IR Spectroscopic Study of M(Benzoic Acid)$_2$Ni(CN)$_4$·(1,4-Dioxane) Clathrate (M = Ni, Cd and Co)

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Z. Naturforsch. **60a,** 469 – 472 (2005); received March 8, 2005

In this study, clathrate of benzoic acid-tetracyanonickel, given by the formula M(benzoic acid)$_2$Ni(CN)$_4$·(1,4-dioxane) (M = Ni, Cd and Co), is obtained for the first time through chemical methods. The similarities of the observed spectra indicate that the obtained clathrate of benzoic acid-tetracyanonickel is a new example of Hofmann-type clathrates. – PACS numbers: 33.20.Ea, 33.20.Tp

Key words: Inclusion Compounds; Benzoic Acid (BA); Infrared Spectroscopy (IR); Hofmann-type Clathrate.

1. Introduction

In various studies, Hofmann-type clathrates, given by the general formula ML$_2$Ni(CN)$_4$·G, were produced. Here M is a transition metal atom, L a ligand molecule or half of a bidentate ligand molecule, and G a guest molecule [1]. The clathrates are of interest because of their inclusion behavior and use as catalysts, anti-oxidants and stabilizing agents [2]. Infrared spectroscopy is one of the best ways for the investigation of the guest-host interactions in Hofmann-type clathrates.

In our previous study we reported Hofmann-type complexes for the benzoic acid (BA) [3]. In this study we used 1,4-dioxane (D) as a guest (G) molecule to produce new Hofmann-type clathrates with the formula M(BA)$_2$Ni(CN)$_4$·G, where M is a transition metal atom (Ni, Cd or Co).

2. Experimental

All chemicals, namely BA ($C_7H_6O_2$, Fluka, $\geq$ 99.5%), $NiCl_2 \cdot 6H_2O$ (Fluka, 98%), $CdCl_2 \cdot 2H_2O$ (Fluka, 96%), $CoCl_2 \cdot 6H_2O$ (Fluka, 99%), ($C_4H_8O_2$, Merck, 99%) and KCN (Fluka, 98%), were used without further purification. First KCN and $NiCl_2 \cdot 6H_2O$ were used for obtaining $K_2Ni(CN)_4$. 1 mmol of $K_2Ni(CN)_4$ was solved in water. 2 mmol of BA were added to this solution. Then 5 mmol of D were added to the mixture. After that, a solution of 1 mmol MCl_2 (M = Ni, Cd and Co) in water was added to the mixtures, which were stirred during 5 d. The compounds prepared were filtered, washed with pure water, ethanol and diethyl ether, and kept in a desiccator containing D vapour. The infrared spectra of the compounds were recorded at room temperature with a Perkin-Elmer BX FT-IR Spectrometer having a resolution of 4 cm^{-1}.

3. Results and Discussion

The IR spectrum of Cd(BA)$_2$Ni(CN)$_4$·D clathrate is shown in Fig. 1 as an example. Owing to the lack of structural clathrate studies, the assignment was made by analyzing the obtained IR spectral data for vibrating a) ligand molecules, b) $[Ni(CN)_4]^{2-}$ ions and c) guest D-molecules.

3.1. Ligand Molecules

The assignment of the IR vibrational frequencies for solid BA has been referred by Stepanian et al. [4]. Some shifted frequencies of the BA molecule can be seen in Table 1. These frequencies were shifted due to the occurence of new clathrates. There are two reasons for the observed small frequency shifts. The first one are changes of the surround of the BA molecule. The second one is the pairing of the internal vibration of the BA molecule with the vibrations of the M-O band [5 – 6].

