Journal of Inclusion Phenomena and Molecular Recognition in Chemistry **28:** 335–347, 1997.

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Infrared Spectroscopic Study of the Hofmann-daon-Type Clathrates : M(1,8-diaminooctane)Ni(CN)$_4$·G (M=Co, Ni or Cd; G=Aromatic Guest Molecules)

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(Received: 15 August 1996; in final form: 11 November 1996)

Abstract. Infrared spectra 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 reported. The 1,8-diaminooctane 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.

Key words: Clathrates, inclusion compounds, 1,8-diaminooctane, infrared spectra, benzene, chlorobenzene, toluene, *p*-xylene, naphthalene, biphenyl, tetracyanonickelate.

1. Introduction

A series of three-dimensional host lattices, Cd(α,ω-diaminoalkane)Ni(CN)$_4$, has been developed from the two-dimensional Hofmann-type host lattice, Cd(NH$_3$)$_2$Ni(CN)$_4$, by replacing the ammonia molecules with bidentate ligands with longer carbon chains [1–3]. The strategy was to enlarge the range of guest molecules which can be accommodated in the host lattices. The α, ω-diamino alkane ligands bridge the cadmium atoms in adjacent two-dimensional [Cd—Ni(CN)$_4$]$_\infty$ sheets giving three-dimensional host structures, and allow the inclusion of bulky guest molecules [4,5].

Recently Iwamoto *et al*. have reported the crystal structures of Cd(daon) Ni(CN)$_4$·G (daon = 1,8-diaminooctane) G = *o*-toluidine in the monoclinic space group $P2/m$ and G = *p*-toluidine in the triclinic space group ($P\bar{1}$) [5]. These [4,5] and other [6,7] crystal structure studies show that the clathrates in this series are not isomorphous with each other, but they have Hofmann-type structures and compare with the Hofmann-type and analogous series which are isostructural [5,6].

In the present work we have extended these studies and prepared M(daon) Ni(CN)$_4$· G (M=Co, Ni or Cd; G=benzene, chlorobenzene, toluene, *p*-xylene, naphthalene or biphenyl) (abbreviated to M-Ni-G) compounds for the first time and report their infrared spectra. We give in detail the infrared wavenumbers of

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Table I. The analytical results ((found%)/calculated%) of M-Ni-G compounds.

