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Infrared spectroscopic studies of the Hofmann-daon-type clathrates: M(1,8-diaminooctane)Ni(CN)$_4$·G (M = Co, Ni or Cd; G = 1,2-dichlorobenzene or1,4-dichlorobenzene)

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Abstract

New Hofmann-daon-type clathrates of the form M(1,8-diaminooctane)Ni(CN)$_4$·G (M = Co, Ni or Cd; G = 1,2-dichlorobenzene or 1,4-dichlorobenzene) were prepared in powder form and their infrared spectra are reported. The spectral features suggest that these compounds are similar in structure to the en-Hofmann-type clathrates and their structure consists of corrugated polymeric layers of $\{M–Ni(CN)_4\}_\infty$ with the 1,8-diaminooctane spaned between two metal (M) atoms, of the consecutive two layers. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Hofmann-type clathrates; Tetracyanonickelate; 1,8-Diaminooctane; Infrared spectra; Dichlorobenzene

1. Introduction

In our previous work [1] we reported that the infrared (IR) spectral results suggest that the structure of M(1,8-diaminooctane)Ni(CN)$_4$·G (M = Co, Ni or Cd; G = benzene, chlorobenzene, toluene, *p*-xylene, naphthalene or biphenyl) compounds are similar to those found in Hofmann-diam-type clathrates given with a general formula M(α,ω-diaminoalkane)-Ni(CN)$_4$·*n*G, where M is transition metals such as Co, Ni or Cd, *n* is the number of G (guest) molecules depending on the bulkiness of the ligands [2]. The Hofmann-type host frame work is formed from infinite $\{M–Ni(CN)_4\}_\infty$ layers with four planar coordination around Ni atom [2–4]. The structure provides a α-type cavity (rectangular box) for the guest molecules [3,4].

In the present work six new clathrates M(daon)-Ni(CN)$_4$·G (M = Co, Ni or Cd; daon = 1,8-diaminooctane; G = 1,2-dichlorobenzene or 1,4-dichlorobenzene) (abbr. M–Ni–G or M–Ni–2Cl and M–Ni–4Cl), were prepared and their IR spectra are reported for the first time.

2. Experimental

The compounds M(daon)Ni(CN)$_4$·G (M = Co, Ni or Cd; G = 1,2-dichlorobenzene or 1,4-dichlorobenzene) were prepared by adding slightly more than 1 mmol of 1,8-diaminooctane to a solution containing 1 mmol of $K_2Ni(CN)_4$, 1 mmol of MCl_2, 20 mmol water and 20 mmol ethanol, saturated with the guest molecules. Infrared spectra of the compounds as nujol

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Table 1
The vibrational wave numbers (cm^{-1}) of 1,8-diaminooctane (*daon*) in the M–Ni–G (M = Co, Ni or Cd; G = 1,2-dichlorobenzene or 1,4-dichlorobenzene) compounds

Assignment [a]	Liquid daon [a]	Co–Ni–G[a,b]	Ni–Ni–G[a,c]	Cd–Ni–G[a,d]	Co–Ni–2Cl	Ni–Ni–2Cl	Cd–Ni–2Cl	Co–Ni–4Cl	Ni–Ni–4Cl	Cd–Ni–4Cl
ν (NH_2)	3381s	3348s	3352s	3350s	3349s	3351s	3353s	3344s	3346s	3348s
ν (NH_2)	3321s	3290s	3296s	3292s	3291s	3293s	3294s	3284s	3286s	3286s
ν (CH_2)	2926vs	2924s	2924s	2924s	2926s	2926s	2925s	2924s	2926s	2924s
ν (CH_2)	2856vs	2852s	2852s	2856s	2854s	2853s	2854s	2852s	2852s	2854s
δ (NH_2)	1584s	1587w	1585m	1589m	1587s	1589m	1588m	1587m	1587m	1585m
δ (CH_2)	1487m	1494vw	1493vw	1495vw	1497vw	1497vw	1497vw	1507vw	1507vw	1507vw
δ (CH_2)	1466s	1470m	1470m	1471m	1469m	1469m	1470m	1469m	1469m	1470m
δ (CH_2)	1440vw	1458w	1459w	1456w	1461w	1461w	1462w	1461w	1462w	1462w
ρ_w (CH_2)	1390w,sh	1396vw	1396vw	1396vw	1395vw	1395vw	1394m	—	—	—
ρ_w (CH_2)	1385w	1387w	1388vw	1387vw	1384vw	1384vw	1384vw	1383vw	1384vw	1383vw
ρ_t (CH_2)	1367vw	1365vw	1367w	1365w	1367w	1367w	1365w	1362w	1360w	1360w
ρ_t (NH_2)	1218vw	1213vw	1215vw	1214vw	1213w	1212w	1213w	1213w	1212w	1213w
ν (CN)	1089vw	1096w	1099vw	1092w	1097m	1098m	1089m	1095m	1095m	1086m
ν (CN)	1066vw	1066vw	1068vw	1066vw	1064vw	1065vw	1065vw	1059vw	1059vw	1059vw
ρ_w (NH_2)	1005vw	996m	999m	993m	995m	998m	992m	991m	995m	987m
ρ_r (CH_2)	951vw	968m	970w	966m	968m	972m	966m	968m	968m	966m
ρ_r (CH_2)	860m,br	841w	841vw	843vw	839vw	840vw	843vw	839vw	840vw	843vw

