FT-IR Spectroscopic Study on Some 4-(3-Cyclohexen-1-yl)pyridine Metal(II) Tetracyanonickelate Complexes

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New Hofmann-type complexes in the form of M(4-Chpy)$_2$Ni(CN)$_4$ [where 4-Chpy = 4-(3-cyclohexen-1-yl)pyridine and M = Ni, Co] were prepared in powder form, and their infrared spectra are reported in the range of 4000 – 400 cm^{-1}. The spectral findings suggest that these compounds are similar in structure to the Hofmann-type complexes, and their structure consists of polymeric layers $|$M-Ni(CN)$_4|_\infty$ with the 4-(3-cyclohexen-1-yl)pyridine molecule bound to the metal atom (M).
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Key words: Hofmann-type Complexes; Tetracyanonickelate; 4-(3-Cyclohexen-1-yl)pyridine; Infrared Spectra.

1. Introduction

Hofmann-type host structures are defined by the general formula M(L$_2$)Ni(CN)$_4$ [1, 2]. In this host structure L$_2$ corresponds to a pair of monodentate ligand molecules and M is a divalent transition metal. Based on this structure, metal(II) tetracyanonickelate complexes have been developed using N-donor ligands such as ammonia [3] and pyridine [4]; O-donor ligands such as water [5], dimethylformamide [6] and dioxane [7] and the S-donor ligand dimethylthioformamide [8]. In this study we prepared M(4-Chpy)$_2$Ni(CN)$_4$ complexes (abbreviated hereafter as M-4-Chpy-Ni), where M = Ni or Co, for the first time, and the spectral properties of them were investigated in the IR region.

2. Experimental

All chemicals used were reagent grade (Merck), and they were used without further purification. The complexes M(4-Chpy)$_2$Ni(CN)$_4$ (M = Ni and Co) were prepared as follows: first 1 mmol of MCl$_2$ was solved in distilled water, then to this solution 1 mmol of K$_2$Ni(CN)$_4$, solved in distilled water, was added under stirring. After a short time slightly more than 2 mmol of 4-Chpy were dropwise added to the mixture, again under stirring. The final mixture was left for stirring for about a week at room temperature. The obtained product was filtered and washed with water, ethanol and diethyl ether successively and dried in a desiccator which included P$_2$O$_5$. Infrared spectra of the complexes as nujol mulls and KBr discs were recorded at 4000 – 400 cm^{-1} via a Perkin-Elmer FTIR 2000 spectrometer. The compounds were analyzed for metal content by a Perkin Elmer 4300 ICP-OES and for C, H and N by a Fisons EA-1108 element analyser. The results were as follows (found % / calculated %):

Co-4-Chpy-Ni: C(57.02/57.81), H(4.1/4.85), N(15.9/15,56), Ni(9.98/10,87), Co(10.1/10.91); Ni-4-Chpy-Ni: C(57.4/57.84), H(4.5/4.85), N(15.5/15.57), Ni(20.86/21.74).

3. Results and Discussions

The infrared spectra obtained for the M(4-Chpy)$_2$Ni(CN)$_4$ (M = Ni and Co) complexes are compatible with each other. This shows that the compounds have analogous spectral features. As an example the spectrum of Ni(4-Chpy)$_2$Ni(CN)$_4$ is shown in Figure 1. The spectral analysis of each compound was performed taking into account the Ni(CN)$_4$ ions and 4-Chpy molecule individually for convenience, explained below, starting with the Ni(CN)$_4$ group vibrations.