However, important frequency shifts were observed at stretched frequencies for C=O str and OH str. For example, the frequencies of C=O str at 1700 cm^{-1} for the solid BA molecule were shifted to lower frequencies

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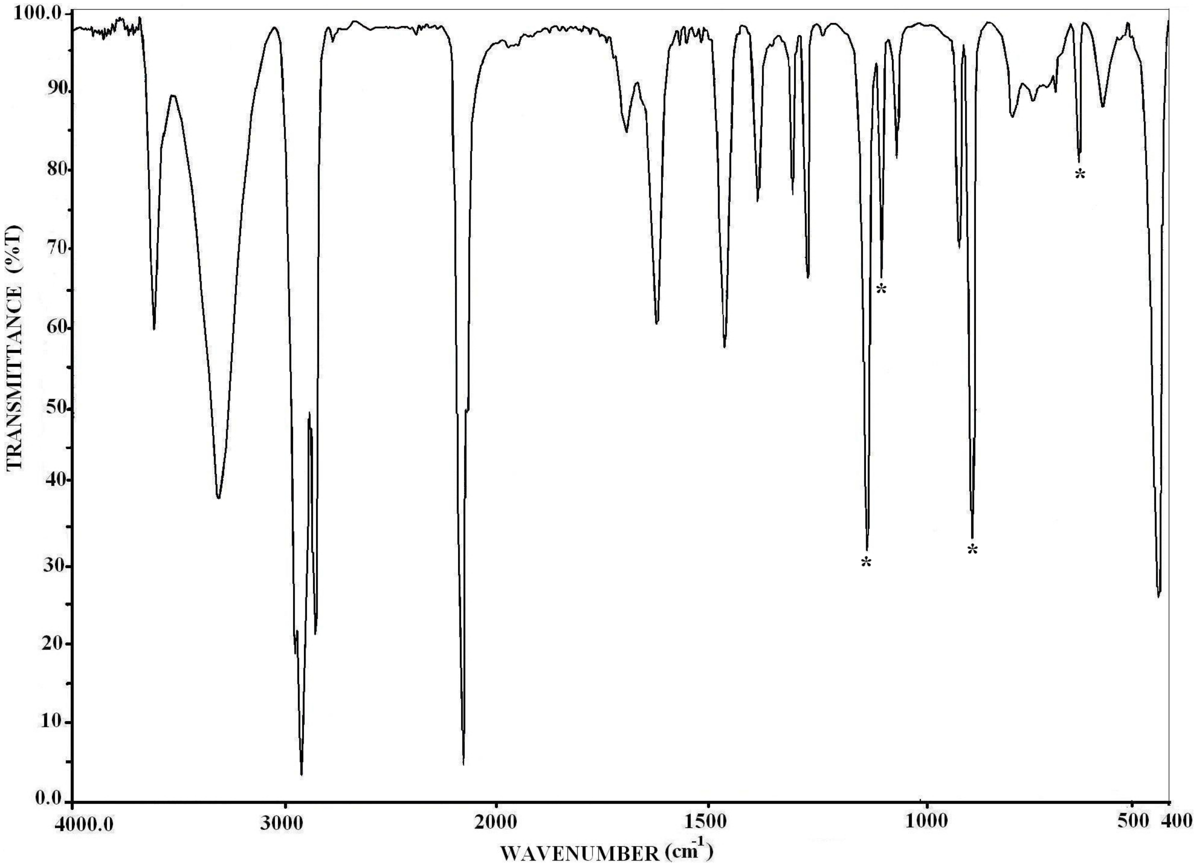

Fig. 1. The infrared spectrum of $Cd(BA)_2Ni(CN)_4\cdot D$ clathrate. The stars indicate dioxane peaks.

by around 50 – 83 cm^{-1} for the obtained clathrates. This shift shows that the BA molecule is connected directly to the metal atom through the oxygen of the carbonyl group. The frequencies of OH str at 3341 cm^{-1} for the solid BA molecule were shifted to lower frequencies by around 28 – 52 cm^{-1} for the obtained clathrates. This shift shows that the C=O bond becomes weak due to interactions of the oxygen atom in the carbonyl group with the metal atom of $MNi(CN)_4$. As a result, the carbon atom extracts electrons of the OH group. In this case, the stretching vibration causes OH shifts to lower frequencies. At the same time, frequency shifts to higher frequencies were observed due to the coupling. For example, the C=O out-of-plane (oop) frequency was shifted to higher frequencies by around 27 – 55 cm^{-1} for the obtained clathrates. This is because by the strength of the (CO-M) band the C=O oop frequency increases [7]. This means that this shift results from the bonding to the metal.

