

FT-IR Spectroscopic Study of $M(\text{Benzoic Acid})_2\text{Ni}(\text{CN})_4$ Complexes ($M = \text{Ni, Cd, Co and Mn}$)

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Complexes of $M(\text{benzoic acid})_2\text{Ni}(\text{CN})_4$ ($M = \text{Ni, Cd, Co and Mn}$) are obtained for the first time. The observed spectra indicate that the obtained complexes are new examples of Hofmann-type complexes. — PACS NO: 33.20.Ea, 33.20.Tp

Key words: Benzoic Acid; Infrared Spectroscopy; Tetracyanonickelate; Hofmann-type Compounds.

1. Introduction

Many Hofmann-type complexes with the general formula $\text{ML}_2\text{Ni}(\text{CN})_4$ were produced by using N-donor ligand molecules such as ammonia [1], pyridine [2], and products of pyridine [3, 4]; O-donor ligand molecules such as water [5], dioxane [6], dimethylsulfoxide [7], urea [8], pyridine-1-oxide [9], and dimethylformamide [10]; S-donor ligand molecules such as 1,3-thiazolidin-2-thion [11] and dimethylthioformamide [12]. In the above formula, M is a transition metal atom having the valence +2, and L is either a bidentate or two monodentate molecules. In the present study we used for the first time benzoic acid (BA) as a ligand to produce new Hofmann-type complexes with the general formula $M(\text{BA})_2\text{Ni}(\text{CN})_4$ ($M = \text{Ni, Cd, Co and Mn}$). These

complexes were investigated in the infrared range of $4000 - 400 \text{ cm}^{-1}$.

The BA molecule contains carboxyl groups, namely *carbonyl* and *hydroxyl* [13]. Each group (carbonyl and hydroxyl) contains an oxygen atom, which can donate electrons. BA has monomer and dimer shapes [14]. The molecular structure of the monomer is shown in Figure 1.

The electron density of the BA monomer was calculated at the restricted Hartree-Fock level using the PM3 method in the MOPAC 97 program package. The calculations indicate that the oxygen atom 9 has a higher electron density than the oxygen atom 8 and the hydrogen atom 15. Hence we expect that the binding happens with the oxygen atom 9. There are various infrared spectroscopy studies reported for the BA molecule [14 – 19].

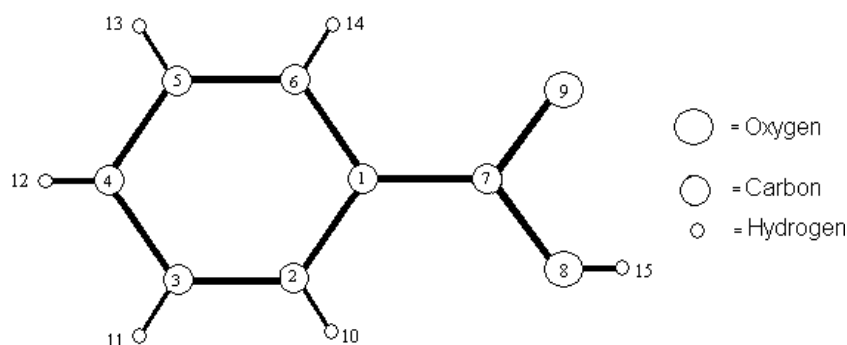


Fig. 1. The molecular structure of the benzoic acid monomer.