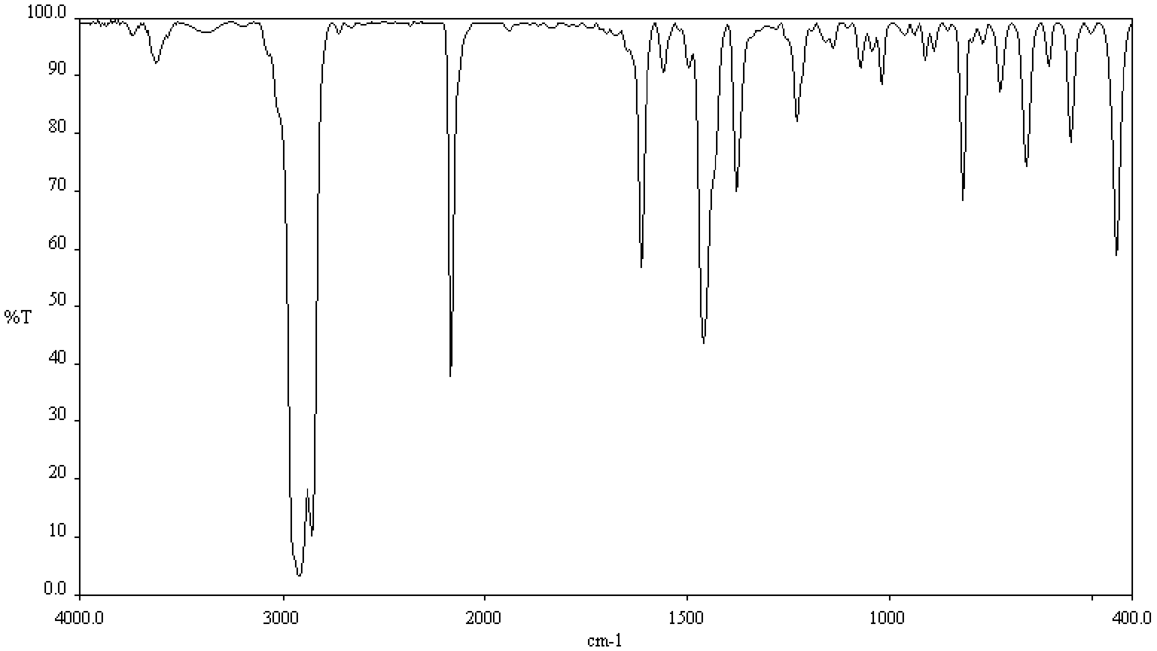

Fig. 1. Infrared spectrum of Ni(4-Chpy)$_2$Ni(CN)$_4$ in nujol.

3.1. Ni(CN)$_4$ Group Vibrations

If the unit cell has D_{4h} symmetry, seven normal modes of vibration are expected in the vibrational spectrum. Four of them are infrared active, and the others are Raman active. The infrared active vibrational modes are $E_u \upsilon$(CN), $E_u \upsilon$(Ni-CN), $A_{2u} \pi$(Ni-CN) and $E_u \delta$(Ni-CN), through which the sheet structure data were explained.

Assignments of the bands for the Ni(CN)$_4$ ion in the spectra of the present compounds were carried out through vibrational data of the $Ni(CN)_4^{2-}$ ion in NaNi(CN)$_4$ reported by McCullough et al. [9]. Since the ion is not coordinated to cations [9], it can be treated as an isolated unit. Therefore we used it as reference for finding out whether coordination to the metals M is taking place. The assignments of the vibrational bands for our complexes are given in Table 1 along with McCullough et al.'s data.

At first place the vibrational frequencies of the Ni(CN)$_4$ ion in the complexes are shifted compared to the isolated unit. Similar frequency shifts have been observed for Hofmann-type complexes [10 – 13]. The shifts arise from the mechanical coupling of the internal modes of Ni(CN)$_4$ with metal atoms as both ends of the CN group are bound to transition metal atoms. Accordingly, the shifts observed in the complexes can be attributed to the mechanical coupling of the internal modes of Ni(CN)$_4$ with a metal atom.

Table 1. The vibrational frequencies (cm^{-1}) of the Ni(CN)$_4$ group in the M-4-Chpy-Ni (M = Ni and Co) compounds.

Assignment[a]	Na$_2$Ni(CN)$_4$[a]	Ni-4-Chpy-Ni	Co-4-Chpy-Ni
ν_8(CN), E$_u$	2132	2169 vs	2163 vs
Hot band	2128	–	–
ν_9(NiC), E$_u$	543	–	–
π(NiC), A$_{2u}$	448	457 sh	453 sh
δ(NiCN), E$_u$	433	441 s	440 s

[a] Taken from [9]. vs, very strong; s, strong; sh, shoulder.

