

# Vibrational Spectroscopic Studies of Three Dimensional Host Lattices Formed by Pyrazine Bridges between Tetracyanonickelate Layers

TANIL AKYÜZ

*Mineral Research and Exploration Institute of Turkey (M.T.A.), Ankara, Turkey.*

SEVİM AKYÜZ\*

*International Centre for Theoretical Physics, Trieste, Italy.*

J. ERIC D. DAVIES

*Department of Chemistry, Lancaster University, Lancaster, LA1 4YA, England.*

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**Abstract.** Three dimensional host lattices have been developed by forming bridges with bidentate pyrazine molecules between adjacent tetracyanonickelate polymeric layers of Ni(II) or Cd(II). The Fourier-transform IR and Raman spectra ( $4000\text{--}200\text{ cm}^{-1}$ ) of the compounds with the general formula  $M(\text{pyz})\text{Ni}(\text{CN})_4$ , (where  $M = \text{Ni}$  or  $\text{Cd}$ ) are reported. These host lattices can include benzene molecules but it is found that aniline molecules cannot be included in these structures. They, however, form complexes with the formula  $M(\text{an})_2\text{Ni}(\text{CN})_4$ , by replacing pyrazine ligands. A monodentate pyrazine complex of Cd(II) with the formula  $\text{Cd}(\text{pyz})_2\text{Ni}(\text{CN})_4$  has also been prepared.

**Key words.** Tetracyanonickelate compounds, benzene clathrate, pyrazine complexes, IR and Raman spectra.

## 1. Introduction

Recently several metal complex hosts have been developed from the two dimensional Hofmann-type host lattices,  $M(\text{NH}_3)_2\text{Ni}(\text{CN})_4$ , by replacing the ammonia molecules by bidentate ligands [1–6]. Mathey *et al.* [5] reported that pyrazine molecules can form bridges between adjacent nickel tetracyanonickelate planes,  $[\text{Ni}—\text{Ni}(\text{CN})_4]$  and they gave the infrared wavenumbers of  $\nu(\text{CN})$  and  $\delta(\text{NiCN})$  modes. To the best of our knowledge no complete vibrational spectroscopic study has been reported on  $\text{Ni}(\text{pyz})(\text{Ni}(\text{CN})_4)$ . On the other hand the  $\text{Cd}(\text{pyz})\text{Ni}(\text{CN})_4$  compound is prepared for the first time. In the course of our investigations, pyrazine molecules were found to act also as monodentate ligands and to give the  $\text{Cd}(\text{pyz})_2\text{Ni}(\text{CN})_4$  complex.

In this work we give further examples of Hofmann-type three dimensional host lattices, and discuss in detail the vibrational wavenumbers of the pyrazine molecule related to its denticity and to the presence of the different transition metals.

\*Author for correspondence. Permanent address: Ondokuz Mayıs University, Department of Physics, Samsun, Turkey.

## 2. Experimental

$M(\text{pyz})\text{Ni}(\text{CN})_4 \cdot n \text{C}_6\text{H}_6$  (where  $M = \text{Ni}$  or  $\text{Cd}$ ,  $n = 0-0.5$ ) compounds (abbreviated hence  $M\text{-Ni-pyz}$ ) were prepared employing a method analogous to that used for 4,4'-bipyridyl benzene clathrates [6]. In some preparations the compounds were found to contain water (both bound and enclathrated) but after being stirred with dimethoxypropane containing a little amount of pyrazine dissolved in benzene for 1-2 days, the samples could be obtained entirely free of water. However, when the  $\text{Cd-Ni-pyz}$  compound was stirred with the methoxypropane/benzene solution containing more pyrazine (for one mole of  $\text{Cd-Ni-pyz}$ , slightly more than one mole of  $\text{pyz}$ ) in a closed flask, by a magnetic stirrer for a week, the  $\text{Cd}(\text{pyz})_2\text{Ni}(\text{CN})_4$  complex was obtained. This complex does not include any benzene molecule in the structure. The samples were analysed for C, H, and N contents by microanalysis and for metal content by X-ray fluorescence methods.

The FT-IR spectra were recorded on a Nicolet MX-IE spectrometer in Nujol and hexachlorobutadiene mulls between CsI windows. The spectrometer was calibrated using  $\text{CO}_2$  bands.

