FT-IR Spectroscopic Study on Some Hofmann-T_d Type Complexes: Ni(4-Phenylpyridine)$_2$M(CN)$_4$ (M = Cd or Hg)

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New Hofmann-T_d type complexes in the form of Ni(4-Phenylpyridine)$_2$M(CN)$_4$ (M = Cd or Hg) were prepared in powder form and their infrared spectra are reported in the region of 4000 – 200 cm^{-1}. From the spectral findings, these compounds are similar in structure to the Hofmann-T_d type complexes. — Pacs numbers: 33.20.Ea, 33.20.Tp, 82.75-z

Key words: Hofmann-T_d Type Complexes; 4-Phenlypyridine; Infrared Spectra; Host Structure.

1. Introduction

Hofmann-T_d type host structures are defined with the general formula of M(L$_2$)M'(CN)$_4$ where M is one of the first row transition metals, L$_2$ corresponds to a pair of monodentate ligand molecules and M' is for Zn, Cd or Hg. The host structure is formed by the chains of -M-L$_2$-M-L$_2$- extending along the *a*- and *b*-axes alternately and the tetrahedral M'(CN)$_4$ ions are arranged between the consecutive crossing chains with the N-ends bound to the M atoms [1 – 4]. This structure possesses two kinds of cavities, namely α and β. The α cavity with the rectangular box is similar to those in the Hofmann type hosts while the β cavity is a twisted biprism [2, 3]. The cavities within the structure can act as a host for the guest molecules.

For the 4-phenylpyridine molecule (4-Phpy), Hofmann type complexes, transition metal(II)-chloro complexes and isothiocyanate complexes were reported [5, 6]. Zawada et al. [7] presented that formation of 4-Phpy complexes with copper ions inhibits the copper corrosion. In the present study we prepared two new compounds in the form of Ni(L$_2$)M(CN)$_4$ (M = Cd and Hg) using 4-Phpy as a ligand for the first time and spectral properties of these complexes were studied in the IR region.

2. Experimental

All the chemicals used were reagent grade (Merck) and they were used without further purification. The compounds were prepared as follows:

For the Ni(4-Phpy)$_2$Cd(CN)$_4$, 1 mmol of K$_2$Cd(CN)$_4$ was dissolved in distilled water, then slightly more than 2 mmol of 4-Phpy dissolved in ethanol were added to this solution under stirring. After a short time, 1 mmol of NiCl$_2$ dissolved in distilled water was added to the mixture drop wise, again under stirring.

For the Ni(4-Phpy)$_2$Hg(CN)$_4$, 1 mmol of Hg(CN)$_2$ dissolved in distilled water was added to the solution of 4-Phpy prepared with ethanol. Then, 1 mmol Ni(CN)$_2$ dissolved in distilled water was added to this mixture under stirring. The final mixtures for both compounds were left for stirring around one week at room temperature. The obtained products were filtered and washed with water, ethanol, diethyl ether successively and dried in desiccators containing P$_2$O$_5$. Infrared spectra of the complexes were recorded in the region of 4000 – 200 cm^{-1} via a Perkin-Elmer FTIR 2000 spectrometer. Samples were prepared as mulls in nujol and hexachloro-1,3-butadiene. The compounds were analyzed for the amounts of Ni, Cd and Hg via a Perkin Elmer 4300 ICP-OES and for C, H and N contents via a Fisons EA-1108 elementel analyser. The results are as follows (found %/calculated %):