Compounds	M (M=Co or Cd)	Ni	C	H	N
$Co(C_8H_{20}N_2)Ni(CN)_4 \cdot C_6H_6$	(12.92)/13.27	(12.85)/13.22	(47.23)/48.68	(5.02)/5.90	(17.76)/18.92
$Ni(C_8H_{20}N_2)Ni(CN)_4 \cdot C_6H_6$		(26.03)/26.45	(47.73)/48.71	(5.16)/5.90	(17.83)/18.93
$Cd(C_8H_{20}N_2)Ni(CN)_4 \cdot C_6H_6$	(21.93)/22.59	(11.16)/11.80	(42.66)/43.45	(4.93)/5.27	(15.90)/16.89
$Co(C_8H_{20}N_2)Ni(CN)_4 \cdot C_6H_5Cl$	(12.04)/12.31	(12.14)/12.27	(44.93)/45.18	(4.96)/5.27	(17.11)/17.56
$Ni(C_8H_{20}N_2)Ni(CN)_4 \cdot C_6H_5Cl$		(24.04)/24.55	(44.82)/45.20	(5.17)/5.27	(17.19)/17.57
$Cd(C_8H_{20}N_2)Ni(CN)_4 \cdot C_6H_5Cl$	(21.22)/21.13	(11.10)/11.03	(39.88)/40.63	(4.38)/4.74	(15.51)/15.80
$Co(C_8H_{20}N_2)Ni(CN)_4 \cdot C_6H_5CH_3$	(12.04)/12.86	(12.51)/12.82	(48.93)/49.81	(5.87)/6.16	(18.11)/18.34
$Ni(C_8H_{20}N_2)Ni(CN)_4 \cdot C_6H_5CH_3$		(25.33)/25.64	(48.82)/49.84	(6.14)/6.16	(18.19)/18.35
$Cd(C_8H_{20}N_2)Ni(CN)_4 \cdot C_6H_5CH_3$	(22.02)/21.97	(11.16)/11.48	(44.26)/44.61	(5.08)/5.52	(16.51)/16.43
$Co(C_8H_{20}N_2)Ni(CN)_4 \cdot p\text{-}C_6H_4(CH_3)_2$	(12.04)/12.48	(12.54)/12.43	(50.34)/50.88	(6.26)/6.40	(17.35)/17.80
$Ni(C_8H_{20}N_2)Ni(CN)_4 \cdot p\text{-}C_6H_4(CH_3)_2$		(24.33)/24.88	(49.42)/50.90	(6.11)/6.41	(17.49)/17.81
$Cd(C_8H_{20}N_2)Ni(CN)_4 \cdot p\text{-}C_6H_4(CH_3)_2$	(21.80)/21.39	(11.16)/11.17	(45.10)/45.70	(5.38)/5.75	(15.53)/15.99
$Co(C_8H_{20}N_2)Ni(CN)_4 \cdot C_{10}H_8$	(11.56)/11.93	(11.00)/11.88	(53.97)/53.47	(5.76)/5.71	(16.81)/17.01
$Ni(C_8H_{20}N_2)Ni(CN)_4 \cdot C_{10}H_8$		(23.18)/23.77	(53.45)/53.50	(5.22)/5.71	(16.99)/17.01
$Cd(C_8H_{20}N_2)Ni(CN)_4 \cdot C_{10}H_8$	(20.05)/20.53	(10.19)/10.72	(47.84)/48.25	(5.13)/5.15	(14.66)/15.35
$Co(C_8H_{20}N_2)Ni(CN)_4 \cdot C_{12}H_{10}$	(11.09)/11.33	(10.95)/11.29	(55.04)/55.42	(5.38)/5.81	(16.04)/16.16
$Ni(C_8H_{20}N_2)Ni(CN)_4 \cdot C_{12}H_{10}$		(22.26)/22.58	(55.42)/55.44	(5.13)/5.82	(15.89)/16.16
$Cd(C_8H_{20}N_2)Ni(CN)_4 \cdot C_{12}H_{10}$	(19.25)/19.60	(10.11)/10.23	(49.82)/50.25	(4.98)/5.27	(14.51)/14.65

Table II. The vibrational wavenumbers (cm^{-1}) of 1,8-diaminooctane in the M-Ni-G compounds.

Assignment[a]	Liquid daon[b]	Cd-Ni[c]	Co-Ni-G G=Benzene	Ni-Ni-G G=Benzene	Cd-Ni-G G=Benzene	Co-Ni-G G=Chlorobenzene	Ni-Ni-G G=Chlorobenzene	Cd-Ni-G G=Chlorobenzene	Co-Ni-G G=Toluene	Ni-Ni-G G=Toluene
$\nu(NH_2)$	3381s	3354s	3350s	3350s	3348s	3348s	3352s	3350s	3346s	3352s
$\nu(NH_2)$	3321s	3296s	3292s	3294s	3290s	3290s	3296s	3292s	3290s	3294s
$\nu(CH_2)$	2926vs	2922s	2924s	2922s	2924s	2924s	2924s	2924s	2926s	2926s
$\nu(CH_2)$	2856vs	2854s	2852s	2852s	2856s	2852s	2852s	2856s	2852s	2854s
$\delta(NH_2)$	1584s	1591s	1587m	1587m	1589m	1587w	1585m	1589m	1587m	1587m
$\delta(CH_2)$	1487m	1493vw	1495vw	1498vw	1493w	1494vw	1493vw	1495vw	1494vw	1495vw
$\delta(CH_2)$	1466s	1470m	1470m	1466m	1471s	1470m	1470m	1471m	1470m	1470m
$\delta(CH_2)$	1440vw	1460vw	1458vw	1460w,sh	1458vw	1458w	1459w	1456w	1456vw	1458w
$\rho_w(CH_2)$	1390w,sh	1395vw	1396w	1396vw	1398w	1396vw	1396vw	1396vw	1396vw	1396vw
$\rho_w(CH_2)$	1385w	1387w	1385vw	–	1385vw	1387w	1388vw	1387vw	1387vw	1389vw
$\rho_t(CH_2)$	1367vw	1365w	1365vw	1371vw	1365w	1365vw	1367w	1365w	1365w	1367vw
$\rho_t(NH_2)$	1218vw	1213w	1213vw	1211vw	1215vw	1213vw	1215vw	1214vw	1213vw	1213vw
$\nu(CN)$	1089vw	1086m	1102w	1104w	1099w	1096w	1099vw	1092w	1099w	1101w
$\nu(CN)$	1066vw	1063vw	1059vw	1059vw	1064vw	1066vw	1068vw	1066vw	1066vw	1066vw
$\rho_w(NH_2)$	1005vw	989m	1001w	1005w	993mw	996m	999m	993m	995m	999m
$\rho_r(CH_2)$	951vw	962m	972m	974w	966m	968m	970w	966m	968m	970m
$\rho_r(CH_2)$	860m,br	843w,br	847w,br	847vw	845vw	841w	841vw	843vw	841vw	843vw