3.2. $[Ni(CN)_4]^{2-}$ Ions

If a unit cell has the symmetry D_{4h}, then seven normal modes are expected to be in a vibration spectrum. Four of them must be active in the IR spectrum, and three in the Raman spectrum. The IR active vibrational modes are δ(CN(E_u)), υ(Ni-CN(E_u)), π(Ni-CN(A_{2u})) and δ(Ni-CN(E_u)). Since we observed these four bands in the infrared spectrum, we assumed that the nickel tetracyanine ion has a square planar environment. Therefore it is reasonable to assume that our clathrate has square planar $Ni(CN)_4$ moieties. In the present study, the frequencies of the $Ni(CN)_4$ group vibrations in the clathrate are assigned on the basis of the work of McCullough [8], who presented vibrational data for the ion $[Ni(CN)_4]^{2-}$ in $Na_2Ni(CN)_4$. These results are listed in Table 2 for comparison with the assignment of groups in our clathrate and in the clathrate of Co(1-PT)-Ni-G [9].

Assignment*	BA	Ni-BA-Ni-D	Cd-BA-Ni-D	Co-BA-Ni-D
OH str [100]	3341 s	3303 s	3313 s	3289 s
C4H str [96]	2975 s	2967 m	2955 s	2982 m
C3H str [49], C5H str [49]	2930 w	2944 s	2924 s	2945 m
C3H str [48], C5H str [48]	2888 m	2890 s	2858 s	2863 m
C=O str [68]	1700 s	1622 m	1617 m	1650 m
ring str [71]	1605 w	–	–	–
ring str [77]	1585 w	1576 w	1576 w	1570 sh
C4H bend [35], ring str [27]	1453 m	1457 s	1456 m	1454 s
CH bend [25], C-COOH str [20]	1381 m	1377 s	1375 m	1374 m
ring str [88]	1273 m	1270 w	1292 m	1293 m
CH bend [67], OH bend [19]	1177 w	1170 w	–	–
C-O str [29], ring bend [15], OH bend [13]	1091 s	–	1082 m	1081 s
CH oop [74], ring oop [22]	1050 s	1043 w	1045 m	1047 m
CH oop [54], ring oop [35]	882 s	875 s	873 s	871 s
CH oop [92]	715 m	723 m	721 w	–
ring bend [49], C-O bend [27]	655 w	622 w	653 w	673 sh
C=O oop [59], ring oop [30], ring bend [30]	434 m	461 m	489 sh	475 sh

Table 1. IR vibrational wavenumbers (cm^{-1}) of the solid BA and BA in the M(BA)$_2$Ni(CN)$_4$·D clathrates.

str, stretching; bend, bending; oop, out-of-plane; s, strong; m, medium; w, weak; vw, very weak; sh, shoulder. Potential energy distributions (%) are given in square brackets. * Taken from [4].

Assignment [8]	Na$_2$Ni(CN)$_4$ [8]	Co-(1-PT)-Ni [9]	Ni-BA-Ni-D	Cd-BA-Ni-D	Co-BA-Ni-D
υ(CN)	2132	2136	2161 s	2159 s	2157 s
Hot band	2128	–	2125 sh	2136 sh	2121 sh
υ(Ni-CN)	543	554 w	544 m	557 m	555 m
π (Ni-CN)	448	477 m	461 m	489 w	465 sh
δ(Ni-CN)	433	433 w	440 s	433 s	437 s

Table 2. IR vibrational wavenumbers (cm^{-1}) of the Ni(CN)$_4$ group in M(BA)$_2$Ni(CN)$_4$·D clathrates.

s, strong; m, medium; w, weak; vw, very weak; sh, shoulder; ν, stretching; π, out-of-plane bending; δ, in-plane bending.

