

An Infrared and Raman Spectroscopic Study of Metal(II) Di(2-Methylpyridine) Tetracyanonickelate Complexes: $\text{Ni}(\text{C}_6\text{H}_7\text{N})_2\text{Ni}(\text{CN})_4$ and $\text{Cd}(\text{C}_6\text{H}_7\text{N})_2\text{Ni}(\text{CN})_4$

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Abstract. The results of an infrared and Raman spectroscopic study are reported for two new metal 2-methylpyridine tetracyanonickelate complexes, $\text{M}(\text{C}_6\text{H}_7\text{N})_2\text{Ni}(\text{CN})_4$, $\text{M} = \text{Ni}$ or Cd . Their structure consists of corrugated polymeric layers of $\{\text{M}-\text{Ni}(\text{CN})_4\}_\infty$ with 2-methylpyridine molecules bound directly to the metal (M). These complexes can act as host lattices in the formation of inclusion compounds with dioxane guest molecules.

Key words: 2-methylpyridine, tetracyanonickelate complex, inclusion compound, infrared and Raman spectra.

1. Introduction

It is known that various *N*-donor ligands such as ammonia [1, 2], pyridine [3] and substituted pyridine [4, 5] can hold adjacent nickel cyanide layers apart and provide unoccupied sites, which, in some cases, can be filled with various guest molecules.

In previous publications [3, 4] we reported the IR and Raman spectra of $\text{ML}_2\text{Ni}(\text{CN})_4$ complexes (where L = pyridine, 3- or 4-methylpyridine). We are now reporting an IR and Raman spectroscopic study of two new tetracyanonickelate complexes of 2-methylpyridine, $\text{Ni}(\text{2-Mepy})_2\text{Ni}(\text{CN})_4$ and $\text{Cd}(\text{2-Mepy})_2\text{Ni}(\text{CN})_4$ (abbreviated henceforth as Ni-Ni-2Mepy and Cd-Ni-2Mepy). The aim of this study is to give further examples of layered tetracyanonickelate complexes and to study their ability with regard to the formation of inclusion compounds with various guest molecules.

2. Experimental

The complexes were prepared by adding slightly more than two moles of 2-methylpyridine and one mole of potassium tetracyanonickelate solution to one mole of M(II) chloride solution using constant stirring. The Cd-Ni-2Mepy complex was also prepared by adding 2-methylpyridine to an aqueous ammoniacal solution of cadmium tetracyanonickelate ($\text{pH} = 9$). Although in the case of Ni, the latter method gave a $\text{Ni}(\text{NH}_3)(\text{2-Mepy})\text{Ni}(\text{CN})_4$ complex, after refluxing in 2-Mepy for two days, it changed into $\text{Ni}(\text{2-Mepy})_2\text{Ni}(\text{CN})_4$.

The complexes were analyzed for metal content using the X-ray fluorescence method.

The inclusion compounds of the M-Ni-2Mepy complexes with dioxane were prepared by stirring these complexes in dioxane at 50°C for 3 h.

The IR spectra of mulls and discs were recorded on a Perkin–Elmer 621 spectrometer. The

Raman spectra of the samples were excited using an argon ion laser and recorded on a Spex Ramalog spectrometer.

3. Results and Discussion

The vibrational wavenumbers of 2-methylpyridine in the IR and Raman spectra of the M-Ni-2Mepy complexes are given in Table I, together with liquid 2-methylpyridine wave-

Table I. The infrared and Raman wavenumbers (cm^{-1}) of 2-methylpyridine molecules in Ni-Ni-2Mepy and Cd-Ni-2Mepy complexes