Table II. Continued

Assignment[a]	Cd-Ni-G G=Toluene	Co-Ni-G G=*p*-Xylene	Ni-Ni-G G=*p*-Xylene	Cd-Ni-G G=*p*-Xylene	Co-Ni-G G=Naphthalene	Ni-Ni-G G=Naphthalene	Cd-Ni-G G=Naphthalene	Co-Ni-G G=Biphenyl	Ni-Ni-G G=Biphenyl	Cd-Ni-G G=Biphenyl
$\nu(NH_2)$	3350s	3351s	3352s	3352s	3342s	3346s	3344s	3338s	3350s	3340s
$\nu(NH_2)$	3290s	3290s	3292s	3292s	3286s	3288s	3286s	3280s	3292s	3282s
$\nu(CH_2)$	2924s	2926s	2924s	2924s	2926s	2926s	2924s	2918s	2922s	2918s
$\nu(CH_2)$	2854s	2853s	2854s	2853s	2856s	2854s	2854s	2850s	2852s	2850s
$\delta(NH_2)$	1589s	1589s	1589m	1589s	1587m	1589m	1587m	1587m	1589m	1587m
$\delta(CH_2)$	1493vw	1495vw	1495vw	1495vw	1495vw	1493vw	1495vw	1497vw	–	1498vw
$\delta(CH_2)$	1471m	1470m	1470m	1470m	1470m	1470m	1469m	1470m	1468m	1470m
$\delta(CH_2)$	1458vw	1458vw	1458vw	1456vw	1461w	1460w	1464w	1462w	1460w	1460w
$\rho_w(CH_2)$	–	1396vw	1396vw	1396vw	–	–	–	–	1396vw	–
$\rho_w(CH_2)$	1385vw	1388vw	1389w	1387w	1389vw	1389vw	1387w	1384vw	1385vw	1380vw
$\rho_t(CH_2)$	1365w	1365w	1367w	1365w	1367vw	1367vw	1365w	1362vw	1363vw	1362w
$\rho_t(NH_2)$	1213vw	1213vw	1213vw	1215vw	1215vw	1213vw	1215vw	1211vw	1211vw	1211vw
$\nu(CN)$	1090m	1095m	1097m	1089m	1103m	1103m	1095m	1101m	1101m	1089m
$\nu(CN)$	1066vw	1064vw	1065vw	1065vw	1063vw	1065vw	1065vw	1059vw	1061vw	1059vw
$\rho_w(NH_2)$	993m	993m	997m	991m	999m	1001m	997m	995m	999m	989m
$\rho_r(CH_2)$	966m	966m	968m	964m	968m	971m	970m	966m	970m	962m
$\rho_r(CH_2)$	843vw	841w	841vw	843vw	839w	842vw	843vw	840w	845vw	841vw

[a] Taken From Ref. [19].
[b] Solution in CCl_4 and $CHCl_3$.
[c] Cd(1,8-diaminooctane)$Ni(CN)_4$.
v = very, s = strong, m = medium, w = weak, br = broad, sh = shoulder.

Table III. The vibrational wavenumbers (cm^{-1}) of the cyanide group in the M-Ni-G compounds.