Raman spectra of the samples were excited using the 488.0 nm line of an  $\text{Ar}^+$  laser, recorded on a Cary 81 spectrometer with a slit width of  $3.2 \text{ cm}^{-1}$ , with the use of a spinning cell.

## 3. Results and Discussion

### 3.1. PYRAZINE VIBRATIONS

The IR spectrum of the  $\text{Cd}(\text{pyz})\text{Ni}(\text{CN})_4 \cdot 0.5\text{C}_6\text{H}_6$  (I) clathrate is given in Figure 1a. The IR spectrum of the  $\text{Cd}(\text{pyz})_2\text{Ni}(\text{CN})_4$  (II) complex, where the pyrazine molecules are bound to cadmium as monodentate ligands, is given in Figure 1b for comparison. The latter complex does not show any tendency of inclusion of benzene molecules. The fundamental vibrational wavenumbers of pyrazine in the IR and Raman spectra of the compounds studied are given in Table I together with the vibrational wavenumbers of pyrazine in solution [7].

Electron diffraction [8, 9] and X-ray diffraction [10, 11] studies have demonstrated the  $D_{2h}$  symmetry of pyrazine in the vapour and solid phases. In complexes in which pyrazine coordinates to two identical metal atoms, as a bidentate ligand, the centre of symmetry of pyrazine will be retained, but is removed in monodentate complexes. Therefore an IR and Raman spectroscopic study gives direct evidence for the denticity of the pyrazine molecule.

The vibrational spectra of the compounds studied show all the principal features found earlier for coordinated pyrazine [12, 14]. Namely several modes of the pyrazine molecule have upward shifts in frequency when compared with the free molecule and the shifts are metal dependent (see Table I). Analogous shifts on coordination were observed in pyridine [15] and 4,4'-bipyridyl complexes [6] and explained as the coupling of the internal modes of the aromatic molecule with the  $M-N$  vibrations [6, 15, 16]. On the other hand, we do not observe any coincidences between the IR and Raman spectra of the  $\text{Ni-Ni-pyz}$  (I) compounds indicating that pyrazine molecules are in a bidentate coordination. However, for

