FT-IR Spectroscopic Study of M(Cyclopentanone)$_2$Ni(CN)$_4$ Complexes (M = Ni, Cd and Co)

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Cyclopentanone-tetracyanonickel complexes, given by the general formula$_4$ of M(cyclopentanone)$_2$Ni(CN)$_4$ (M = Ni, Cd and Co), were obtained for the first time. The similarities of the observed spectra with Hofmann-type complexes indicate that the obtained compounds are new examples of Hofmann-type complexes. – PACS: 33.20.Ea, 33.20.Tp

Key words: Cyclopentanone (CPN); Infrared Spectroscopy (IR); Tetracyanonickelate; Hofmann-type Compounds.

1. Introduction

Hofmann-type complexes, given by the general formula of ML$_2$Ni(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]; and S-donor ligand molecules, such as 1,3-thiazolidin-2-thion [11] and dimethylthioformamide [12]. In the formulas given above, M is a transition metal atom having the valence +2, and L is either a bidentate or two monodentate molecules. In this study we used for the first time the cyclopentanone (CPN) molecule as a ligand to produce new Hofmann-type complexes of the general formula M(CPN)$_2$Ni(CN)$_4$ (M = Ni, Co and Cd). These complexes were investigated in the infrared range of 4000 – 400 cm^{-1}.

The CPN molecule (Fig. 1) contains a carbonyl group, in which oxygen can donate an electron.

We expect that the bonding occurs from the oxygen atom of the carbonyl group of the CPN. There are various infrared studies reported for the CPN molecule [13 – 18].

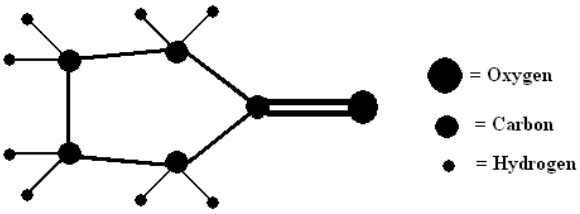

Fig. 1. The molecular structure of cyclopentanone.

2. Experimental

All the chemicals, namely cyclopentanone, C_5H_8O (Fluka, 98%), $NiCl_2{\cdot}6H_2O$ (Fluka, 98%), $CdCl_2{\cdot}2H_2O$ (Fluka, 96%) $CoCl_2{\cdot}6H_2O$ (Fluka, 99%) and KCN (Fluka, 98%), were used without further purification. First, 1 mmol $K_2Ni(CN)_4$ was dissolved in distilled water and 2 mmol CPN were added to the solution under stirring. Then 1 mmol of MCl_2 (M = Ni, Cd or Co), dissolved in distilled water, was added to this mixture. The whole mixture was stirred for 5 d. The obtained compounds were filtered, washed with pure water, ethanol and diethyl ether, and kept in desiccators containing P_2O_5. Infrared spectra of these compounds were recorded at room temperature with a Mattson 1000 FTIR spectrometer having a resolution of 4 cm^{-1}.

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

$Ni(C_5H_8O)_2Ni(CN)_4$: C = 43.08/43.15, H = 04.14/04.14, N = 14.35/14.38.

$Cd(C_5H_8O)_2Ni(CN)_4$: C = 37.77/37.92, H = 03.61/03.63, N = 12.59/12.63.

$Co(C_5H_8O)_2Ni(CN)_4$: C = 43.10/43.12, H = 04.12/04.13, N = 14.36/14.37.