Assignment[a]	$Na_2Ni(CN)_4$[a]	Cd-Ni-Bz[b,c]	Cd-Ni[d,e]	Cd-Ni[f]	Co-Ni-G G=Benzene	Ni-Ni-G G=Benzene	Cd-Ni-G G=Benzene	
ν_8(CN),E_u	2132	2156vs	2147vs	2148vs	2160vs	2167vs	2148vs	
	2128	–	–	–	–	–	–	
ν_9(NiC),E_u	543	554m,br	548sh	546vw	550m	573m	538m	
ν_9(NiC),E_u	–	–	–	525m	–	557vw	523vw	
π(NiC),A_{2u}	448	446w	447sh	–	455vw	457vw	447vw	
δ(NiCN),E_u	433	425vs	423vs	424vs	436s	438s	424s	
Assignment[a]	Co-Ni-G G=Chlorobenzene	Ni-Ni-G G=Chlorobenzene	Cd-Ni-G G=Chlorobenzene	Co-Ni-G G=Toluene	Ni-Ni-G G=Toluene	Cd-Ni-G G=Toluene	Co-Ni-G G=*p*-Xylene	Ni-Ni-G G=*p*-Xylene
ν_8(CN),E_u	2154vs	2166vs	2146vs	2145vs	2160vs	2146vs	2154vs	2160s
	–	–	–	–	–	–	–	–
ν_9(NiC),E_u	557m	579m	536m	559m	580m	538m	553m	575m
ν_9(NiC),E_u	528vw	–	523vw	528vw	552vw	523vw	526vw	532vw
π(NiC),A_{2u}	451vw	457vw	–	451vw	455vw	434vw	451vw	455vw
δ(NiCN),E_u	434vs	440vs	424vs	434vs	438vs	424vs	434vs	436vs
Assignment[a]	Cd-Ni-G G=*p*-Xylene	Co-Ni-G G=Naphthalene	Ni-Ni-G G=Naphthalene	Cd-Ni-G G=Naphthalene	Co-Ni-G G=Biphenyl	Ni-Ni-G G=Biphenyl	Cd-Ni-G G=Biphenyl	
ν_8(CN),E_u	2146vs	2152vs	2168vs	2164	2162vs	2168vs	2154vs	
	–	–	–	–	–	–	–	
ν_9(NiC),E_u	532m	561m	582m	550m	556m	579m	534m	
ν_9(NiC),E_u	523vw	528vw	532vw	525vw	543vw	546vw	517vw	
π(NiC),A_{2u}	–	451vw	453vw	–	–	457vw	–	
δ(NiCN),E_u	424vs	432vs	435vs	422vs	436vs	440vs	424vs	

[a] Taken From Ref.[8]. [b] $Cd(NH_3)_2Ni(CN)_4 \cdot 2C_6H_6$ [c] Taken From Ref.[9]. [d] $Cd(3,4\text{-Lutidine})_2Ni(CN)_4$.
[e] Taken From Ref.[10]. [f] Cd(1,8-diaminooctane)$Ni(CN)_4$.
v=very, s=strong, m=medium, w=weak, br=broad, sh=shoulder.

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

Assignment[a]	Liquid Benzene[b]	Cd-Cd-G[d,e] G=Benzene	Cd-Ni-G[f,g] G=Benzene	Co-Ni-G G=Benzene	Ni-Ni-G G=Benzene	Cd-Ni-G G=Benzene
ν_{20},E_{1u}	3073	3080m	3029w	3088m	3088m	3085m
$\nu_8+\nu_{19}$,E_{1u}	3086[c]	3064m	3082m	3069w	3068w	3064w
ν_{13},B_{1u}	3063[c]	3028s	3063w	3033m	3032m	3026m
$\nu_5+\nu_{17}$ E_{1u}	1965[c]	–	1986m	1967vw	1966w	1967vw
$\nu_{10}+\nu_{17}$, E_{1u}	1820[c]	–	1848m	1820w	1820w	1825w
ν_{19},E_{1u}	1479	1477m	1474s	1478w	1478w	1476w
ν_{14},B_{2u}	1309	–	1313vw	1306vw	1304w	1301w
ν_{15},B_{2u}	1149	1145sh	1146s	1136vw	1138vw	1151w
ν_{18},E_{1u}	1036	1032w	1032vs	1037m	1036m	1037w
ν_{17},E_{2u}	966	–	984m	–	–	–
ν_{11},A_{2u}	670	698s	700vs	685vs	684vs	687vs
	–	686vs	–	–	–	–
ν_{16},E_{2u}	404	–	405w	–	–	–

[a] Taken From Ref. [20].
[b] Taken From Ref. [12].
[c] Taken From Ref. [21]. [d] $Cd(NH_3)_2Cd(CN)_4{\cdot}2C_6H_6$.
[e] Taken From Ref.[18].
[f] $Cd(NH_3)_2Ni(CN)_4{\cdot}2C_6H_6$.
[g] Taken From Ref.[9].
v = very, s = strong, m = medium, w = weak, sh = shoulder.

the daon molecule related to its interaction with different guest molecules and to the presence of the different transition metals. The infrared spectrum of the $Cd(daon)Ni(CN)_4$ host is also reported for comparison.

