.o.	554m	573m	535m	549m	572m	532m	553m	573m	536m	565m	579m	537m

[a] v: very, s: strong, m: medium, w: weak, sh: shoulder, n.o.: not observed.
[b] Taken from [7].
[c] Taken from [6].

Table 2
The vibrational wavenumber (cm^{-1}) of the $Ni(CN)_4$ group for the M-Ni-1,5G (M = Co, Ni or Cd; G = chlorobenzene, 1,2-dichlorobenzene, 1,3-dichlorobenzene, 1,4-dichlorobenzene) clathrates[a]

Assignment[b]	$Na_2Ni(CN)_4$[b]	Co-Ni-ClBz	Ni-Ni-ClBz	Cd-Ni-ClBz	Co-Ni-1, 2ClBz	Ni-Ni-1, 2ClBz	Cd-Ni-1, 2ClBz	Co-Ni-1, 3ClBz	Ni-Ni-1, 3ClBz	Cd-Ni-1, 3ClBz	Co-Ni-1, 4ClBz	Ni-Ni-1, 4ClBz	Cd-Ni-1, 4ClBz
ν_8(CN), E_u	2132, 2128	2158vs	2167vs	2148vs	2157vs	2167vs	2148vs	2156vs	2163vs	2148vs	2163vs	2167vs	2148vs
Hot band	–	2123vw,sh	2130vw,sh	2128vw,sh	2125vw,sh	2128vw,sh	2132vw,sh	2133vw,sh	2131vw,sh	2122vw,sh	2125vw,sh	2130vw,sh	2124vw,sh
$\nu(^{13}C–N)$, E_u	2087	n.o.	n.o.	2110vw	2107vw	2109vw	2110vw	2113vw	2109vw	2108vw	2110vw	2110vw	2109vw
ν_9, ν(NiC), E_u	543	500vw	500vw	498vw	487vw	487vw	489vw	532vw	526vw	522vw	539vw	538vw	515vw
ν_{12}, π(NiC), A_{2u}	448	455vw	453vw	445vw	453vw	457vw	445vw	452vw	456vw	434vw	455vw	455vw	444vw
ν_{10}, δ(NiCN), E_u	433, 421	437vs	440vs	424vs	436vs	439vs	423vs	435vs	437vs	424vs	437vs	439vs	422vs

[a] v: very, s: strong, m: medium, w: weak, sh: shoulder, n.o.: not observed.
[b] Taken from [8].

Table 3
The vibrational wavenumber (cm^{-1}) of chlorobenzene in the M-Ni-1,5G (M = Co, Ni or Cd; G = chlorobenzene) clathrates[a]

Assignment[b]	Chlorobenzene in CCl_4 or CS_2[b]	Co-Ni-ClBz	Ni-Ni-ClBz	Cd-Ni-ClBz
ν(CH), A_1	3087w,sh	n.o.	3079vw	n.o.
ν(CH), B_2	3072s	3069vw	3065vw	3065vw
ν(CH), A_1	3060w,sh	n.o.	n.o.	n.o.
ν(CH), A_1	3030w,sh	n.o.	n.o.	n.o.
ν(CH), B_1	3006w	n.o.	n.o.	n.o.
ν(CC), B_2	1586s	1584s	1584s	1584s
ν(CC), A_1	1571w,sh	1561vw	1562vw	1561vw
ν(CC), A_1	1479vs	1477vs	1477vs	1470vs
ν(CC), B_2	1447s	1445vw	1445vw	1444vw
β(CH), A_1	1123w	n.o.	1120vw	n.o.
β(CH), B_2	1084s	1082w	1082w	1083w
β(CH), B_2	1069vw	1065vw	1065vw	1066vw
β(CH), A_1	1023m	1020w	1020w	1020w
γ(CH), B_1	1003vw	n.o.	1005vw	n.o.
γ(CH), B_1	902vw	904vw	907vw	907vw
γ(CH), B_1	741vs	747vs	747vs	748vs
δ(ring), B_1	702s	703s	702s	702s
δ(ring), B_2	687s	686m	689m	687m
δ(ring), B_1	471m	469w	469w	469w

[a] v: very, s: strong, m: medium, w: weak, sh: shoulder, n.o.: not observed.
[b] Taken from [12,13].