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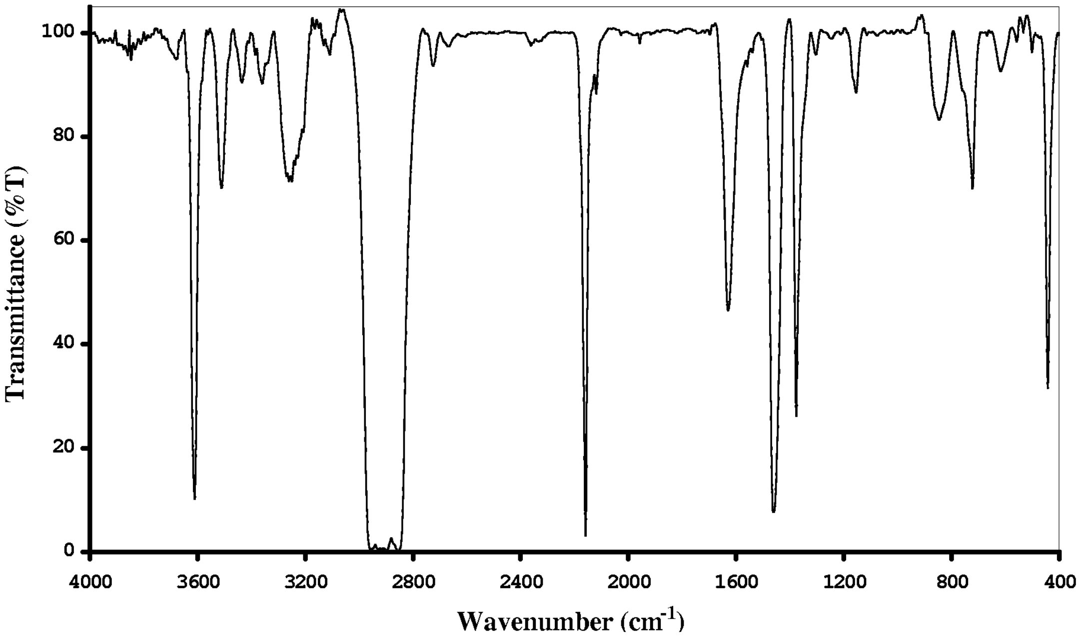

Fig. 2. The infrared spectrum of Ni(CPN)$_2$Ni(CN)$_4$ (in nujol).

3. Results and Discussion

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

3.1. Ligand Vibrations

The CPN has a puckered structure and belongs to the C_{2v} symmetry. It has 36 normal vibrations, namely 9A$_1$, 6B$_1$, 1A$_2$ and 9B$_2$, and these vibrations are IR active [18]. The assignments and the wavenumbers of the IR bands for the CPN molecule observed in the IR spectra of the M(CPN)$_2$Ni(CN)$_4$ complexes are given in Table 1, together with the wavenumbers of liquid phase CPN.

The observed small frequency shifts are due to changes of the surround of the CPN molecule and to the pairing of the internal vibration of the CPN molecule with the vibrations of the (M-O) band. The small frequency shifts were reported in other studies [2, 19]. The noticeable frequency shifts were observed at stretched frequencies of the C=O. The observed stretched frequencies of the C=O at 1745 cm^{-1}

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

Assignment*	CPN	Ni-CPN-Ni	Cd-CPN-Ni	Co-CPN-Ni
C-O def(⊥), B$_1$	445 w	447 w	445 w	450 w
C-O def(‖), B$_2$	472 vs	483 w	508 m	502 w
ring mode (‖), A$_1$	566 sh	570 w	559 m	560 w
ring mode (‖), B$_2$	584 s	595 w	620 w	617 w
ring mode (‖), A$_1$	710 w	712 w	709 w	710 w
ring mode (‖), A$_1$	810 m	795 w	810 w	789 m
ring mode (‖), B$_2$	837 vs	842 s	845 w	849 w
ring mode (‖), A$_1$	894 w	889 m	885 s	876 s
CH$_2$ rock, A$_2$	917 m	921 w	938 w	921 w
ring mode (‖), B$_2$	960 vs	966 w	971 w	957 w
CH$_2$ rock, B$_1$	1025 m	1050 s	1041 s	1027 w
CH$_2$ rock, B$_1$	1153 vs	1157 m	1157 vs	1156 m
CH$_2$ twist, B$_1$	1182 sh	1178 w	1208 w	–
CH$_2$ twist, B$_1$	1233 m	1240 w	1247 w	1246 w
CH$_2$ wag, A$_1$	1266 sh	1268 w	1253 m	1260 w
CH$_2$ wag, B$_2$	1279 s	1278 w	1279 w	-
CH$_2$ wag, B$_2$	1316 m	1308 w	1304 m	1304 w
CH$_2$ def, B$_2$	1408 vs	1390 m	1382 s	1385 s
CH$_2$ def, A$_1$	1457 s	1459 vs	1459 vs	1465 vs
CH$_2$ def, B$_2$	1470 sh	–	–	–
C=O stretch, A$_1$	1745 vs	1627 vs	1619 vs	1631 vs
C-H stretch, A$_1$	2885 sh	2880 sh	2858 sh	2860 sh
C-H stretch, A$_2$	–	2900 m	–	2903 m
C-H stretch, B$_2$	2919 sh	–	2922 sh	2928 sh
C-H stretch, B$_1$	2945 sh	2942 sh	2947 sh	2947 sh
C-H stretch, A$_1$	2966 vs	2960 s	2959 s	2962 s

str, stretching; bend, bending; oop, out-of-plane; s, strong; m, medium; w, weak; vw, very weak; sh, shoulder. (⊥) and (‖) refer to vibrations perpendicular and parallel to C_2 symmetry axis. * Taken from [18].