Assignment ^a	Liquid ^b		Ni-Ni-2Mepy		Cd-Ni-2Mepy	
	IR	R	IR	R	IR	R
A'						
ν_1 CH str.	3080	3089	3086 <i>w</i>	–	3075 <i>m</i>	3080 <i>w</i>
ν_2 CH str.	–	3046	3071 <i>w</i>	–	3063 <i>sh</i>	–
ν_3 X-Sens.	1233	1236	{ 1234 <i>w</i> 1223 <i>w</i>	{ – 1225 <i>w</i>	1221 <i>w</i>	–
ν_4 ring str.	1590	{ 1589 1591	1611 <i>vs</i>	1610 <i>w</i>	1607 <i>vs</i>	1608 <i>w</i>
ν_5 ring str.	1475	1479	1491 <i>vs</i>	–	1491 <i>vs</i>	–
ν_6 i.p. $\delta(\text{CH})$	1143	1149	1163 <i>s</i>	1151 <i>w</i>	1158 <i>s</i>	1160 <i>w</i>
ν_7 i.p. $\delta(\text{CH})$	1047	1050	1065 <i>s</i>	1066 <i>s</i>	1063 <i>s</i>	1065 <i>s</i>
ν_8 X-Sens.	798	800	806 <i>m</i>	809 <i>m</i>	804 <i>m</i>	808 <i>s</i>
ν_9 ring str.	994	998	1013 <i>s</i>	1016 <i>vs</i>	1011 <i>s</i>	1014 <i>vs</i>
ν_{10} X-Sens.	548	548	554 <i>m</i>	–	552 <i>m</i>	554 <i>m</i>
ν_{11} CH str.	3080	3089	3086 <i>w</i>	–	3075 <i>m</i>	3080 <i>w</i>
ν_{12} CH str.	–	3046	3030 <i>w</i>	–	3022 <i>m</i>	3028 <i>w</i>
ν_{13} ring str.	1565	1568	1572 <i>s</i>	–	1572 <i>s</i>	1575 <i>w</i>
ν_{14} ring str.	1440	1428	1458 <i>sh</i>	–	1447 <i>s</i>	–
ν_{15} ring str.	1376	1376	–	–	–	–
ν_{16} i.p. $\delta(\text{CH})$	1291	1295	1309 <i>s</i>	–	1308 <i>s</i>	1314 <i>vw</i>
ν_{17} X-Sens.	358	360	396 <i>w</i>	–	380 <i>m</i>	385 <i>vw</i>
ν_{18} i.p. $\delta(\text{CH})$	1099	1100	1111 <i>m</i>	1111 <i>w</i>	1107 <i>m</i>	–
ν_{19} i.p. ring def.	628	629	640 <i>m</i>	–	640 <i>m</i>	653 <i>vw</i>
A''						
ν_{20} o.p. $\delta(\text{CH})$	972	–	982 <i>vw</i>	–	980 <i>vw</i>	–
ν_{21} o.p. $\delta(\text{CH})$	883	883	–	–	–	–
ν_{22} o.p. ring def.	403	403	426 <i>sh</i>	–	415 <i>s</i>	–
ν_{23} o.p. $\delta(\text{CH})$	940	–	962 <i>vw</i>	–	959 <i>vw</i>	–
ν_{24} o.p. $\delta(\text{CH})$	751	–	754 <i>vs</i>	–	752 <i>vs</i>	–
ν_{25} o.p. ring. def.	729	726	725 <i>s</i>	–	721 <i>s</i>	–
ν_{26} o.p. $\delta(\text{CH})$	470	470	476 <i>m</i>	–	471 <i>m</i>	–
ν_{27} X-Sens.	–	207	–	–	–	198
ν_s (CH_3)	2925	2925	2922 <i>m</i>	–	2924 <i>m</i>	2930 <i>w</i>
ν_a (CH_3)	2950	2960	2947 <i>m</i>	–	2950 <i>w</i>	–
δ_s (CH_3)	1376	1376	1385 <i>m</i>	–	1383 <i>m</i>	1387 <i>vw</i>
δ_a (CH_3)	1440	1428	1437 <i>vs</i>	–	1433 <i>vs</i>	–
CH_3 rock	1040	1036	1040 <i>m</i>	1041 <i>vw</i>	1036 <i>m</i>	–

^a Assignment is done by correlating 2-methylpyridine vibrations [6] with those of pyridine [3].