2. Experimental

All chemicals used were reagent grade (Merck) and used without further purification.

The compounds $M(daon)Ni(CN)_4{\cdot}$ G (M=Co, Ni or Cd; G=benzene, chlorobenzene, toluene, *p*-xylene, naphthalene or biphenyl) were prepared by adding slightly more than one millimole of 1,8-diaminooctane to one millimole of $K_2Ni(CN)_4$ and one millimole of MCl_2 solution in water saturated with guest. The precipitate was filtered, washed with water, ethanol and ether, successively, and kept in a desiccator containing molecular sieves and saturated guest vapour.

The freshly prepared compounds were analyzed for M (M=Co, Ni or Cd) by AAS (Philips, PU 9200), and C, H and N by a LECO CHNS-932 analyzer (Table I). The poor results (in Table I) are due to the instability under ambient conditions of compounds with small guest molecules, such as benzene and chlorobenzene.

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

Assignment[a]	Liquid Chlorobenzene[a]	Co-Ni-G G=Chlorobenzene	Ni-Ni-G G=Chlorobenzene	Cd-Ni-G G=Chlorobenzene
$\nu(CH)$,A_1	3087w,sh	–	3087vw	–
$\nu(CH)$,B_2	3072s	3078vw	3070vw	3076vw
$\nu(CH)$,A_1	3060w,sh	–	–	–
$\nu(CH)$,A_1	3030w,sh	–	3032vw	–
$\nu(CH)$,B_1	3006w	–	–	–
$\nu(CC)$,B_2	1586s	1580w,sh	–	1579w,sh
$\nu(CC)$,A_1	1571w,sh	1560vw	1562w,sh	1562vw
$\nu(CC)$,A_1	1479vs	1479w	1477w	1479w
$\nu(CC)$,B_2	1447s	1444vw	1444vw	1444vw
$\beta(CH)$,A_1	1123w	–	–	–
$\beta(CH)$,B_2	1084s	1081w	1082w	1080w
$\beta(CH)$,B_2	1069vw	–	–	–
$\beta(CH)$,A_1	1023m	1021w	1022vw	1022vw
$\gamma(CH)$,B_1	1003vw	1002vw,sh	–	1001vw
$\gamma(CH)$,B_1	902vw	907vw	–	908vw
$\gamma(CH)$,B_1	741vs	749s	748s	750s
$\delta(ring)$,B_1	702s	701m	702m	700m
$\delta(ring)$,B_2	687s	688m	685m	687m
$\delta(ring)$,B_1	471m	470w	469w	469w

[a] Taken From Ref. [13].
v = very, s = strong, m = medium, w = weak, sh = shoulder.

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 polystyrene film and indene solution. The samples were prepared as mulls in Nujol and hexachlorobutadiene in a KBr cell.

3. Result and Discussion

The infrared (IR) spectra of the compounds M-Ni-G (M=Co, Ni or Cd; G=benzene, chlorobenzene, toluene, p-xylene, naphthalene or biphenyl) are very similar. The similarities between the IR spectral features of the compounds suggest that they also have similar structural features. These in turn suggest that the degrees of the interactions of the guest molecules, the daon ligand and the $Ni(CN)_4$ species with their surroundings are almost the same for each compound. It will be most convenient to divide the infrared vibrations into three groups arising from the daon ligands, from the $Ni(CN)_4$ units and from the guest molecule moieties, respectively. The infrared wavenumbers of the bands in the spectra of these species are

