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INFRARED SPECTROSCOPIC STUDY OF THE HOFMANN-DIAM-TYPE CLATHRATES : M(1,6-DIAMINOHEXANE)Ni(CN)$_4$ ·C$_6$H$_6$ (M=Ni, Co or Cd)

Keywords: IR spectra, Hofmann-diam-type , tetracyanonickelate, 1,6-diaminohexane, benzene.

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ABSTRACT

Infrared spectra of M(1,6-diaminohexane)Ni(CN)$_4$·C$_6$H$_6$ (M=Co, Ni or Cd) are reported. The spectral data suggest that the compounds are similar in structure to Cd(1,6-diaminohexane)Ni(CN)$_4$·m-Toluidine and have Hofmann-diam-type structure.

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

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ligands by the α,ω-diaminoalkane ligands behaving ambidently, with the aim of enlarging the range of guest molecules that can be accommodated in the host lattices [1-5]. Recently, Iwamoto et al. are determined to the crystal structure of $Cd(dahxn)Ni(CN)_4 \cdot G$ (dahxn=1,6-diaminohexane, G=o-toluidine [2] and p-toluidine[4] in the monoclinic space group P2/m, G=m-toluidine [4] in the triclinic space group $P\bar{1}$) by single crystal X-ray diffraction methods. These [1-5] and other [6,7] studies show that the series of the Hofmann-diam-type clathrates are not isomorphous with each other.

This paper reports the two newly prepared $M(dahxn)Ni(CN)_4 \cdot C_6H_6$ (M=Co or Ni) (abbreviated to M-Ni-Bz) compounds and we are also reported the $Cd(dahxn)Ni(CN)_4 \cdot G$ (G=Benzene or m-toluidine) for a comparison. The infrared spectral features of the $M(dahxn)Ni(CN)_4 \cdot C_6H_6$ (M=Co, Ni or Cd) compounds are similar to that of $Cd(dahxn)Ni(CN)_4 \cdot$m-toluidine clathrate.

EXPERIMENTAL

The compounds $M(dahxn)Ni(CN)_4 \cdot C_6H_6$ (M= Ni , Co or Cd) were prepared by adding slightly more than one millimole of 1,6-diaminohexane to one millimole of $K_2Ni(CN)_4$ and one millimole of MCl_2 solution in water saturated with the guest molecule. The compound $Cd(dahxn)Ni(CN)_4 \cdot m\text{-}MeC_6H_4NH_2$ were prepared by a procedure similar to those already reported [2]. Infrared spectra of the compounds as mulls in nujol and KBr discs were recorded on MATTSON 1000 FTIR spectrometer in the range of the 4000 to 400 cm^{-1}. The freshly prepared compounds were analyzed for C, H and N by a LECO CHNS-932 analyzer. The results are as follows (found%/ calculated%):

$Co(C_6H_{16}N_2)Ni(CN)_4 \cdot C_6H_6$: C=46.07/46.19, H=5.14/5.33, N=20.02/20.20;

$Ni(C_6H_{16}N_2)Ni(CN)_4 \cdot C_6H_6$: C=45.94/ 46.22, H=5.12/5.33, N=19.86/20.21;

$Cd(C_6H_{16}N_2)Ni(CN)_4 \cdot C_6H_6$: C=39.87/40.93, H=4.29/4.72, N=17.84/17.90;

RESULT AND DISCUSSION

The infrared (IR) spectral features of the compounds M-Ni-Bz (M=Ni, Co or Cd) are found to be similar to each other. The similar spectral features of the

compounds suggest that they have similar analogous structural features and degrees of the interactions suggest that they have similar structural features and degrees of the interaction of the benzene, *dahxn* ligand and $Ni(CN)_4$ species with their surroundings are almost the same for each compound. The symmetry restrictions of the compounds with different crystal symmetry possibilities are not effective. It may be most convenient to divide the vibrations into three groups arising from the *dahxn* ligands, from the $Ni(CN)_4$ units and from the benzene moieties, respectively. The vibrational wavenumbers of the bands in the spectra of these species are tabulated in Tables 1-3, respectively, together with some pertinent spectral data for a comparison.

No complete vibrational assignment has been reported for the free *dahxn* molecule in the literature. The assignments and the wavenumbers of the vibrational bands of the free *dahxn* molecule observed in the spectra of the compounds studied are given in Table 1, together with our spectral data for *dahxn* molecule in the liquid phase and in solution in CCl_4 on which the assignments are based. The NH_2 stretching frequencies which are lower than the corresponding values of the free *dahxn* molecule (in Table 1) show that ligand molecules bound directly to the metal M (M=Co, Ni or Cd). Several modes of the coordinated *dahxn* molecule have upward shifts in freqency in comparison with those of liquid *dahxn* and the shifts are metal dependent. General increase in frequency of the *dahxn* modes with the different metals in our compounds is in the order: Cd≤Co<Ni, which is in agreement with the increasing order of the second ionization potential of the metals. The similar observation were also reported in Hofmann-type clathrates [9]. Considering the present spectral data it is not possible to give an account on the conformation of the *dahxn* ligand in our compounds. However, some implication may be deduced from the Cd(dahxn)$Ni(CN)_4$ .G (G=m-, o- or p-toluidine): X-ray difraction studies have shown that the *dahxn* molecules in Cd(dahxn)$Ni(CN)_4$ .G (G=m-, o- or p-toluidine) are in all *trans* conformation [2,4]. Therefore the flexible *dahxn* molecule is also expected to be in *trans* form in the compounds studied.

