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The FT-IR spectra of pyrazinamide complexes of transition metal(II) tetracyanonickelate

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Abstract

$M(PZA)_2Ni(CN)_4$ {where M = Mn, Co, Fe, Ni or Cd; PZA = pyrazinamide} complexes have been prepared for the first time and their FT-IR spectra are reported in the 400–4000 cm^{-1} region. The spectral features suggest that the compounds are similar in structure to the Hofmann type two dimensional coordination polymer compounds, formed with $Ni(CN)_4^{-2}$ ions bridged by $M(PZA)_2^{+2}$ cations. PZA is coordinated to M(II) through the oxygen atom of the carbonyl group.

Keywords: Infrared spectra; Hofmann type complexes; Tetracyanonickelate; Transition metal; Pyrazinamide; Pyrazine carboxamide

1. Introduction

Pyrazinamide (pyrazine carboxamide), is a well known anti tubercle bacillus drug [1]. The parent molecule and some of its complexes are widely used due to their antimycobacterial properties [1,2]. Although vibrational frequencies of pyrazine are extensively studied [3–6], IR and Raman data on pyrazinamide (PZA) [7–8] and its complexes are not plentiful in the literature [9–11]. The only detailed analysis of IR and polarized Raman spectra of PZA was reported by Kalkar et al. [7]. To the best of our knowledge no complete IR spectroscopic investigation on PZA complexes was reported in the literature. Only the wavenumbers of ν(C=O), $\nu(NH_2)$ and few ring modes were given [9–11]. Therefore, it would be interesting to investigate vibrational frequencies of PZA in a series of Hofmann type tetracyanonickelate complex hosts [12]. In this study, the two dimensional coordination polymer compounds, $M(PZA)_2Ni(CN)_4$ {where M = Mn, Co, Fe, Ni or Cd; PZA = pyrazinamide, and abbreviated henceforth M–Ni–PZA}, in which the sheet is constructed by the linkage between the square planar $Ni(CN)_4^{2-}$ and the octahedral M(II) through cyano bridges; have been prepared for the first time and their FT-IR spectra are reported in the 400–4000 cm^{-1} region.

2. Experimental

All the chemicals used were reagent grade (Merck) and used without further purification. The complexes were prepared using the method given in Ref. [13]. The samples were analysed for the metal content

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using an X-ray fluorescence method. The relative ratios of M and Ni atoms were found to be 1:1. The C, H, N analysis results for M=Ni and Cd complexes are: *Anal. Found* for Ni–Ni–PZA: C; 35.41%, H; 2.40%, N; 29.42%, *Calcd.* for $Ni(PZA)_2Ni(CN)_4$: C; 35.84%, H; 2.15%, N; 29.89%, *Anal. Found* for Cd–Ni–PZA: C; 31.85%, H; 1.90%, N; 26.43%, *Calcd.* for $Cd(PZA)_2Ni(CN)_4$: C; 32.22%, H; 1.93%, N; 26.87%. The differences in elemental analysis indicate non-stoichiometry of the coordination polymer and defects in the polymer structure. It must be noted that samples are found to contain small amounts of water as guest species. The IR spectra of nujol mulls or KBr discs were recorded on a Jasco 300E FT-IR spectrometer (2 cm^{-1} resolution).

3. Results and discussion

The structural formula of PZA is given in Fig. 1. The FT-IR spectra of Fe-Ni–PZA and Ni–Ni–PZA complexes are given in Fig. 2(a) and (b), respectively. The IR spectra of the M–Ni–PZA complexes are very similar indicating that they have analogous structures. The vibrational wavenumbers of PZA are tabulated in Table 1 together with the relevant data [7].

PZA can coordinate through the pyrazine ring nitrogens, the >C=O and/or $-NH_2$ groups. IR technique is diagnostic of the coordination mode of PZA in complexes. When the aromatic ring nitrogen involves in complex formation, certain ring modes, particularly the ring breathing mode and the two ring stretching modes around 1400–1600 cm^{-1} increase in value both due to the coupling with M–N(ligand) bond vibrations [14–16] and due to alterations of the ring force field [17]. On the other hand when amino nitrogen is involved in coordination, drastic changes occur in amino group vibrational wavenumbers [18–21], and when coordination occurs through the oxygen of the carbonyl group, a negative shift of the ν(C=O) mode of the coordinated molecule with respect to the free ligand is expected [22]. Therefore in order to determine the coordination mode of PZA in M–Ni–PZA complexes, the wavenumbers of PZA in complexes are compared with those of free PZA.