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

Assignment[a]	Liquid Toluene[a]	Co-Ni-G G=Toluene	Ni-Ni-G G=Toluene	Cd-Ni-G G=Toluene
$\nu(CH), A_1$	3085	3080vw	3086vw	3083vw
$\nu(CH), A_1$	3070	–	–	–
$\nu(CH), A_1$	3058	3061vw	3065vw	–
$\nu(CH), B_2$	3037	3030w	3033w	3030vw
$\nu(CH), B_2$	3028	–	–	–
$\nu(CH_3), B_1$	2979	2987m	2989m	2980m
$\nu(CH_3), B_2$	2950	2964vw	2960vw	2954vw
$\nu(CH_3), A_1$	2920	–	–	–
$\nu(CC), A_1$	1604	1602vw	1603vw	1600vw
$\nu(CC), B_2$	1584	1581s,sh	1578s,sh	1581m,sh
$\nu(CC), A_1$	1493	–	–	–
$\delta(CH_3), B_2$	1455	1477m	1478m	1477m
$\delta(CH_3), A_1$	1378	–	–	–
$\nu(CC), B_2$	1331	–	–	–
$\beta(CH), B_2$	1313	1309vw	1304vw	1310vw
$\nu(C-CH_3)_{X-sens}, A_1$	1208	–	–	–
$\beta(CH), A_1$	1176	1173vw	1171vw	1300w
$\beta(CH), B_2$	1153	1155w	1157w	1155w
$\beta(CH), B_2$	1080	1081w	1082w	1082w,sh
$r(CH_3), B_1$	1040	1043vw	1040vw	1041vw
$\beta(CH), A_1$	1028	1022w	1022w	1021w
$Ring, A_1$	1002	–	–	–
$\gamma(CH), B_1$	983	–	–	–
$\gamma(CH), B_1$	893	–	–	–
$\alpha(CCC)_{X-sens}, A_1$	784	795w	793w	796w
$\gamma(CH), B_1$	734	749s	749s	750s
$\phi(CC), B_2$	690	701m	702m	701m
?	–	687m	685m	688m
$\alpha(CCC), B_2$	620	–	–	–
$\alpha(CCC)_{X-sens}, A_1$	524	530vw	528vw	523vw
$\phi(CC)_{X-sens}, B_1$	467	470vw	469vw	–

[a] Taken From Ref. [14].
v = very, s = strong, m = medium, w = weak, sh = shoulder.

tabulated in Tables II–IX, respectively, together with some relevant spectral data for comparison.

From the present spectral data it is not possible to obtain the conformation of the daon molecules in the compounds. However, some results can be found from the structure of Cd(daon)Ni(CN)$_4$· G (G= *o*-toluidine or *p*-toluidine): the daon ligand

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

Assignment[a]	Liquid *p*-Xylene[a]	Co-Ni-G G = *p*-Xylene	Ni-Ni-G G = *p*-Xylene	Cd-Ni-G G = *p*-Xylene
$\nu(CH), B_{1u}$	3044	–	–	–
$\nu(CH), B_{2u}$	3017	3018vw	3018vw	3020vw
$\nu(CH_3), B_{2u}$	2975	2985w	2989w	2978w
	2947	–	–	–
$\nu(CH_3), B_{3u}$	2923	–	–	–
$\nu(CC), B_{1u}$	1529	1516w	1516w	1516w
$\delta(CH_3), B_{3u}$	1458	1475w,sh	1477w,sh	1474w,sh
	1452	–	–	–
$\nu(CC), B_{2u}$	1421	1435vw	1436vw	1433vw
$\delta(CH_3), B_{1u}$	1379	–	–	–
$\alpha(CCC), B_{2u}$	1324	–	–	–
$X-sens, B_{1u}$	1220	–	–	–
$\beta(CH), B_{2u}$	1120	1119vw	1119vw	1118vw
$r(CH_3), B_{2u}$	1041	1049m	1049m	1043m
$\beta(CH), B_{1u}$	1023	1022vw	1022vw	1020vw
$\gamma(CH), B_{3u}$	795	796s	795s	796s
$X-sens, B_{1u}$	725	729m	729m	733m
$\phi(CC), B_{3u}$	483	484w	484w	484w

[a] Taken From Ref. [15].
v = very, s = strong, m = medium, w = weak, sh = shoulder.

molecules bridging the cadmium atoms in adjacent cyanometal complex sheets are in a $trans$ conformation [5]. The shape of the unit cell is distorted by the bending of the two-dimensional cyanometal complex sheets [4–7]. Some of the cavities in the unit cell are occupied by the ligand molecules in place of the guest [5–7].

3.1. VIBRATIONS OF 1,8-DIAMINOOCTANE

The assignments and the wavenumbers of the infrared bands of the daon molecule observed in the spectra of the compounds under study are given in Table II, together with the spectral data for the daon molecule in the liquid phase and in solution in CCl_4 and $CHCl_3$ on which the assignments are based. To the best of our knowledge no vibrational assignment has been reported for the free daon molecule in literature.