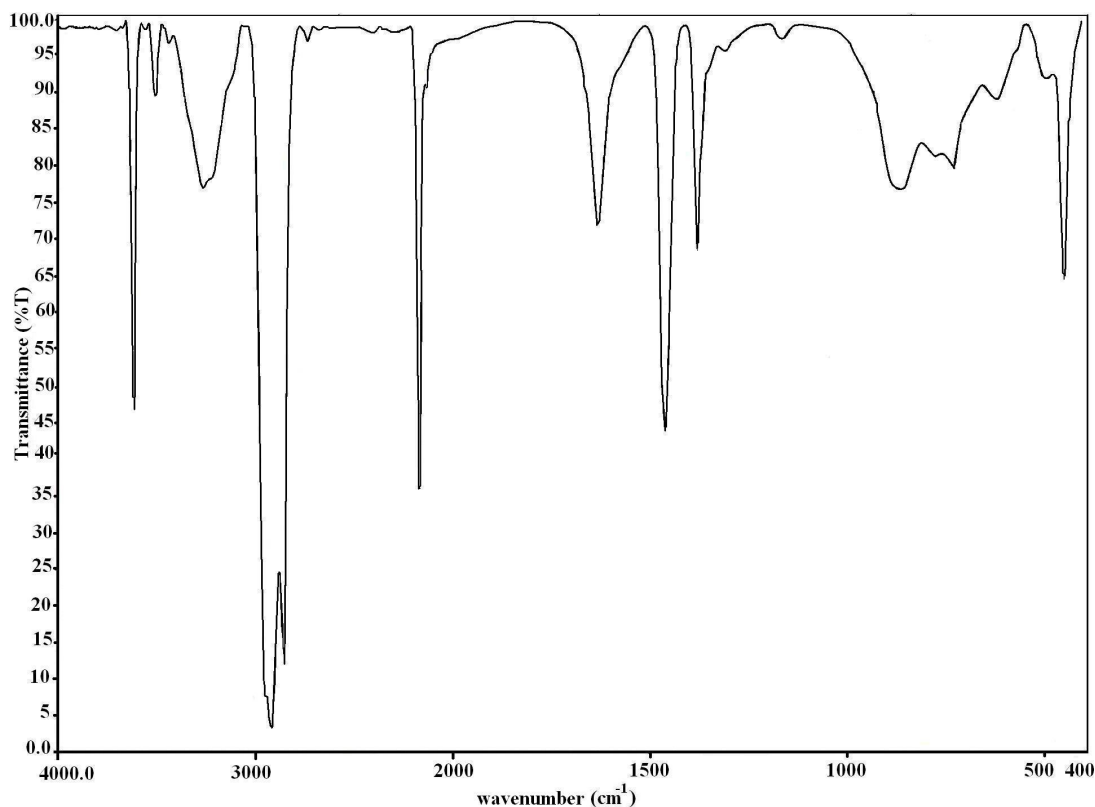


Fig. 2. The infrared spectrum of $\text{Ni}(\text{BA})_2\text{Ni}(\text{CN})_4$.

2. Experimental

In this study all chemicals, namely BA ($\text{C}_7\text{H}_6\text{O}_2$; Fluka, $\geq 99.5\%$), $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (Fluka, 98%), $\text{CdCl}_2 \cdot 2\text{H}_2\text{O}$ (Fluka, 96%), $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (Fluka, 99%), $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ (Fluka, 99%), and KCN (Fluka, 98%), were used without further purification. First, 1 mmol $\text{K}_2\text{Ni}(\text{CN})_4$ was solved in distilled water, and then 2 mmol BA were solved in distilled water. After that, the second solution was added to the first under stirring. Then 1 mmol of MCl_2 ($\text{M} = \text{Ni}, \text{Cd}, \text{Co}$ and Mn), solved in distilled water, was added to the mixture, which was stirred for 5 d. The compounds obtained were filtered, washed with pure water, ethanol and ether, and kept in a desiccator containing P_2O_5 . Infrared spectra of these compounds were recorded at room temperature with a Perkin-Elmer BX FT-IR Spectrometer having a resolution of 4 cm^{-1} .