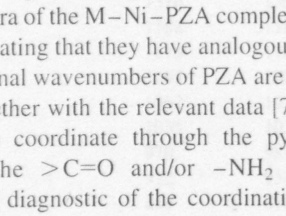

Fig. 1. Structural formula of pyrazinamide.

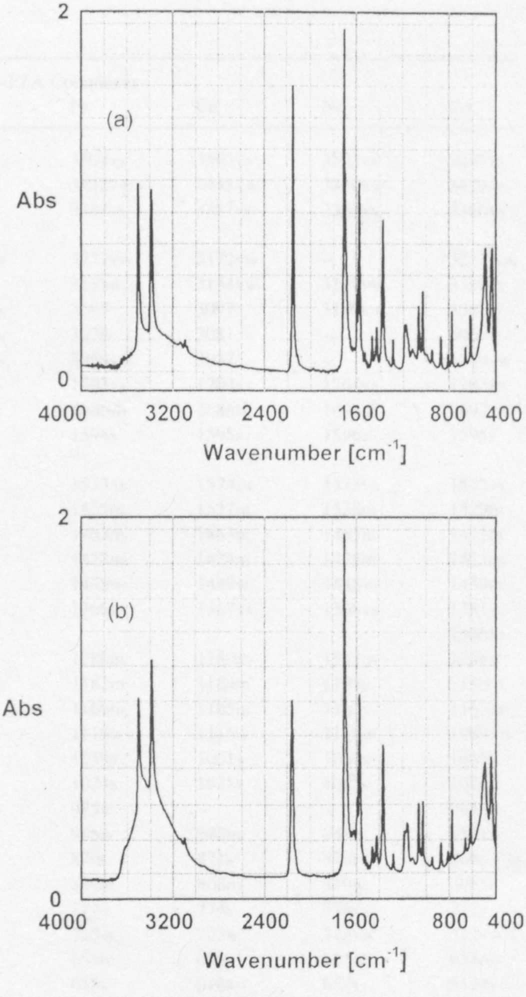

Fig. 2. The FT-IR spectra of $Fe(PZA)_2Ni(CN)_4$ (a) and $Ni(PZA)_2Ni(CN)_4$ (b).

In the IR spectra of the PZA complexes studied, the $\nu_a(NH_2)$ and $\nu_s(NH_2)$ modes are found to be higher in value than those of microcrystalline PZA (Table 1). Since it is well known that a coordinated amino group shows a negative shift, $\Delta = 150–220\ cm^{-1}$, in the NH_2 stretching modes, in comparison to the free