^b Wavenumbers are taken from [6].

vs = very strong, *s* = strong, *m* = medium, *w* = weak, *vw* = very weak, *sh* = shoulder.

numbers [6]. The spectra of both of the compounds (Ni and Cd) show all the principle features found earlier for coordinated pyridine [3, 7] and coordinated pyridine derivatives [4, 5, 8]. Namely several modes of the 2-methylpyridine have upward shifts in frequency when compared with the free molecule and the shifts are metal dependent. Analogous shifts on coordination were observed in pyridine, 3- and 4-methylpyridine complexes [3, 4, 7, 8] and explained as the coupling of the internal modes of the aromatic molecule with the M—N vibrations. Thus we have obtained direct evidence from the vibrational spectra of M-Ni-2Mepy that 2-methylpyridine molecules coordinate to metal (M = Ni or Cd).

The vibrational wavenumbers of the Ni(CN)₄ group are tabulated in Table II, along with the vibrational wavenumbers of the M(py)₂Ni(CN)₄ complexes [3]. The characteristic $\nu(\text{CN})$ and $\delta(\text{NiCN})$ frequencies are found to be similar to those known for the Hofmann-type clathrates [9] and pyridine complexes [3], indicating that the $\{\text{M-Ni}(\text{CN})_4\}_\infty$ layers have been preserved. The presence of just one IR active (E_u) and two Raman active (A_{1g} and B_{1g}) CN stretching vibrations normally confirms the square planar environment around the Ni(CN)₄ ion. On the other hand we also observed one $\nu(\text{CN})$ band (E_u) in the IR and two other $\nu(\text{CN})$ bands (A_{1g} and B_{1g}) in the Raman spectra of both Cd(py)₂Ni(CN)₄ [3] and Cd(4-Clpy)(NH₃)Ni(CN)₄ (4-Clpy = 4-chloropyridine) [4] complexes, the crystallographic studies of these complexes [10, 11] proved that the square planar environment around the tetracyanonickelate ion is slightly distorted when compared with the Hofmann-type clathrates which have tetragonal symmetry [2]. The structure of both complexes also consists of polymeric two-dimensional networks made up of tetracyanonickelate ions coordinated to cadmium, but the $\{\text{Cd-Ni}(\text{CN})_4\}_\infty$ layers are not planar, like Hofmann's benzene clathrate [1], they are undulated [10, 11]. This undulation in the layers occurs because of a departure from linearity in the Ni—C—N—Cd sequence of atoms at the carbon and nitrogen positions. Thus the effect of a slight deviation from a square planar environment may not be apparent in the vibrational spectra of tetracyanocomplexes. Although there is no crystallographic study of M-Ni-2Mepy complexes, the present spectroscopic data do not disagree with our proposal that the M-Ni-2Mepy complexes have structures closely related to Mpy₂Ni(CN)₄ with the undulated $\{\text{M-Ni}(\text{CN})_4\}_\infty$ layers.

Table II. The infrared and Raman wavenumbers (cm⁻¹) of the Ni(CN)₄ group vibrations of the M(2-Mepy)₂Ni(CN)₄ and M(py)₂Ni(CN)₄ complexes

Assignment	Ni-Ni-py ^a		Cd-Ni-py ^a		Ni-Ni-2Mepy		Cd-Ni-2Mepy		Relative intensity
	IR	R	IR	R	IR	R	IR	R	
$\nu(\text{CN})$ (A_{1g})	—	2186	—	2172	—	2196	—	2178	<i>vs</i>
$\nu(\text{CN})$ (B_{1g})	—	2177	—	2160	—	2175	—	2167	<i>s</i>
$\nu(\text{CN})$ (E_u)	2170	—	2154	—	2166	—	2157	—	<i>vs</i>
$\nu(^{13}\text{CN})$	2129	—	2111	—	2127	—	2116	—	<i>vw</i>
$\nu(\text{NiC})$ (E_u)	550	—	543	—	^b	—	^b	—	<i>w</i>
$\pi(\text{NiCN})$ (A_{2u})	453	—	—	—	459	—	449	—	<i>w</i>
$\delta(\text{NiCN})$ (E_u)	441	—	425	—	444	—	428	—	<i>s</i>

The symbols ν , δ and π refer to valence, in-plane and out-of-plane vibrations respectively.

^a Taken from [3].