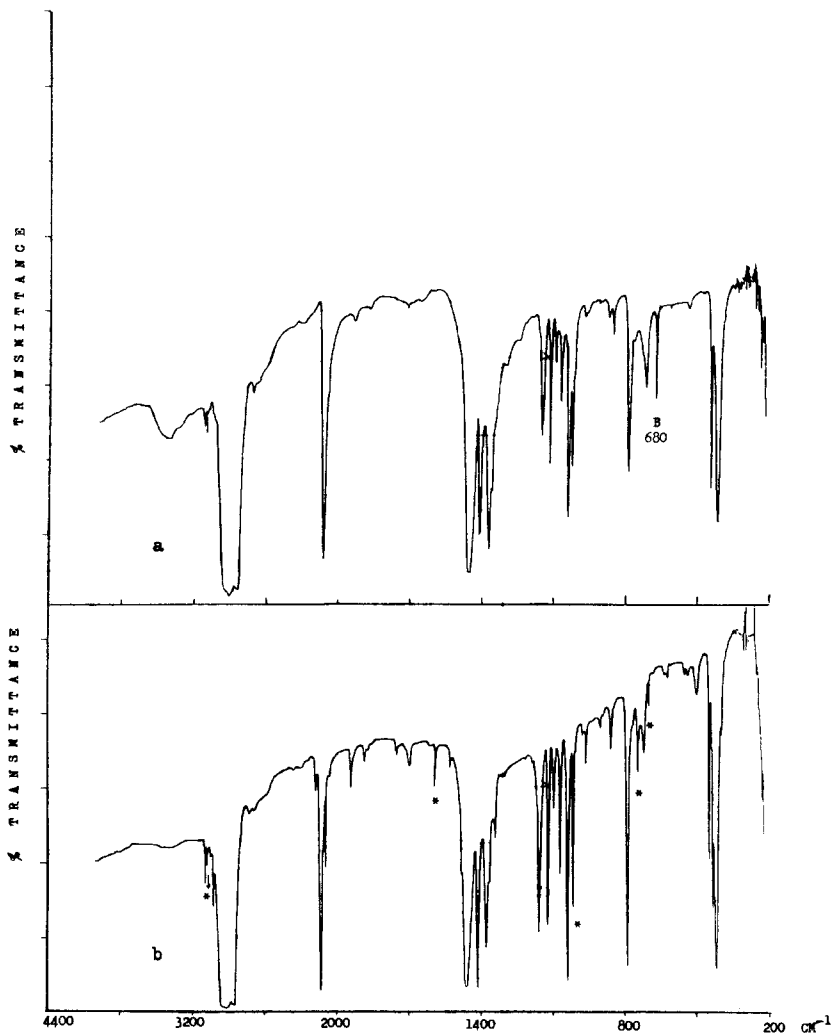


Fig. 1. Infrared spectra of Nujol mulls of the  $\text{Cd}(\text{pyz})\text{Ni}(\text{CN})_4 \cdot 0.5 \text{C}_6\text{H}_6$  (a) and  $\text{Cd}(\text{pyz})_2\text{Ni}(\text{CN})_4$  (b) compounds. B = benzene. The most predominant differences between the monodentate pyrazine complex and the bidentate complex are marked\*.

Cd-Ni-pyz (**II**) a large number of such coincidences are found largely fulfilling the predicted behaviour for monodentate pyrazine coordination although intensity considerations restrict the number of observable coincidences (see Table I).

On the basis of the vibrational spectroscopic results we therefore propose that in the case of the Ni-Ni-pyz and Cd-Ni-pyz (**I**) compounds the pyrazine molecules are bound to metal atoms (Ni or Cd, respectively) of the adjacent layers of  $[\text{M}-\text{Ni}(\text{CN})_4]_\infty$  as bidentate ligands. However, in the case of Cd-Ni-pyz (**II**) complex, the pyrazine molecules are bound to Cd as monodentate ligands and this compound of composition  $\text{Cd}(\text{pyz})_2\text{Ni}(\text{CN})_4$  is correctly formulated as a true

Table I. Fundamental vibrational wavenumbers of pyrazine in Ni(py<sub>z</sub>)Ni(CN)<sub>4</sub>·0.5 C<sub>6</sub>H<sub>6</sub>, Cd(py<sub>z</sub>)Ni(CN)<sub>4</sub>·0.5 C<sub>6</sub>H<sub>6</sub> (I) and Cd(py<sub>z</sub>)<sub>2</sub>Ni(CN)<sub>4</sub> (II) compounds.

Symmetry and assignment <sup>a</sup>	Pyrazine solution <sup>a</sup>		Ni		Cd I		Cd II		Relative intensity
	IR	R	IR	R	IR	R	IR	R	
16a, A <sub>u</sub> 'ring	422 <sup>b</sup>	—	438	—	435	—	435 s	—	sh
16b, B <sub>2u</sub> 'ring	418	—	485	—	451	—	450	—	s
6a, A <sub>g</sub> δ <sub>ring</sub>	—	600	—	—	—	—	—	—	—
6b, B <sub>2g</sub> δ <sub>ring</sub>	—	701	—	704	—	702	703w	702	m
4, B <sub>3g</sub> 'ring	—	756	—	—	—	748	748	748	w
11, B <sub>3u</sub> ν(CH)	785	—	810	—	796	—	792	797vw	vs
10a, B <sub>1g</sub> ν(CH)	—	919	—	915	—	913	912	913	vw
5, B <sub>3g</sub> ν(CH)	—	983	—	—	—	—	—	—	—
17a, A <sub>u</sub> ν(CH)	997 <sup>b</sup>	—	—	—	—	—	1028	—	vw
?	—	—	—	—	1031	—	—	—	s
1, A <sub>g</sub> 'ring	—	1011	—	1038	—	1027	1018	1021	vs
12, B <sub>1u</sub> δ <sub>ring</sub>	1019	—	1060	—	1047	—	1042m	1042	vs
15, B <sub>3u</sub> δ(CH)	1061	—	1089 s	—	1078	—	1072	1074 vw	m
18a, B <sub>1u</sub> δ(CH)	1130	—	1132	—	1125	—	1124	—	s
14, B <sub>3u</sub> 'ring	1150	—	1164	—	1157	—	1159	—	s
9a, A <sub>g</sub> δ(CH)	—	1231	—	—	—	1230	—	1230	w
3, B <sub>2g</sub> δ(CH)	—	1343	—	—	—	1370	—	1370	w
19b, B <sub>3u</sub> ν <sub>ring</sub>	1412	—	1424	—	1419	—	1414	1416vw	vs
19a, B <sub>1u</sub> ν <sub>ring</sub>	1483	—	1494	—	1481	—	1481	—	w
8b, B <sub>2g</sub> ν <sub>ring</sub>	—	1524	—	1525	—	1522	1530	1533 vw	m
8a, A <sub>g</sub> ν <sub>ring</sub>	—	1574	—	1607	—	1587	1590	1587	m
13, B <sub>1u</sub> ν(CH)	3011	—	3049	—	3043	—	3049	—	m
7b, B <sub>2g</sub> ν(CH)	—	3040	—	—	—	—	—	—	—
2, A <sub>g</sub> ν(CH)	—	3054	—	3081	—	3078	3079	3078	m
20b, B <sub>3u</sub> ν(CH)	3061	—	3100	—	3095	—	3095	—	m