The bands observed in the range 3350–3280 cm^{-1} (Table II) assigned to the NH_2 symmetric and asymmetric stretching frequencies which are lower than the corresponding values of the free daon molecule are characteristic of coordinated —NH_2 groups.

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

Assignment[a]	Naphthalene[a]	Co-Ni-G G=Naphthalene	Ni-Ni-G G=Naphthalene	Cd-Ni-G G=Naphthalene
ν_{41}, B_{3u}	3072	3066w	3064w	3062w
?		3047w	3049w	3048w
ν_{29}, B_{2u}	3014	3012vw	3012vw	3012vw
ν_{42}, B_{3u}	2976	2987m	2989m	2979m
ν_{30}, B_{2u}	2947	2964vw	2960vw	2960vw
ν_{43}, B_{3u}	1680	–	–	–
ν_{31}, B_{2u}	1595	1593s,sh	1593s,sh	1593s,sh
ν_{44}, B_{3u}	1510	1504m	1506m	1504m
ν_{32}, B_{2u}	1387	1389w	1389w	1387w
ν_{33}, B_{2u}	1268	1269m	1267m	1269m
ν_{45}, B_{3u}	1211	–	–	–
ν_{34}, B_{2u}	1139	1130w	1128w	1130w
ν_{46}, B_{3u}	1012	1009w	1010w,sh	1011w
ν_{22}, B_{1u}	957	–	–	–
ν_{47}, B_{3u}	876	–	879vw	–
ν_{23}, B_{1u}	782	795vs	793vs	796vs
ν_{35}, B_{2u}	752	752vw	752vw	754vw
ν_{48}, B_{3u}	618	619w	619w	619w
ν_{24}, B_{1u}	475	480s	478s	480s

[a] Taken From Ref. [16].
v = very, s = strong, m = medium, w = weak, sh = shoulder.

3.2. $Ni(CN)_4$ GROUP VIBRATIONS

The bands of the $Ni(CN)_4$ ion in the compounds were assigned on the basis of the work of McCullough et al. who presented vibrational data for the $Ni(CN)_4^{2-}$ ion in $Na_2Ni(CN)_4$ [8].

The assigned wavenumbers for $Ni(CN)_4$ groups in our compounds are given in Table III, together with the vibrational wavenumbers of $Na_2Ni(CN)_4$. Table III also lists the wavenumbers of the IR spectra of the $Ni(CN)_4$ group in the benzene clathrates $Cd(NH_3)_2Ni(CN)_4{\cdot}2C_6H_6$ [9] and in the complex compound Cd(3,4-lutidine)$_2$Ni(CN)$_4$ [10] for comparison.

If the unit cell has the D_{4h} symmetry, only four fundamental vibrations are expected in the infrared spectrum above 400 cm^{-1} [11]. Four fundamental bands are assigned in the infrared spectra of the compounds (Table III). Therefore, since no splitting of the infrared E_u mode occurs, the slight distortion from tetragonal symmetry seems to be too small to have any effect on the vibrational spectra. The characteristic frequencies of the $Ni(CN)_4$ group suggest that the $[Cd—Ni(CN)_4]_\infty$ layers have been preserved.

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

Assignment[a]	Biphenyl[a]	Co-Ni-G G=Biphenyl	Ni-Ni-G G=Biphenyl	Cd-Ni-G G=Biphenyl
ν_1, B_{3u}	3080	3084w	3078vw	3082w
ν_2, B_{3u}	3072[b]	3064w	3062vw	3070w
ν_{12}, B_{2u}	3069[b]	3047vw	3043vw	3045vw
ν_{13}, B_{2u}	3068[b]	3034w	3030w	3030m
ν_4, B_{3u}	1597	1599m	1599m,sh	1600s
ν_{14}, B_{2u}	1570	1570m	1568m	1570m
ν_5, B_{3u}	1482	1480s	1479s	1481s
ν_{15}, B_{2u}	1432	1431m	1431m	1429m
ν_{16}, B_{2u}	1383	–	–	–
ν_{17}, B_{2u}	1283	1269vw	1267vw	1269vw
ν_6, B_{3u}	1176	1180vw	1178vw	1178vw
ν_{18}, B_{2u}	1156	1157vw	1159vw	1163vw
ν_{19}, B_{2u}	1074	1076m	1076m	1076m
ν_7, B_{3u}	1040	1043w	1043w	1039w
ν_8, B_{3u}	1008	1009vw	1009vw	1009vw
ν_9, B_{3u}	965	–	–	–
ν_{23}, B_{1u}	903	903w	908w	908w
ν_{24}, B_{1u}	736	739s	744s	740s
ν_{25}, B_{1u}	698	700s	700s	700s
ν_{19}, B_{2u}	626	–	–	–
ν_{10}, B_{3u}	609	609w	609w	609w
ν_{26}, B_{1u}	484	486vw,br	484vw,br	–