^b Overlapped by the ν_{10} band of 2-methylpyridine.

vs = very strong, *s* = strong, *w* = weak, *vw* = very weak.

We have tried to prepare inclusion compounds of these complexes with aniline, benzene, thiophene and dioxane; however, we have so far only succeeded with dioxane. The IR spectra of the Cd-Ni-2Mepy complex and its inclusion compound with dioxane are given in Figure 1 a and b, respectively. All the vibrational frequencies of the dioxane guest molecules in the IR spectra of M-Ni-2Mepy compounds correspond closely in frequency and intensity to those in the IR spectra of $M(\text{NH}_3)_2\text{Ni}(\text{CN})_4 \cdot 2\text{C}_4\text{H}_8\text{O}_2$ (M = Ni or Cd) clathrates [12]. It is found that dioxane escapes slightly from dioxane-treated samples upon grinding or under reduced pressure without any change in the vibrational frequencies of the host structure. Dioxane bands disappeared totally after washing the dioxane-treated samples with water several times; but by that time the sample contained water as guest molecules.

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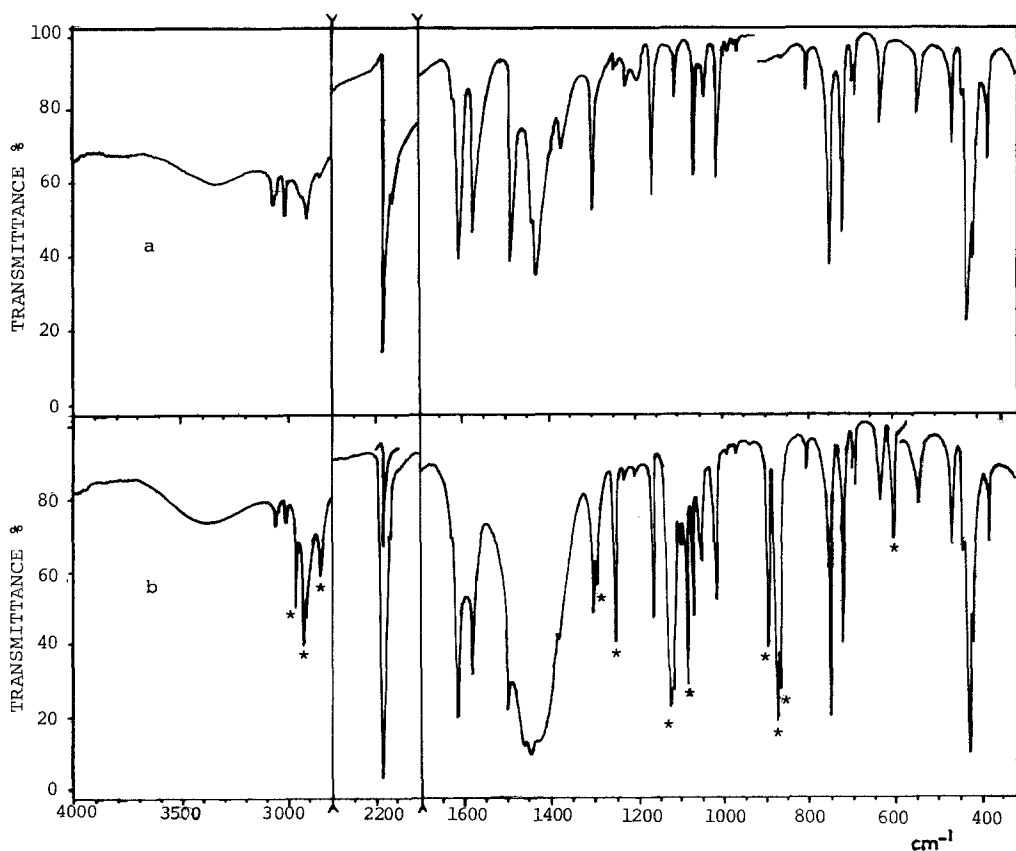


Fig. 1. The infrared spectra of KBr discs of $\text{Cd}(2\text{-Mepy})_2\text{Ni}(\text{CN})_4$ complex (a) and of its inclusion compound with dioxane (b). Dioxane bands marked*.

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