<sup>a</sup>Taken from Ref. 7, <sup>b</sup>Solid phase value.

compound and not as an inclusion compound such as Cd(py<sub>z</sub>)Ni(CN)<sub>4</sub>·py<sub>z</sub>. Mathey *et al.* [5] however reported that excess pyrazine could be included in the structure of Ni–Ni-py<sub>z</sub> leading to Ni(py<sub>z</sub>)Ni(CN)<sub>4</sub>·0.5 py<sub>z</sub>. We do not observe pyrazine bands which do not show coordination properties, i.e. closer in frequency to those of free pyrazine, in the vibrational spectra of the compounds studied. Instead we do have mixtures of the monodentate and bidentate pyrazine complexes, Ni(py<sub>z</sub>)Ni(CN)<sub>4</sub> and Ni(py<sub>z</sub>)<sub>2</sub>Ni(CN)<sub>4</sub>, depending on the preparation. The predominant spectral difference observed in the IR spectra of the complexes containing monodentate pyrazine with compounds containing a bidentate bridging ligand is the appearance of the absorptions at about 3079 (2, A<sub>g</sub>), 1590 (8a, A<sub>g</sub>), 1018 (1, A<sub>g</sub>), 748 (4, B<sub>3g</sub>), and 703 (6b, B<sub>2g</sub>) cm<sup>-1</sup> which are not allowed in the IR spectra of the bidentate complexes. These bands are marked with asterisks in Figure 1b.

### 3.2. TETRACYANONICKELATE GROUP VIBRATIONS

The vibrational wavenumbers of the Ni(CN)<sub>4</sub> group vibrations of the compounds studied are tabulated in Table II. The wavenumbers of the ν(CN) and δ(NiCN)

Table II. Fundamental vibrational wavenumbers of the tetracyanonickelate group in sodium crystal and in M-Ni-pyz compounds.<sup>a</sup>

Assignment <sup>b</sup>	Na <sup>b</sup>	Ni I	Cd I	Cd II	Relative intensity
1, $A_{1g}$ , $\nu(\text{CN})$	2149	(2193)	(2159)	(2158)	vs
4, $B_{1g}$ , $\nu(\text{CN})$	2141	(2182)	(2145)	(2143)	vs
	2132				
8, $E_u$ , $\nu(\text{CN})$	2128	2173	2135	2133	vs
9, $E_u$ , $\nu(\text{NiC})$	543	558	544	544	w
12, $A_{2u}$ , $\pi(\text{NiCN})$	448	458	—	—	sh
	433				
10, $E_u$ , $\delta(\text{NiCN})$	421	443	423	423	vs

<sup>a</sup>The bands observed in the infrared spectra are given without parentheses, those observed in the Raman spectra are given in parentheses.