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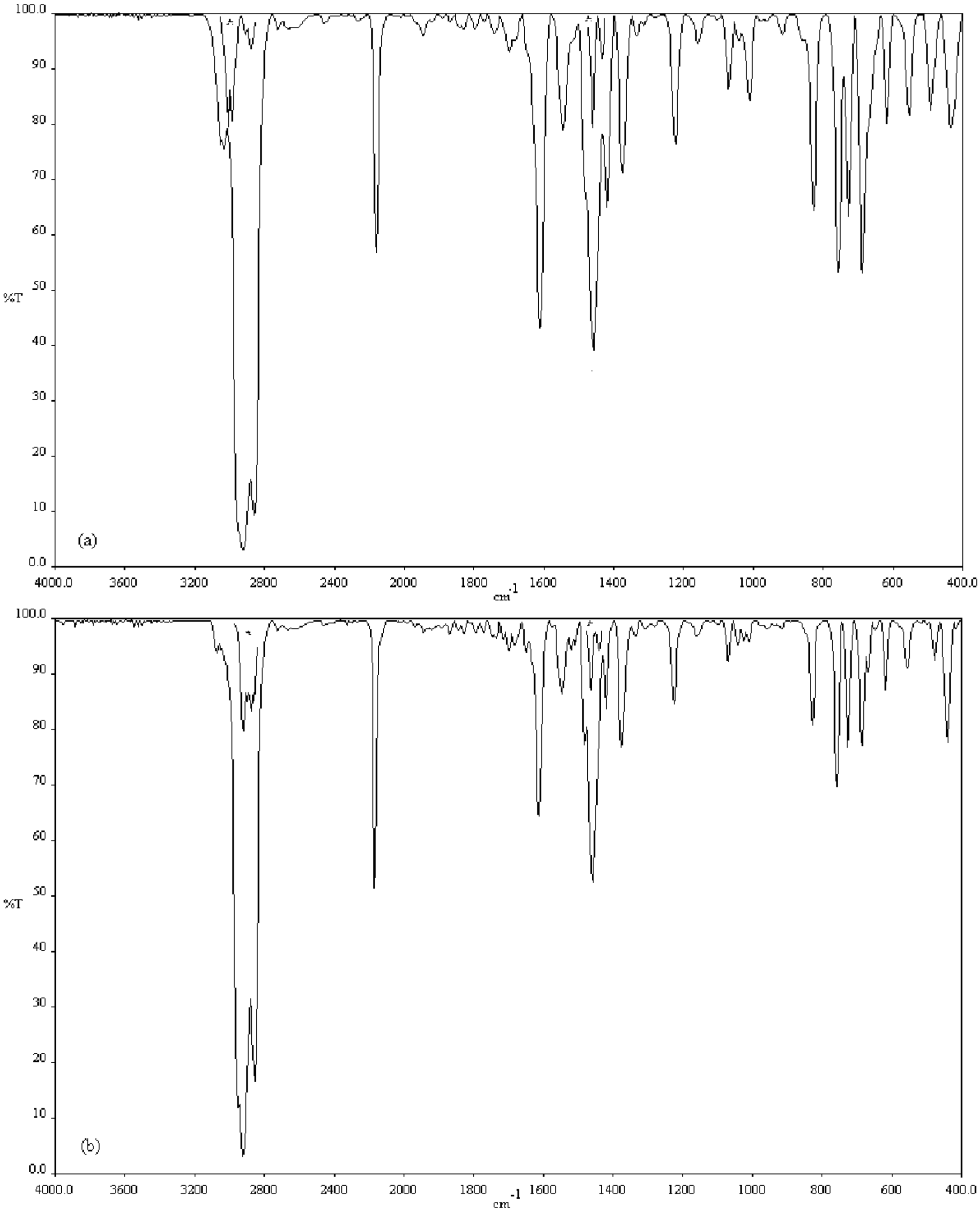

Fig. 1. Infrared spectrum of (a) Ni(4-Phpy)$_2$Cd(CN)$_4$ and (b) Ni(4-Phpy)$_2$Hg(CN)$_4$ compounds in nujol (* in hexacholoro-1,3-butadiene).

Ni(4-Phpy)$_2$Cd(CN)$_4$: C (54.5/53.33), H (3.8/3.10), N (13.7/14.35), Ni (9.81/10.02), Cd (19.01/19.20).

Ni(4-Phpy)$_2$Hg(CN)$_4$: C (47.7/46.35), H (3.3/2.70), N (11.8/12.47), Ni (8.30/8.71), Hg (28.63/29.77).

3. Results and Discussions

The infrared spectra obtained for the Ni(4-Phpy)$_2$M(CN)$_4$ (M = Cd and Hg) complexes are compatible with each other. This shows that the compounds have analogous spectral features. The spectra of the complexes are given in Figure 1. The spectral analysis for each compound was performed taking into account the 4-Phpy molecule and M(CN)$_4$ (M = Cd and Hg) ions individually to follow the shifts taking place on the complexing.