[a] Taken from Ref. [1].
[b] Co(1,8-diaminooctane)$Ni(CN)_4$.chlorobenzene.
[c] Ni(1,8-diaminooctane)$Ni(CN)_4$.chlorobenzene.
[d] Cd(1,8-diaminooctane)$Ni(CN)_4$.chlorobenzene. v = very, s = strong, m = medium, w = weak, br = broad, sh = shoulder.

Table 2
The vibrational wave numbers (cm^{-1}) of cyanide group for the M–Ni–G compounds (M = Co, Ni or Cd, G = 1,2-dichlorobenzene or 1,4-dichlorobenzene)

Assignment [a]	$Na_2Ni(CN)_4$ [a]	Co–Ni–G [b,c]	Ni–Ni–G [b,d]	Cd–Ni–G [b,e]	Co–Ni–2Cl	Ni–Ni–2Cl	Cd–Ni–2Cl	Co–Ni–4Cl	Ni–Ni–4Cl	Cd–Ni–4Cl
ν_8 (CN), E_u	2132	2154vs	2166vs	2146vs	2152vs	2159vs	2146vs	2154vs	2162vs	2150vs
Hot band?	2128	—	—	—	2129	2130	—	—	2131	—
ν_9 (NiC), E_u	—	557m	579m	536m	559m	580m	538m	557m	580m	534m
ν_9 (NiC), E_u	543	528vw	—	523vw	529w	534w	525w,sh	523vw	528vw	518w,sh
π(NiC), A_{2u}	448	451vw	457vw	—	452w	454w	445vw	453vw	453w	438w
δ(NiCn), E_u	433	434vs	440vs	424vs	434s	437s	424s	436s	438s	426s

[a] Taken from Ref. [6].
[b] Taken from Ref. [1].
[c] Co(1,8-diaminooctane)$Ni(CN)_4$.chlorobenzene.
[d] Ni(1,8-diaminooctane)$Ni(CN)_4$.chlorobenzene.
[e] Cd(1,8-diaminooctane)$Ni(CN)_4$.chlorobenzene. v = very, s = strong, m = medium, w = weak, sh = shoulder.

Table 3
The vibrational wave numbers (cm^{-1}) of 1,2-dichlorobenzene in the M–Ni–2Cl (M = Co, Ni or Cd; 2Cl = 1,2-dichlorobenzene) compounds

Assignment [a]	1-2 dichlorobenzene [a]	Co–Ni–2Cl	Ni–Ni–2Cl	Cd–Ni–2Cl
ν (CH), A_1	3072	3078vw	3083vw	3082w
ν (CC), A_1	1576	1571m	1571m	1570m
ν (CC), A_1	1458	1455s	1455s	1454s
ν (CC), B_2	1438	1434m	1434m	1434m
β(CH), B_2	1252	1249w	1250w	1259w
X-sens, A_1	1155	1157m	1157vw	1157vw
X-sens, B_2	1130	1122m	1122m	1123m
β (CH), B_2	1038	1037s	1036s	1035s
γ (CH), A_2	975	—	—	—
γ (CH), B_1	940	947vw	947vw	947vw
γ (CH), A_2	850	859vw	860vw	843vw
γ (CH), B_1	748	760vs	760vs	760vs
X-sens, B_2	740	736vs	736vs	736s
X-sens,A_1	660	660s	660s	659s
X-sens,A_1	480	486vw	485vw	481vw
ϕ (CC), B_1	435	—	—	—
X-sens, B_2	427	—	—	—

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

mulls and KBr discs were recorded in the range of 4000–400 cm^{-1} on MATTSON 1000 FTIR spectrometer. The freshly prepared compounds were analyzed for C, H and N with the following results (found %/calculated %).