The freshly prepared samples were analyzed (CHNS-932, LECO) to determine the amount of C, H, and N with the following results (found% / calculated %):

- $\text{Ni}(\text{BA})_2\text{Ni}(\text{CN})_4$: C = 46.40/46.42, H = 02.59/02.60, N = 12.02/12.03,
- $\text{Cd}(\text{BA})_2\text{Ni}(\text{CN})_4$: C = 41.63/41.62, H = 02.31/02.33, N = 10.78/10.79,
- $\text{Co}(\text{BA})_2\text{Ni}(\text{CN})_4$: C = 46.37/46.40, H = 02.59/02.60, N = 12.01/12.02,
- $\text{Mn}(\text{BA})_2\text{Ni}(\text{CN})_4$: C = 46.77/46.80, H = 02.61/02.62, N = 12.12/12.13.

3. Results and Discussion

The IR spectrum of the $\text{Ni}(\text{BA})_2\text{Ni}(\text{CN})_4$ complex is shown in Fig. 2 as an example. The assignments were made by treating the ligand BA molecules and the $[\text{Ni}(\text{CN})_4]^{2-}$ ion as isolated units to determine the shifts for each one. The results obtained from the IR spectral data can be analyzed for a) vibrating ligand molecules, b) $[\text{Ni}(\text{CN})_4]^{2-}$ ion units.

3.1. Ligand Vibrations

The BA monomer have a planar structure and belongs to the C_s point group. It has 39 normal vi-

Assignment [14]	BA	Ni-(BA)-Ni	Cd-(BA)-Ni	Co-(BA)-Ni	Mn-(BA)-Ni
OH str (100)	3341 s	3260 m	3298 s	3268 s	3288 m
C4H str (96)	2975 s	2970 sh	2968 sh	2972 sh	2965 sh
C3H str (49), C5H str (49)	2930 w	2920 w	2926 w	2925 w	2925 w
C3H str (48), C5H str (48)	2888 m	2856 s	2856 s	2856 s	2856 s
C=O str (68)	1700 s	1630 m	1633 s	1630 s	1621 s
Ring str (71)	1605 w		1600 w	1600 w	
Ring str (77)	1585 w	1580 w	1582 w	1586 w	1583 w
C4H bend (35), ring str (27)	1453 m	1461 s	1461 m	1460 m	1461 m
CH bend (25), C-COOH str (20)	1381 m	1377 m	1377 m	1377 w	1379 w
Ring str (88)	1273 m		1220 w	1217 w	1218 w
CH bend (67), OH bend (19)	1177 w	1156 w	1164 w	1170 w	1180 vw
C-O str (29), ring bend (15), OH bend (13)	1091 s	1086 w	1092 w	1094 w	1090 w
CH oop (74), ring oop (22)	1050 s	1054 w	1060 w	1042 w	1046 w
CH oop (54), ring oop (35)	882 s	864 m	874 w	859 m	870 sh
CH oop (92)	715 m	725 m	720 m	723 m	724 m
Ring bend (49), C-O bend (27)	655 w	620 w	609 w	686 w	660 sh
C=O oop (59), ring oop (30), Ring bend (30)	434 m	488 w	475 w	485 m	474 w

Table 1. IR vibrational wavenumbers (cm^{-1}) of the solid BA and BA in the M-(BA)-Ni complexes.

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 brackets.

brations, namely 27 A' (planar) and 12 A'' (out-of-plane). These vibrations are IR active [14]. The assignments and the wavenumbers of the IR bands of the BA molecule observed in the IR spectra of the M(BA)₂Ni(CN)₄ complexes are given in Table 1, together with the wavenumbers of solid phase BA.

The observed small frequency shifts are due to changes of the environment of the BA molecule and the pairing of the internal vibration of the BA molecule with the vibrations of the M-O band. Small frequency shifts were reported in other studies [2, 20]. Noticeable frequency shifts were observed as stretched frequencies of C=O and OH. For the solid BA molecule the frequencies of C=O at 1700 cm^{-1} are shifted to lower frequencies by around $67-79 \text{ cm}^{-1}$. This shift shows that the BA molecule is directly connected to the metal through the oxygen of the carbonyl group. The frequencies of OH at 3341 cm^{-1} for the solid BA molecule are shifted to lower frequencies by around $43-81 \text{ cm}^{-1}$ for the obtained complexes. This shift indicates that the C=O bond becomes weak due to the interaction of the oxygen atom in the carbonyl group with the metal atom of [M-Ni(CN)₄]. As a result, the carbon atom extracts the electrons of the OH group.