In assigning the bands characteristic to the $Ni(CN)_4^{2-}$ ion in the spectra of the compounds under study we refer to the work of McCullough et al. whose

TABLE 1

The vibrational wavenumbers (cm^{-1}) of 1,6-diaminohexane in the M-Ni-Bz compounds.

Assignment[a]	Liquid dahxn[b]	Cd-Ni-G[c]	Co-Ni-Bz	Ni-Ni-Bz	Cd-Ni-Bz
ν (NH_2)	3377s	3342s	3344s	3348s	3348s
ν (NH_2)	3286s	3284s	3286s	3288s	3290s
ν (CH_2)	2927vs	2924vs	2926vs	2927vs	2924vs
ν (CH_2)	2854vs	2855vs	2858vs	2860vs	2858vs
δ (NH_2)	1578s	1591m	1585m	1587m	1587m
δ (CH_2)	1485s	1493m	1495w	1495w	1494w
δ (CH_2)	1437w	1448vw	1442vw	1443vw	1443vw
ρ_w (CH_2)	1389w	1387vw	1383vw	1383vw	1383vw
ρ_w (CH_2)	1338w	1338vw	1336vw	1338vw	1336vw
ρ_r (NH_2)	1305vw	1294vw	-	-	-
ν (CN)	1075m	1079m	1090m	1092m	1080m
ρ_w (NH_2)	1052vw	1058w	1066w	1066w	1062w,sh
?	-	1011w	1014w	1016vw	1014m
ρ_r (CH_2)	975vw	962m	968m	972m	964m
ρ_r (CH_2)	832m,br	868vw	860vw	868vw	858vw
ρ_r (CH_2)	725w	740w	737w	736w	737w

[a] Taken From Ref. [8]. [b] The solution in CCl_4. [c] Cd(dahxn)Ni(CN)$_4$.m-toluidine. v=very, s=strong, m=medium, w=weak, br=broad, sh=shoulder.

TABLE 2

The vibrational wavenumbers (cm^{-1}) of Cyanide group for the M-Ni-Bz compounds.

Assignment [a]	$Na_2Ni(CN)_4$[a]	Cd-Ni-G[b,c]	Cd-Ni-G[d]	Co-Ni-Bz	Ni-Ni-Bz	Cd-Ni-Bz
ν_8 (CN), E_u	2132	2156vs	2150vs	2154vs	2160vs	2146vs
	2128	-	-	-	-	
ν_9 (NiC), E_u	543	554m,br	555m	563m	584m	550m
ν_9 (NiC), E_u	-	-	536w	548w	551w	542w
π (NiC), A_{2u}	448	446vw	457vw	451vw	453vw	467vw
δ (NiCN), E_u	433	425vs	424vs	434s	436s	424s

[a] Taken From Ref. [10]. [b] $Cd(NH_3)_2Ni(CN)_4 .2C_6H_6$. [c] Taken From Ref. [9]. [d] Cd(dahxn)Ni(CN)$_4$.m-toluidine. v=very, s=strong, m=medium, w=weak, br=broad.

TABLE 3

The vibrational wavenumbers (cm^{-1}) of guest benzene molecule in the M-Ni-Bz compounds.

Assignments[a]	Liquid Benzene[b]	Cd-Cd-Bz[c,d]	Co-Ni-Bz	Ni-Ni-Bz	Cd-Ni-Bz
ν_{20}, E_{1u}	3073	3080m	3080m	3082m	3078m
$\nu_8 + \nu_{19}$	3075	3064m	3061w	3062m	3060m
ν_{13}, B_{1u}	-	3028s	3022s	3023s	3022s
$\nu_5 + \nu_{17}, E_{1u}$	1955	-	1977w	1977w	1979w
$\nu_{10} + \nu_{17}$	1815	-	1828w	1830w	1830w
ν_{19}, E_{1u}	1479	1477m	1474m	1475m	1474m
ν_{14}, B_{2u}	1309	-	1311vw	1306vw	1309vw
ν_{15}, B_{2u}	1149	1145sh	1146vw	1148vw	1146vw
ν_{18}, E_{1u}	1036	1032w	1034w	1032w	1034w
ν_{11}, A_{2u}	670	698s	690vs	690vs	690vs
	-	686vs	-	-	-

[a] Taken From Ref. [13]. [b] Taken From Ref. [11]. [c] $Cd(NH_3)_2Cd(CN)_4.2C_6H_6$. [d] Taken From Ref. [12]. v=very, s=strong, w=weak, m=medium. sh=shoulder.

presented vibrational data for the ion $Ni(CN)_4^{2-}$ in $Na_2Ni(CN)_4$ [10]. The ion $Ni(CN)_4^{2-}$ can be entertainment 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 considered are given in Table 2, together with the vibrational wavenumbers of $Na_2Ni(CN)_4$. The wavenumbers of the IR spectra of the $Ni(CN)_4$ group in the clathrate, $Cd(NH_3)_2Ni(CN)_4.2C_6H_6$ [9], are also listed for a 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 [9] 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 (Co, Ni or Cd)-NC vibrations. The characteristic frequencies of $Ni(CN)_4$ 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 benzene molecule observed in the IR spectra of M-Ni-Bz (M=Co, Ni and Cd) compounds together with that of the benzene in liquid phase [11] are given in Table 3. Our band assignment of the benzene molecules in the IR spectrum for the compounds studied agrees with that Hofmann-type [9] and Hofmann Td-type clathrates [12], and host-guest interactions in the clathrate structure are not effective due to the long *dahxn* ligand, and the benzene molecules are also kept free molecule symmetry (D_{6h}).

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