for the liquid phase CPN molecule shifted to a low frequency region around 114 – 126 cm^{-1}. This shift shows that the CPN molecule is directly connected to the metal atom through the oxygen atom of the carbonyl group.

The frequency shifts to higher frequencies were also observed for the complexes. For example, the C-O def($\perp$), B$_1$, frequency shifted to the high frequency around 2 – 7 cm^{-1} and the C-O def($\|$), B$_2$, frequency shifted to the high frequency around 11 – 36 cm^{-1}. These occur because the bonding of the (CO-M) makes difficult the C-O deformation motion for the C=O. Similar shifts were observed in Şenyel's study [10]. We think that the observed peaks between 3613 and 3100 cm^{-1} result from the 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$_u\delta$(CN), E$_u\upsilon$(Ni-CN), A$_{2u}\pi$(Ni-CN) and E$_u\delta$(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)$_4$ group vibrations in complexes are assigned on the basis of the work of McCullough [20], who presented vibrational data for the ion [Ni(CN)$_4$]$^{2-}$ in Na$_2$Ni(CN)$_4$. The vibrational wavenumbers of the Ni(CN)$_4$ group in our complexes are given in Table 2, together with the McCullough data and the data for the complexes of Co-(1-PT)-Ni-Bz [21] for comparison.

As the stretched vibrations of the CN group of K$_2$Ni(CN)$_4$ were observed in the 2122 cm^{-1} region, the band υ(CN) for the complex of M-CPN-Ni shifted to the high frequency range around 35 – 52 cm^{-1}. The same shift appeared also in the in-plane bending δ(Ni-CN) for some complexes around 2 – 5 cm^{-1}. The shifts show that both bands are connected to the metal atom. The stretching band of υ(Ni-CN) were observed at 570 cm^{-1} for the Ni-CPN-Ni complex, at 558 cm^{-1} for the Cd-CPN-Ni complex and at 559 cm^{-1} for the Co-CPN-Ni complex.

Table 2. IR vibrational wavenumbers (cm^{-1}) of the Ni(CN)$_4$ group in the M-CPN-Ni complexes.

Assignment*	Na$_2$ Ni(CN)$_4$*	Co-(1-PT) -Ni**	Ni -CPN-Ni	Cd -CPN-Ni	Co -CPN-Ni
υ(CN)	2132	2136 s	2174 vs	2157 s	2165 vs
Hot band	2128	–	2118 sh	–	2121 sh
υ(Ni-CN)	543	554 w	570 m	558 w	559 m
π(Ni-CN)	448	477 m	450 s	475 w	438 vs
δ(Ni-CN)	433	433 w	438 w	435 s	419 w

s, strong; m, medium; w, weak; vw, very weak; sh, shoulder. ν, stretching; π, out-of-plane bending; δ, in-plane bending. * Taken from [20]. ** Taken from [21].

The characteristic υ(CN) and δ(Ni-CN) frequencies observed are similar to the Hofmann-type complexes indicating that the $|$M-Ni(CN)$_4|_\infty$ layers were preserved [22]. These polymeric layers are hold in parallel by Van der Waals interactions between the CPN. The α type cavity occurs in these complexes. The cavities have a volume depending on type of transition metal. The CPN molecules are located below and above the plane. Nickel atoms are surrounded by four carbon atoms of cyanide groups, and M atoms are also surrounded by four nitrogen atoms of the cyanide groups, and at the same time two oxygen atoms of the carbonyl group of the CPN molecules are bonded to the metal atoms in the regular square plane.

As a conclusion, the compounds M(cyclopentanone)$_2$Ni(CN)$_4$ (M = Ni, Cd and Co) are new examples of Hofmann-type complexes.

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