- $Co(C_8H_{20}N_2)Ni(CN)_4\cdot$ (1,2-$C_6H_4Cl_2$):C = 42.09/42.14, H = 5.54/4.71, N = 16.04/16.38;
- $Ni(C_8H_{20}N_2)Ni(CN)_4\cdot$ (1,2-$C_6H_4Cl_2$): C = 41.46/42.16, H = 4.47/4.72, N = 16.04/16.39;
- $Cd(C_8H_{20}N_2)Ni(CN)_4\cdot$ (1,2-$C_6H_4Cl_2$): C = 37.18/38.16, H = 4.32/4.27, N = 14.76/14.83;
- $Co(C_8H_{20}N_2)Ni(CN)_4\cdot$ (1,4-$C_6H_4Cl_2$): C = 41.32/42.14, H = 4.45/4.71, N = 16.69/16.38;
- $Ni(C_8H_{20}N_2)Ni(CN)_4\cdot$ (1,4-$C_6H_4Cl_2$): C = 41.80/42.16, H = 4.68/4.72, N = 16.41/16.39;

Table 4
The vibrational wave numbers (cm^{-1}) of 1,4-dichlorobenzene in the M–Ni–4Cl (M = Co, Ni or Cd; 4Cl = 1,4-dichlorobenzene) compounds

Assignment [a]	1-4 dicholorobenzene [a]	Co–Ni–4Cl	Ni–Ni–4Cl	Cd–Ni–4Cl
ν (CH), B_{2u}	3087	—	—	—
ν (CH), B_{1u}	3078	—	—	—
ν (CC), B_{1u}	1477	—	—	—
ν (CC), B_{2u}	1394	1399vw	1399vw	1399vw
α (CCC), B_{2u}	1220	1222vw	1223vw	1223vw
β (CH), B_{2u}	1107	1105w,sh	1105w,sh	1103w,sh
X-sens, B_{1u}	1090	1076m	1068m	1070m
β (CH), B_{1u}	1015	1014m	1015m	1015m
γ (CH), A_u	951	—	—	—
γ (CH), B_{3g}	934	—	—	—
γ (CH), B_{3u}	819[b]	823s	823s	823s
X-sens, B_{1u}	550	—	550vw	550vw
ϕ (CC), B_{3u}	485[b]	488m	488m	487m
ϕ (CC), A_u	405	—	—	—

[a] Taken from Ref. [10].
[b] Band contour of vapour spectrum. v = very, s = strong, m = medium, w = weak, sh = shoulder.

- $Cd(C_8H_{20}N_2)Ni(CN)_4\cdot$ $(1,4\text{-}C_6H_4Cl_2)$: C = 37.93/38.16, H = 4.70/4.27, N = 15.03/14.83;

These analytical results are paltry for the samples obtainable in powder form because of partial decomposition. Such instabilities were reported for clathrates having low boiling guest molecules [5].

3. Results and discussion

The IR spectral features of the host moieties of the M–Ni–G (M = Co, Ni or Cd; G = 1,2-dichlorobenzene or 1,4-dichlorobenzene) compounds are found to be similar to each other suggesting that they also have similar structural features. These in turn suggest that the degrees of the interactions of the *daon* 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 *daon* ligands, from the $Ni(CN)_4$ units and from the guest moieties. The IR wave numbers of the bands in the spectra of these species are tabulated in Tables 1–4, respectively, together with some relevant spectral data for comparison.

From the present spectral data alone it is not possible to obtain the conformation of the *daon* molecules in the compounds. The bands assigned to the NH_2 stretching frequencies in the range 3350–3290 cm^{-1} (Table 1), which are lower than the corresponding values of the free *daon* molecule, are characteristic of coordinated $-NH_2$ groups.

In assigning the bands owing to the $Ni(CN)_4^{2-}$ ion in the spectra of the compounds under study, we refer to the work of McCullough et al. [6]. The vibrational data for $Ni(CN)_4$ groups in the compounds considered are given in Table 2, together with the vibrational wave numbers of $Na_2Ni(CN)_4$ and some other relevant data for comparison. The assigned wave numbers for the $Ni(CN)_4$ group in the compounds studied appear to be much higher than those for the isolated $Ni(CN)_4$ units (Table 2). Such frequency shifts were observed for other Hofmann-diam-type [7,8] and Hofmann-type [5] clathrates, where both the ends of the CN group coordinated and explained as the mechanical coupling of the internal modes of $Ni(CN)_4$ with the metal (Ni–NC) vibrations [5]. The characteristic frequencies of the $Ni(CN)_4$ group are found to be similar to those of the en-Hofmann-type clathrates [1,2].

The assignments and the wave numbers of the bands arising from the guest molecules in the liquid phase [9,10] and in the M–Ni–G (M = Co, Ni or Cd; G = 1,2-dichlorobenzene and 1,4-dichlorobenzene) compounds are given in Tables 3 and 4 on which the assignments are based. Our band assignment of the guest molecules in the compounds are in agreement with that of the literature [9,10]. The IR spectral data of the compounds studied suggest that the guest molecules retain the symmetry of free molecule.

The preceding discussion when considered together leads to the conclusion that the compounds M(daon)-$Ni(CN)_4\cdot$G (M = Co, Ni or Cd; G = 1,2-dichlorobenzene or 1,4-dichlororbenzene) are similar in structure to the Hofmann-daon-type clathrates M(1,8-diaminooctane)$Ni(CN)_4\cdot$G (M = Co, Ni or Cd; G = benzene, chlorobenzene, toluene, *p*-xylene, naphthalene, biphenyl).

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