The IR wavenumbers of the bands in the spectra of these species are tabulated in Tables 1–6, respectively, together with some relevant spectral data for comparison.

Up to the time of writing, there have been no studies concerning the spectral data for free dadn or dadn in metal complexes. Therefore, the assignments were made in terms of characteristic group frequen-

Table 4
The vibrational wavenumber (cm^{-1}) of 1,2-dichlorobenzene in the M-Ni-1,5G (M = Co, Ni or Cd; G = 1,2-dichlorobenzene) clathrates[a]

Assignment[b]	1,2-Dichlorobenzene (gas phase)[b]	Co-Ni-1,2ClBz	Ni-Ni-1,2ClBz	Cd-Ni-1,2ClBz
ν(CH), A_1	3072	3061vw	3060vw	3058vw
ν(CC), A_1	1576	1588vs	1588vs	1587vs
ν(CC), A_1	1458	1456s	1456s	1456s
ν(CC), B_2	1438	1436m	1437m	1435m
β(CH), B_2	1252	1252w	1252w	1252w
X-sens., A_1	1155	1157m	1157m	1155m
X-sens., B_2	1130	1126m	1126m	1124m
β(CH), B_2	1038	1036s	1036s	1036s
γ(CH), A_2	975	972w,sh	973w,sh	969w,sh
γ(CH), B_1	940	945vw	947vw	944vw
γ(CH), A_2	850	864vw	868vw	863vw
γ(CH), B_1	748	759vs	760vs	759vs
X-sens., B_2	740	739s	739s	737s
X-sens., A_1	660	659s	659s	659s
X-sens., A_1	480	486vw	487vw	484vw
ϕ(CC), B_1	435	436s	439s	437s,sh
X-sens., B_2	427	419vw	419vw	411vw

[a] v: very, s: strong, m: medium, w: weak, sh: shoulder.
[b] Taken from [14].

Table 5
The vibrational wavenumber (cm^{-1}) of 1,3-dichlorobenzene in the M-Ni-1,5G (M = Co, Ni or Cd; G = 1,3-dichlorobenzene) clathrates[a]

Assignment[b]	1,3-Dichlorobenzene (gas phase)[a]	Co-Ni-1,3ClBz	Ni-Ni-1,3ClBz	Cd-Ni-1,3ClBz
ν(CH), A_1	3071	3061w	3065w	3060w
ν(CC), A_1	1580	1577vs	1577vs	1577vs
ν(CC), B_2	1464	1460vs	1461vs	1461vs
ν(CC), A_1	1412	1406m	1405m	1405m
β(CH), B_2	1258	1255w	1254w	1255w
X-sens., B_2	1161	1161m	1162m	1162m
X-sens., A_1	1127	1123m	1123m	1122m
β(CH), B_2	1079	1079m	1079m	1079m
γ(CH), B_1	966	996m,sh	998m,sh	996m,sh
γ(CH), A_2	896	894w	893w	894w
γ(CH), A_2	n.o.	n.o.	n.o.	n.o.
X-sens., B_2	784	782vs	782vs	781vs
γ(CH), B_1	775	n.o.	n.o.	n.o.
X-sens., A_1	663	668w	n.o.	668w
X-sens., A_1	428	436s	437s	435s,sh
ϕ(CC), B_1	397	n.o.	n.o.	n.o.
X-sens., B_2	n.o.	n.o.	n.o.	n.o.

[a] v: very, s: strong, m: medium, w: weak, sh: shoulder, n.o.: not observed.
[b] Taken from [14].

cies. These assignments are given in Table 1, along with some relevant spectral data. The bands assigned to the NH_2 stretching frequencies in the range 3365–3287 cm^{-1} (Table 1), which are lower than the corresponding values of the free dadn molecule, are characteristics of coordinated $-NH_2$ groups. That is, on coordination, the N–H stretching frequencies should decrease due to the consecutive inductive effects; in other words, on coordination, the N–H bond should become weaker, resulting in lower frequencies.