Ni:  $\text{Ni}(\text{pyz})\text{Ni}(\text{CN})_4 \cdot 0.5 \text{C}_6\text{H}_6$ , Cd(I):  $\text{Cd}(\text{pyz})\text{Ni}(\text{CN})_4 \cdot 0.5 \text{C}_6\text{H}_6$ , Cd (II):  $\text{Cd}(\text{pyz})_2\text{Ni}(\text{CN})_4$  <sup>b</sup>Taken from Ref. 18.

bands observed in the IR spectrum of the Ni-Ni-pyz compound are found to be similar to those given by Mathey *et al.* [5]. Since we observed only one  $\nu(\text{CN})$  ( $E_u$ ) band in the IR spectrum and the other two  $\nu(\text{CN})$  bands ( $A_{1g}$  and  $B_{1g}$ ) in the Raman spectrum of the M-Ni-pyz compounds, we propose a square planar environment around the tetracyanonickelate ion. The cyanide stretching vibrational modes of the Cd-Ni-pyz (I) compound are observed at 2135 (IR,  $E_u$ ), 2145 ( $R_a$ ,  $B_{1g}$ ), and 2159 ( $R_a$ ,  $A_{1g}$ )  $\text{cm}^{-1}$  which are rather low in comparison with those of the other compounds that have  $[\text{Cd}-\text{Ni}(\text{CN})_4]_\infty$  polymeric layers (e.g. in the range between 2144–2154  $\text{cm}^{-1}$ ) [6, 15–17]. However these vibrational modes are found to be still higher than those of the corresponding ones of the free  $\text{Ni}(\text{CN})_4^{2-}$  ion [18]: For example in the case of sodium tetracyanonickelate crystal these modes were observed at 2132 and 2128 ( $E_u$ ), 2141 ( $B_{1g}$ ), and 2149 ( $A_{1g}$ )  $\text{cm}^{-1}$  [18]. It is known that cyanide stretching modes shift to higher wavenumber in the case of the compounds that have  $[\text{M}-\text{Ni}(\text{CN})_4]_\infty$  polymeric layers, due to the mechanical coupling with M—NC modes, mostly  $\nu(\text{M}-\text{N})$  [15] thus the stronger this (M—N) bond, the higher its frequency and the higher become the  $\nu(\text{CN})$  frequencies. Therefore we may suggest that the Cd—NC bond in the Cd-Ni-pyz compound is rather weak in comparison with the other known  $\text{Cd}(\text{L})_2\text{Ni}(\text{CN})_4$  compounds (L = 4,4'-bipy, py or  $\text{NH}_3$ ) that have Cd-tetracyanonickelate polymeric layers [6, 15, 17]. On the other hand in the IR spectra of the  $\text{Cu}(\text{L})_2\text{Ni}(\text{CN})_4$  complexes (where L = pyridine, 2-, 3- or 4-methylpyridine) [15, 19] the  $\nu(\text{CN})$  ( $E_u$ ) IR active mode is observed as doublet pairs and the wavenumber of the lower one of this pair is in the range between 2142–2136  $\text{cm}^{-1}$ , which is close to our observations in Cd-Ni-pyz.

The  $\text{Ni}(\text{CN})_4$  vibrational modes of the monodentate pyrazine complex, Cd-Ni-pyz (I), are found to be similar to those of the corresponding bidentate compound (II), indicating that the polymeric layers are the same for both compounds. We observed a very weak band at 2178  $\text{cm}^{-1}$  in the IR spectrum of the Cd-Ni-pyz (II) complex and assume it to arise from the decomposed structure where the tetra-

cyanonickelate ion is still coordinated to Cd atoms which have lost their pyrazine molecules, consistent with the decomposition studies of the Hofmann-type clathrates [17, 20].

### 3.3. INCLUSION PROPERTIES OF THE M-Ni-pyz COMPOUNDS

It is found that both the Ni-Ni-pyz and Cd-Ni-Pyz (I) compounds can include benzene in their structures. The  $\nu_{11}(A_{2u})$  vibrational mode of benzene is observed at  $680\text{ cm}^{-1}$  in the IR and the  $\nu_1(A_{1g})$  mode is observed at  $991\text{ cm}^{-1}$  in the Raman spectra of the compounds. However we have never observed any inclusion of aromatic molecules whose volumes are greater than that of benzene in these compounds. When we have tried to prepare inclusion compounds with aniline, we have found that aniline molecules form a complex with the formula,  $M(\text{an})_2\text{Ni}(\text{CN})_4$  by replacing pyrazine molecules.

The  $\text{Cd}(\text{pyz})_2\text{Ni}(\text{CN})_4$  complex does not show any tendency of adsorption of benzene.

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