Another spectral feature is related to the characteristic υ(CN) and δ(NiCN) frequencies. The frequencies are similar to Hofmann-type complexes [10 – 13]. The similarity shows that the $|M\text{-}Ni(CN)_4|_\infty$ layers have been preserved. The presence of just one IR active $E_u \upsilon$(CN) stretching vibration in both spectra indicates that the local symmetry around the nickel atom is D_{4h}.

3.2. 4-(3-Cyclohexen-1-yl)pyridine Vibrations

To the best of our knowledge the vibrational assignments of the 4-Chpy molecule have not yet been reported. Therefore the spectral features due to the ligand molecule in the complexes were evaluated through the measured IR vibrational frequencies of

Table 2. The vibrational frequencies (cm^{-1}) of the 4-Chpy ligand in the M-4-Chpy-Ni (M = Ni and Co) compounds.

Ass.[a]	Cyclohexene[a]	Ass.[b]	Pyridine[b]	4-Chpy (measured)	4-Chpy (calculated)	Ni-4-Chpy-Ni	Co-4-Chpy-Ni
–	–	(CH)	3079	–	–	–	–
ν_{23}	3067	–	–	3067 w	3075 s	3068 vw	3068 vw
–	–	(CH)	3053	–	–	–	
–	–	(CH)	3053	–	–	–	
–	–	(CH)	3036	–	–	–	
ν_1	3026	(CH)	3026	3024 vs	3020 vs	–	
ν_{24}	2960	–	–	–	–	–	–
ν_2	2940	–	–	–	–	–	–
ν_3	2916	–	–	2917 vs	3006 s	2919 vs	2916 vs
ν_{25}	2898	–	–	–	–	–	–
ν_{26}	2882	–	–	–	–	–	–
ν_4	2865	–	–	–	–	–	–
ν_{27}	2860	–	–	–	–	–	–
ν_5	2839	–	–	2837 s	2586 s	2836 s	2835 s
ν_6	1656	–	–	1684 vw	no	1677 vw	1672 vw
–	–	$\nu_9 + \nu_{10}$	1598	1651 w	1653 s	1649 vw	1650 vw
–	–	ν_{ring}	1582	1600 vs	1608 s	1614 vs	1614 vs
–	–	ν_{ring}	1574	1556 m	1546 m	1558 m	1557 w
–	–	ν_{ring}	1482	1491 m	1505 m	1496 w	1499 w
ν_7	–	–	–	–	–	–	–
ν_{28}	1450	–	–	1450 sh	no	–	–
ν_{29}	1443	–	–	–	–	–	–
ν_8	1436	ν_{ring}	1438	1435 s	1458 s	1440 vs	1461 vs
–	–	combination	1374	1372 w	1363 m	1372 w	1377 w
–	–	ν_{ring}	1355	–	–	–	–
ν_9	1353	–	–	–	–	–	–
ν_{10}	1343	–	–	–	–	1340 sh	1344 sh
ν_{30}	1338	–	–	–	–	–	–
ν_{31}	1321	–	–	1321 m	1322 m	1320 vw	1319 vw
ν_{32}	1265	–	–	1267 w	1265 w	1266 vw	1266 vw
ν_{11}	1241	δ(CH)	1235	1247 w	1245 vw	1244 sh	1243 vw
ν_{12}	1222	–	–	–	–	–	–
	–	δ(CH)	1217	1220 m	1209 vw	1228 m	1229 m
ν_{33}	–	–	–	–	–	–	–
–	–	δ(CH)	1147	1188 w	1176 w	1193 w	1188 vw
ν_{13}	–	–	–	–	–	–	–
ν_{34}	1139	–	–	1142 w	1139 w	1139 w	1139 sh
ν_{14}	–	–	–	–	–	–	–
–	–	δ(CH)	1080	1092 vw	1105 w	1103 vw	1105 vw
ν_{15}	1068	δ(CH)	1068	1072 m	1072 m	1071 m	1072 m
ν_{35}	1040	–	–	–	–	–	–
–	–	ν_{ring}	1029	1044 w	1051 w	1043 vw	1044 vw
ν_{36}	1009	–	–	–	–	–	–
ν_{16}	996	–	–	–	–	–	–
–	–	ν_{ring}	990	994 m	1015 m	1023 m	1020 m
–	–	γ(CH)	–	–	–	–	–
–	–	unassigned	980	971 vw	973 w	964 vw	965 vw
–	–	γ(CH)	939	941 w	934 w	941 vw	942 w
ν_{37}	917	–	–	914 m	916 w	914 w	915 vw
ν_{17}	905	–	–	904 w	894 w	903 w	903 w
–	–	γ(CH)	–	–	–	–	–
–	–	γ(CH)	882	858 vw	868 w	859 w	842 vw
ν_{38}	878	–	–	–	–	–	–
ν_{18}	822	–	–	818 vs	806 s	821 s	824 s
ν_{19}	789	–	–	–	–	–	–
–	–	γ_{ring}	746	745 vw	761 vw	773 w	772 w
ν_{39}	721	–	–	725 m	733 m	728 m	724 w
–	–	γ(CH)	703	659 vs	687 m	664 s	666 s
–	–	δ_{ring}	650	616 w	no	–	–
ν_{40}	643	–	–	596 m	627 m	610 m	616 w
–	–	ν_{ring}	604	550 s	549 m	554 s	557 s
ν_{20}	495	–	–	503 w	498 w	504 w	504 w
ν_{41}	455	–	–	457 w	479 w	–	–
–	–	ν_{ring}	405	–	402 vw	–	–