3.1. Phenylpyridine Vibrations

The molecular structure of 4-phenylpyridine was studied by Bayari et al. [5] and Zawada et al. [7]. The latter study covers the IR range from 438 cm^{-1} to 1609 cm^{-1}. The molecule belongs to the $C_{2\upsilon}$ point group possessing 57 vibrational modes. The vibrational bands consist of 39 planar bands with 20 being of class A$_1$ and 19 of class B$_1$, and 18 non planar bands with 7 being of class A$_2$ and 11 of class B$_2$. The vibrations of A$_1$, B$_1$ and B$_2$ classes are infrared active. The assignments and wavenumbers of the vibrational bands for the 4-Phpy ligand observed in the infrared spectra of the Ni(4Phpy)$_2$Cd(CN)$_4$ and Ni(4Phpy)$_2$Hg(CN)$_4$ complexes are listed in Table 1 together with wavenumbers of the 4-Phpy in solid state, with that the analysis was carried out.

From Table 1, the shifts for the vibrational modes of the A$_1$ class are more noticeable pointing out that the vibrational modes were perturbated strongly by complexing. At the higher frequency region the strong band at 1588 cm^{-1} shifted around 25 cm^{-1} as an intense band for both compounds. Another strong band at 1001 cm^{-1} shifted to the 1012 cm^{-1}. In the lower frequency region, a shift taking place for the strong band at 608 cm^{-1} is around 12 cm^{-1} for both compounds. The strong band at 438 cm^{-1} shifted 57 cm^{-1} for Ni(4Phpy)$_2$Cd(CN)$_4$ and 41 cm^{-1} for Ni(4Phpy)$_2$Hg(CN)$_4$ compounds. Analogous shifts upon coordination were reported for the Hofmann-T_d type complexes [8, 9] and Hofmann-T_d type clathrates [10, 11] and the frequency shifts were explained as a coupling of the internal vibrational modes of the ligand molecule with M-N vibrations. On this

Table 1. The vibrational frequencies (cm^{-1}) of the 4-Phpy ligand in the Ni-4Phpy-M' (M' = Cd and Hg) compounds.

Assignment[a]	Solid 4-Phpy[a]	Ni-4Phpy-Cd	Ni-4Phpy-Hg
A$_1$			
ν(CH)	3083 w	3089 vw	3086 vw
ν(CH)	3060 m	3061 m	–
ν(CH)	3038 w	3051 w	3053 w
ν(CH)	3028 w	3034 w	3029 w
ν(CH)	–	–	–
ν_{ring}	1609 vw	1632 w	1634 vw
ν_{ring}	1599 vw	–	–
ν_{ring}	1588 s	1612 s	1614 s
ν_{ring}	1512 m	1519 w	1521 w
ν_{ring}	1484 s	1485 s	1484 s
δ(CH)	1410 ms	1420 m	1421 m
$\nu_{\text{ring}} + \delta$(CH)	1279 w	1282 w	1281 w
δ(CH)	1233 s	1225 s	1227 s
ν_{ring}	1042 s	1045 m	1044 m
Ring breathing	1001 s	1012 s	1012 s
δ_{ring}	832 vs	829 vs	830 vs
$\delta_{\text{ring}} + \nu_{\text{ring}}$	762 vs	759 vs	760 vs
δ_{ring}	608 s	620 s	621 s
δ_{ring}	438 s	495 s	479 m
δ_{ring}	–	–	–
B$_2$			
ν(CH)	–	3074 sh	3074 w
ν(CH)	3008 w	3012 sh	3011 w
ν(CH)	–	–	–
ν(CH)	–	–	–
ν_{ring}	1630 w	1650 w	1651 w
ν_{ring}	1543 s	1545 s	1547 s
ν_{ring}	1447 w	1445 w	1449 w
ν_{ring}	1341 mw	1336 w	1337 w
ν_{ring}	1314 mw	1314 w	1308 w
δ(CH)	–	–	–
δ(CH)	1190 m	1185 w	1187 w
δ(CH)	1163 m	1160 m	1160 m
δ(CH)	1104 ms	1103 w	1101 w
ν_{ring}	1073 s	1072 m	1071 m
δ(CH)	1017 mw	1026 w	1027 w
δ_{ring}	868 m	864 w	865 w
δ_{ring}	561 s	556 s	558 m
δ_{ring}	–	–	–
δ_{ring}	–	–	–
B$_1$			
γ(CH)	–	980 w	978 w
γ(CH)	965 w	960 w	959 w
γ(CH)	918 m	919 m	918 w
γ(CH)	887 w	893 w	893 w
γ(CH)	731 s	730 s	729 s
γ_{ring}	687 vs	691 vs	688 vs
γ_{ring}	–	–	–
γ_{ring}	–	–	–
γ_{ring}	–	–	–