Assignment*	Liquid dioxane	Ni-BA-Ni-D	Cd-BA-Ni-D	Co-BA-Ni-D
$\upsilon_{11}(a_u)$, $\upsilon_{28}(b_u)$	2961 vs	2967 s	2954 s	2945 w
$\upsilon_{12}(a_u)$, $\upsilon_{29}(b_u)$	2854 vs	2869 s	2857 s	2863 w
$\upsilon_{30}(b_u)$	1453 s	1457 vs	1456 m	1454 m
$\upsilon_{14}(a_u)$	1366 s	1377 s	1375 m	1374 m
$\upsilon_{32}(b_u)$	1289 s	1294 m	1293 m	1293 m
$\upsilon_{15}(a_u)$	1255 s	1258 s	1258 m	1260 s
$\upsilon_{16}(a_u)$	1122 vs	1122 s	1121 s	1120 s
$\upsilon_{17}(a_u)$	1084 s	1084 m, 1079 m	1082 m	1081 m
$\upsilon_{33}(b_u)$	1048 s	1049 m, 1043 w	1045 m	1047 m
$\upsilon_{18}(a_u)$	874 s	875 s, 866 s	873 s, 866 w	871 s
$\upsilon_{35}(b_u)$	614 s	622 m, 611 m	614 m	614 m

Table 3. IR vibrational wavenumbers (cm^{-1}) of 1,4-dioxane in M(BA)$_2$Ni(CN)$_4$·D clathrates.

s, strong; m, medium; w, weak; vw, very weak; sh, shoulder. * Taken from [10].

Stretched vibrations of the CN group of K$_2$Ni(CN)$_4$ were observed in the 2122 cm^{-1} region, the stretched vibrations band υ(CN) for the clathrate of M-BA-Ni-D shifted to the high frequency range by 35–39 cm^{-1}. The same shift also appeared for the in-plane bending δ(Ni-CN). The vibrations band δ(Ni-CN) for the clathrate M-BA-Ni-D shifted to the high frequency range by 4–7 cm^{-1}. This shows that both bands are connected to the metal atom.

This shift is due to the coupling of the stretching vibration of the metal-nitrogen bond and the CN bond. The stretching vibrations of υ(Ni-CN) were observed as a medium strength band at 544 cm^{-1} for Ni-BA-Ni-D clathrate, at 557 cm^{-1} for Cd-BA-Ni-D clathrate and at 555 cm^{-1} for Co-BA-Ni-D clathrate.

The characteristic υ(CN) and δ(Ni-CN) frequency values belonging to the group of the clathrate Ni(CN)$_4$ are similar to the Hofmann-type clathrate showing polymeric layer structure. The obtained spectrum of the clathrate shows that the clathrate consists of infinite polymeric layers in the form of $|\mathrm{MNi(CN)_4}|_\infty$. In the layer structure, the $[\mathrm{Ni(CN)_4}]^{-2}$ ions are surrounded by M(BA)$^{2+}$ cations.

3.3. Guest D-Molecules

The assignment and the frequencies of the vibrational bands arising from the enclathrated D observed in the spectrum of M(BA)$_2$Ni(CN)$_4$·D are given in Table 3 along with the wavenumbers of D in the liquid phase found by Sopková and Bubanec for comparison [10]. The vibrational studies show that the D molecule has a chair conformation with a centre of symmetry (C_{2h}) in the gas and liquid phases [11]. In some of our clathrates, several D bands are split into doublets to guest D molecules. Similar observations have also been made for Hofmann-type D clathrates [12] and Hofmann-T_d-type D clathrates [13]. As a result, from investigation of the infrared bands of D in the spectra of our compounds it can be concluded that the D molecule is centro-symmetric and is thus most likely in a chair conformation (Table 3). Same situations have been observed for metal halide complexes [14], for Hofmann-type D clathrates [15] and Hofmann-T_d- type D clathrates [13].

It is thought that these polymeric layers are hold in parallel by Van der Waals interactions between the BA. Various cavities occur in this clathrate. The cavities are formed either at the same volume (Ni-Ni) or at two different volumes (Cd-Ni and Co-Ni), depending on the type of metal. The BA molecules are located below and above of the plane. The nickel atoms are surrounded by four carbon atoms of cyanide groups, and metal atoms are surrounded by four nitrogen atoms of the cyanide groups and two oxygen atoms of the carbonyl group of the BA molecules in the regular square plane. In octahedral configuration, metal atoms interact with the atoms of the ligand molecules below and above of the plane, which can give their electron.

The explanation given above indicates that the clathrate obtained in this study is a new examples of Hofmann-type clathrates. These clathrate can be used as molecular sieves for the chemical purification and separation of isomers.

Acknowledgement

The author thanks the Anadolu University Plant Drug and Scientific Research Centre (AÜBİBAM) for providing technical support.

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