[a,b] Taken from [15] and [10], respectively. vs, very strong; s, strong; m, medium; w, weak; vw, very weak. Ass: assignments.

the free ligand molecule. The vibrational frequencies for the free ligand were tabled according to vibrational frequencies of cyclohexene [14, 15] and pyridine [10], since the ligand molecule consists of both molecular structures. Additionally, normal mode frequencies of 4-Chpy (in gas phase) have been calculated at the b31yp/6-31g(d) level by using the package Gaussian 98 [16]. The calculated and measured IR data for the free molecule and the ligand molecule of the 4-Chpy in the complexes, together with the data for the cyclohexene and pyridine molecules, are given in Table 2.

The studies regarding Hofmann-type complexes [10 – 13] and also the Hofmann-type clathrates [17 – 19] manifest that typical spectral features of coordinations are frequency shifts of ligand molecules in complexes compared to free ligand molecules resulting from the ligand molecule complexed to the metal atom. As well as these shifts, small shifts also take place due to changes in the environment.

As can be seen from Table 2, the vibrational frequencies of the 4-Chpy molecule generally increase on complexing. However, among the vibrational modes the modes attributed to the pyridine molecule are more strongly perturbated. The strong band at 1600 cm^{-1} is shifted to 1614 cm^{-1} as an intense band. Another strong band at 1435 cm^{-1} shifts to 1440 cm^{-1} for Ni-4-Chpy-Ni, and to 1461 cm^{-1} for the Co-4-Chpy-Ni compounds. A shift takes place for the medium band at 1220 cm^{-1} around 8 cm^{-1}. The medium band at 999 cm^{-1} shifted to 1023 cm^{-1} for Ni-4-Chpy-Ni and to 1022 cm^{-1} for Co-4-Chpy-Ni. Similar upward shifts are also observed for the vibrational band of the ligand molecule in the frequency range from 457 to 818 cm^{-1}. The observed general increase of the vibrational frequencies is consistent with the Hofmann-type complexes of pyridine molecules reported in [10]. The upward shifts in frequencies were explained in terms of coupling of the internal vibration of the ligand molecule with M-N vibrations [10 – 13, 17 – 19]. In this respect, the strong perturbation of the pyridine molecule together with the general increase in vibration frequencies indicate that the pyridine molecule within the 4-Chpy ligand molecule is complexed to the metal atom. Regarding the cyclohexene molecule, the vibrational bands of the molecule possess small shifts. This shows that the molecule causes the environmental changes on complexing.

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

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