In assigning the bands due to the $Ni(CN)_4^{2-}$ ion in the spectra of the compounds under study, we refer to the work of McCullough et al. [8] who

Table 6
The vibrational wavenumber (cm^{-1}) of 1,4-dichlorobenzene in the M-Ni-1,5G (M = Co, Ni or Cd; G = 1,4 dichlorobenzene) clathrates[a]

Assignment[b]	1,4-Dichlorobenzene (gas phase)[b]	Co-Ni-1,4ClBz	Ni-Ni-1,4ClBz	Cd-Ni-1,4ClBz
ν(CH), B_{2u}	3087	n.o.	n.o.	n.o.
ν(CH), B_{1u}	3078	n.o.	n.o.	n.o.
ν(CC), B_{1u}	1477	1476s	1475s	1475s,sh
ν(CC), B_{2u}	1394	1395m	1392m	1392m
α(CCC), B_{2u}	1220	1222vw	1223vw	1223vw
β(CH), B_{2u}	1107	1100w,sh	1102w,sh	1097w,sh
X-sens., B_{1u}	1090	1069w	1068w	1069w
β(CH), B_{1u}	1015	1008m,sh	1013m,sh	1011m,sh
γ(CH), A_u	951	963m	957m	955m
γ(CH), B_{3g}	934	940w,sh	943w,sh	943w,sh
γ(CH), B_{3u}	819[c]	817m,sh	815m,sh	815m,sh
X-sens., B_{1u}	550	552w,sh	548w,sh	547w,sh
ϕ(CC), B_{3u}	485[c]	487m	487m	487m
ϕ(CC), A_u	405	n.o.	n.o.	n.o.

[a] v: very, s: strong, m: medium, w: weak, sh: shoulder, n.o.: not observed.
[b] Taken from [14].
[c] Band contour of vapour spectrum.

presented vibrational data for the ion $Ni(CN)_4$ in $Na_2Ni(CN)_4$. The vibrational data for $Ni(CN)_4$ groups in the compounds under study are given in Table 2, together with the vibrational wavenumbers of $Na_2Ni(CN)_4$. 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-diam-type [9,10] and Hofmann-type [11] clathrates in which both ends of the CN group coordinated and explained as the mechanical coupling of the internal modes of $Ni(CN)_4$ with the metal M–NC vibrations [9–11]. 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 Ni atom is square, and that $[M\text{-}Ni(CN)_4]_\infty$ layers have been conserved.

The assignments and the wavenumbers of the bands arising from the guest molecules chlorobenzene (vapour phase, in-plane vibrations [12], out-of-plane vibrations [13]), 1,2-, 1,3- and 1,4-dichlorobenzene (in solutions in CCl_4 and CS_2) [14] are given in Tables 3–6, respectively, on which the assignments are based. Our band assignments of the guest molecules in the compounds are in agreement with those of the literature [12–14]. The IR spectral data of the compounds studied suggest that the guest molecules retain the symmetry of the corresponding free molecules.

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 3–6) than those of guest molecules in solutions. Similar positive frequency shifts were observed for Hofmann-type clathrates [15] 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. Therefore, we may reasonably suggest that the frequency shifts in our clathrates are due to the π-electron donation from the benzene ring to the hydrogen atoms of the dadn which has a more electrophilic character caused by the bidentate coordination.

It should be noted that, in our clathrates, the number of guest molecules is 1,5. A similar number has been found in other Hofmann-diam-type clathrates [5,6,15]. Therefore, the decrease in the number of the guest molecules from 2 in Hofmann-type [11] to 1,5 in the present series is due to the fact that one of the four cavities may be occupied by the dadn ligand molecules, and the remainder three by the guest molecule [4,5]. Similar results have been obtained in the Hofmann-pn-type clathrate, $Cd[NH_2\text{-}CH(CH_3)\text{-}CH_2NH_2]Ni(CN)_4 \cdot 3/2C_6H_6$ [16].

The proceeding discussion considered together leads to the conclusion that the host frameworks of the clathrates studied have layered structures of $[M\text{-}Ni(CN_4)]_\infty$ sheets. The adjacent sheets are bridged by the bidentate ligand molecules. These structures provide rectangular box-type cavities. The NH_2 groups of the ligand molecules are hydrogen-bonded to the π-electrons of the aromatic guest molecules.

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