[a] Taken from [5]. The initials are: vs, very strong; s, strong; m, medium; w, weak; vw, very weak.

Assignment[a]	$K_2Cd(CN)_4$[a]	$K_2Hg(CN)_4$[a]	Ni-4Phpy-Cd	Ni-4Phpy-Hg
ν_1(CN), A_1	(2149)	(2149)	–	–
ν_5(CN), F_2	2145	2146	2161 vs	2168 vs
Hot band	–	–	2130 sh	2133 sh
ν_2(MC), A_1	(327)	(335)	–	–
$\nu_6[\nu(MC)+\delta(NCM)]$, F_2	316	330	372 s	352 s
$\nu_7[\nu(MC)+\delta(NCM)]$, F_2	250	235	245 w	260 w

Table 2. The vibrational frequencies (cm^{-1}) of the M(CN)$_4$ (M = Cd or Hg) ions group in the Ni-4Phpy-M (M = Cd or Hg) compounds.

[a] Taken from [12]. vs, very strong, s, strong, w, weak, sh, shoulder. The values in parentheses are the Raman values.

basis the frequency shifts observed for the 4-Phpy molecule in the present compounds arise from the coupling of the internal vibrational modes of the 4-Phpy with M-N vibrations revealing the metal dependence.

As well as the strong shifts, another spectral feature caused by coordination are the small frequency shifts resulting from the environmental changes of the ligand molecule [8 – 11]. Hence the observed small frequency shifts for the B_1 and B_2 classes of the ligand molecule are resulting from the environmental changes caused by the 4-Phpy molecule upon coordination.

3.2. *M(CN)$_4$ Group Vibrations*

Assigments of the bands for the M(CN)$_4$ (M = Cd or Hg) ions in the spectra of the compounds were performed through the vibrational data of the $K_2M(CN)_4$ (M = Cd or Hg) salts in the solid phase reported by Jones [12] who assigned the vibrational data on the basis of T_d symmetry. The studies on these salts showed that the K-CN distances are 2.9 Å in $K_2Cd(CN)_4$ [13], $K_2Hg(CN)_4$ [14] while the Cd-NC distances are 2.3 Å in the T_d symmetry. Therefore we used them as references to account for the vibrational changes when the stiffer M-NC bonding takes place. The vibrational data for M(CN)$_4$ groups in the compounds are given in Table 2 along with the vibrational wavenumbers of $K_2Cd(CN)_4$ and $K_2Hg(CN)_4$. From Table 2, the vibrational frequencies of the M(CN)$_4$ ion groups in the complexes are shifted compared with those for the M(CN)$_4$ groups in $K_2M(CN)_4$ (M = Cd or Hg). Similar frequency shifts have been observed for the Hofmann-T_d type complexes [8, 9] and also for the Hofmann-T_d type clathrates [10, 11], and explained that the shifts arise from the mechanical coupling of the internal modes of M(CN)$_4$ (M = Cd or Hg) groups with metal atoms as both ends of the CN group are bound to the transition metals. Accordingly the shifts observed in the compounds can be attribute to the mechanical coupling of the internal modes of M(CN)$_4$ with metal atoms.

As a result, the similarities obtained for the spectral features of the present compounds with the Hofmann-T_d type structures let us to conclude that the compounds presented in this study are further examples of the Hofmann-T_d type complexes.

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