Frequency shifts to higher frequencies were also observed for the complexes. For example, the C=O (out-of-plane) frequencies shifted by around $40-54 \text{ cm}^{-1}$. This is because the bonding of the (CO-M) makes difficult the out-of-plane bending motion for the C=O. Similar shifts were observed in Şenyel's study [10]. We think that the observed peaks at 3613 and 3502 cm^{-1} result from water molecules in the complexes.

3.2. [Ni(CN)₄]²⁻ Vibrations

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 the remaining in the Raman spectrum. The IR active vibrational modes are $E_u\delta(\text{CN})$, $E_u\nu(\text{Ni-CN})$, $A_{2u}\pi(\text{Ni-CN})$ and $E_u\delta(\text{Ni-CN})$. Since we observed these four bands in the infrared spectrum, our complexes have a square planar environment. The frequencies of the [Ni(CN)₄]²⁻ group vibrations in complexes are assigned on the basis of the work of McCullough [21], who presented vibrational data for the ion [Ni(CN)₄]²⁻ in Na₂Ni(CN)₄. The vibrational wavenumbers of [Ni(CN)₄]²⁻ in our complexes are given in Table 2, together with McCullough's data and the data for complexes of Co(1-PT)-Ni-Bz [22] for comparison.

As the stretched vibrations of the CN group of K₂Ni(CN)₄ were observed in the 2122 cm^{-1} region, the band $\nu(\text{CN})$ for the complex of M-(BA)-Ni shifted to the high frequency range by around $33-44 \text{ cm}^{-1}$. The same shift also appeared in the plane bending $\delta(\text{Ni-CN})$ for the complexes around $2-13 \text{ cm}^{-1}$. The shifts show that both bands are connected to the metal.

The stretch of $\nu(\text{Ni-CN})$ was observed at 560 cm^{-1} for the Ni-(BA)-Ni complex, at 558 cm^{-1} for the Cd-(BA)-Ni complex and at 561 cm^{-1} for the Mn-(BA)-Ni complex.

The characteristic $\nu(\text{CN})$ and $\delta(\text{Ni-CN})$ frequencies observed are similar to the Hofmann-type complexes, indicating that the [M-Ni(CN)₄]_∞ layers were

Table 2. IR vibrational wavenumbers (cm⁻¹) of the [Ni(CN)₄]²⁻ group in the M-(BA)-Ni complexes.

Assignment [21]	Na ₂ Ni(CN) ₄ [21]	Co-(1-PT)-Ni [22]	Ni-(BA)-Ni	Cd-(BA)-Ni	Co-(BA)-Ni	Mn-(BA)-Ni
ν(CN)	2132	2136	2166 s	2157 s	2161 s	2155 s
Hot band	2128		2127 sh	2115 sh	2120 w	2116 sh
ν(Ni-CN)	543	554 w	560 w	558 w		561 m
π (Ni-CN)	448	477 m	488 w	475 w	485 w	479 vw
δ(Ni-CN)	433	433 w	446 m	431 s	442 s	438 s

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

preserved [23]. These polymeric layers are hold in parallel by Van der Waals interactions between the BA. The α type cavity occurs in these complexes. The cavities have a volume depending on the type of the transition metal. The BA molecules are located below and above the plane. The nickel atoms are surrounded by four carbon atoms of the cyanide groups, and the metal atoms M are also surrounded by four nitrogen atoms of the cyanide groups, and at the same time two oxygen atoms of the carbonyl groups of the BA molecules are bonded to the metal atoms in the regular square plane.

As a conclusion, the compounds M(benzoic acid)₂Ni(CN)₄ (M = Ni, Cd, Co and Mn) are new examples of Hofmann-type complexes.

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