[a] Taken From Ref. [17].
[b] Calculated value [17].
v = very, s = strong, m = medium, w = weak, br = broad, sh = shoulder.

The vibration frequencies of the $Ni(CN)_4$ group in the compounds studied appear to be shifted relative to isolated $Ni(CN)_4$ units. Such frequency shifts have been observed for other Hofmann-type clathrates, $M(NH_3)_2Ni(CN)_4 \cdot 2C_6H_6$ (M=Ni, Cd, Cu, Zn) [9], and Hofmann-type host complexes M(3,4-lutidine)$_2$ $Ni(CN)_4$ (M=Mn, Fe, Co, Zu, Ni, Cu or Cd) [10], in which both ends of the CN group are bonded to transition metals and explained as the mechanical coupling of the internal modes of $Ni(CN)_4$ with the metal (M—NC) vibrations [9-11].

3.3. Vibrations of Guest Molecules

The assignments and the wavenumbers of the bands arising from the guest molecules observed in the IR spectra of M-Ni-G (M=Co, Ni or Cd; G=benzene, chlorobenzene, toluene, *p*-xylene, naphthalene or biphenyl) compounds are given

in Tables IV–IX, respectively, together with the wavenumbers of the free guest molecule on which the assignments are based. The assignment of the guest molecule wavenumbers in the infrared spectra of the clathrate compounds were based on the studies of Painter and Koening [12], Steel and Lippincott [13], Hitchcock and Laposa [14], Green [15], Lippincott and O'Reilly [16], Zerbi and Sandroni [17], respectively. The most outstanding spectral features are the following.

Our assignment of the guest molecule bands in the IR spectrum of M-Ni-G clathrates agrees with that of the literature [12–17]. The infrared spectral data of the compounds under study suggest that the guest molecules retain the free molecule symmetry.

The CH out-of-plane (ν_{11}, A_{2u}) vibrational band in the infrared spectra of the benzene compounds M-Ni-G (M=Co, Ni or Cd; G=benzene) (Table IV), is found to be shifted to higher frequency from that of liquid benzene. Similar positive shifts were observed for Hofmann-type [9] and T_d-type [18] clathrates. This upward shift was explained by weak hydrogen bonding between π electrons located above and below the plane of the benzene ring and the daon molecule of the host lattice [9,18]. The shift of the CH out-of-plane vibrational band of the studied compounds is smaller than that in Hofmann-type and T_d-type clathrate compounds because of the weaker host-guest interaction.

We assigned the wavenumbers in the infrared spectra of the chlorobenzene clathrates by comparision with the assignment of the C_6H_5F molecule in the work of Steel and Lippincott [13].

Several modes of the toluene or *p*-xylene molecules (—CH_3 vibrations, Tables VI–VII, respectively) and of the naphthalene or biphenyl molecules (CH stretching vibrations, Tables VIII–IX, respectively) have upward shifts in frequency compared to those in the free guest molecules. These shifts may occur due to the effect of weak hydrogen bonding. The vibration mode ($\phi(CC)$) at about 690 cm^{-1} was split by Fermi resonance (Table VI), and two bands at about 687 cm^{-1} and 701 cm^{-1} were observed for the toluene molecule.

The preceeding discussion considered together leads us to the conclussion that the compounds M(daon)Ni$(CN)_4$·G (M= Co, Ni or Cd; G=benzene, chlorobenzene, toluene, *p*-xylene, naphthalene or biphenyl) are similar in structure to the Hofmann-daon-type clathrates Cd(daon)Ni$(CN)_4$·G (G=*o*-toluidine or *p*-toluidine) [5]. Similar studies for 1,12-diaminododecane based compounds are in progress.

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