Table 1
The wavenumbers (cm^{-1}) of PZA in M–Ni–PZA complexes

Tentative assignment [7]	PZA[a]		M–Ni–PZA Complexes				
	[7]	This study	Mn	Fe	Co	Ni	Cd
$\nu_{a}NH_{2}$) a$'$	3515M	3412vs	3487vs	3504vs	3503vs	3503vs	3489vs
	3420D		3446sh	3432vw	3448vw	3450vw	3436m
νsNH_{2}) a$'$	3370	3368sh	3377vs	3387vs	3387vs	3387vs	3380vs
	3170D	3290m					
$2\delta NH_{2}$)?		3210sh	3253vw	3272vw	3172vw	–	3257 vw
		3163s	3137w	3135w	3134vw	3137vw	3139m
ν(CH) a$'$	3088	3088	3088vw	3093	3097	3100vw	3087w
ν(CH) a$'$	3065	3066	3076vw	3078	3081	–	3069w
ν(CH) a$'$	3050	3052	3048vw	3058vw	3057	–	3049vw
ν(C=O), amide I, a$'$	1710	1714vs	1704sh	1703vs	1704vs	1704vs	1703sh
			1690vs	1686sh	1686sh	1690sh	1697vs
$\delta(NH_{2})$, amide II, a$'$	1610D	1610s	1595s	1594s	1595s	1596s	1594s
	1565M						
ν_{ring}, a$'$	1589	1581s	1575vs	1573vs	1574vs	1573vs	1575vs
ν_{ring}, a$'$	1530	1525m	1528m	1525m	1527m	1528m	1529m
ν_{ring}, a$'$	1480	1479m	1472m	1463m	1463m	1465m	1472m
ν_{ring}, a$'$	1443	1437m	1430w	1423m	1424m	1425m	1425sp
			1441m	1448w	1449w	1448w	1439m
ν(CN), amide III, a$'$	1385	1378vs	1382s	1366s	1367vs	1368vs	1381s
							1366m
δ(CH), a'	1316	1305w	1290m	1280m	1280m	1281m	1288w
δ(CH), a$'$	1188	1183m	1181[b]m	1182m	1184m	1185s	1180m
ν_{ring}, a$'$	1175	1166m	1165m	1166m	1165m	1162s	1163m
NH_{2} twist, a$''$	1095	1087m	1090w	1116w	1116w	1118w	1099vw
δ(CH), a$'$	1062	1054s	1065s	1059s	1061s	1063s	1065s
Ring breath, a$'$	1035	1025s	1023s	1024s	1025s	1025s	1024s
γ(CH), a$''$	970	988vw	981vw	975w	–	–	981vw
γ(CH), a$''$	922	954vw	948w	946w	946m	946w	959vw
δ_{ring}, a$'$	882	870s	866s	870s	871s	870m	866s
CO i.p. bend, amide IV, a$'$	815	800sh	809m	806m	808m	810w	808m
γ(CH), a$''$	791	786s	770s	774s	774s	775s	771s
γ_{ring}, a$''$	705	702w	723w	722w	723w	723vw	722vw
NH_{2} wag., a$''$	678	670vs	656m	659m	660m	661m	658ms
δ_{ring}, a$'$	615	619m	611ms	615s	616s	617s	612m
δ_{ring}, a$'$	562	543vs	521vs	512sh	513sh	516sh	510vs
		518vs					
CO o.p. bend, amide VI a$''$	450	–	–	489s	489s	494s	490sh
$C-NH_{2}$ i.p. bend, a$'$	435	431vs	438vs	439vs	440vs	439vs	442m
γ_{ring}, a$''$	412	419m	420sh	**	**	420sh	420sh
γ_{ring}. a$''$		413m	409m	414m	–	415m	–

**Overlapped with δ(NiCN) mode. i.p. = in plane, o.p. = out of plane.

[a] Solid pyrazinamide (KBr). M = value of monomer structure, D = value of dimer structure.

[b] Mean of doublet.

ligand [18–21], we can conclude that this group does not take part in coordination. On the other hand the $\nu(C-NH_{2})$ mode of aniline and aniline derivatives shows a negative shift, $\Delta = 50-60\ cm^{-1}$, upon coordination [18–21], but we do not observe such a shift of this mode in M–Ni–PZA complexes, which is a further proof of a non-coordinated amide nitrogen. In solid PZA, amide group hydrogens are involved inter and intra H-bonds [7]. We could not record IR spectrum of PZA dissolved in a non-polar solvent (free PZA), due to its poor solubility. Nevertheless, the slight up shift of $\nu(NH_2)$ of M–Ni–PZA complexes indicates that the NH_2 group of the PZA forms weaker H-bonds than in the pure solid. The IR data show that the amide NH_2 of PZA does not take part in coordination, but forms weak hydrogen bonds, probably with guest water molecules. It must be noted that samples are found to contain small amount of water as guest species.

In the IR spectra, the ring-breathing mode of PZA is observed at 1025 cm^{-1} for solid PZA and around 1023–1025 cm^{-1} for M–Ni–PZA complexes. The lack of blue shift of ring breathing suggests that the PZA molecule does not coordinate to the metal(II) in M–Ni–PZA complexes through the heterocyclic ring nitrogen. We also do not observe any blue shift in certain ring modes due to formation of M–Ni–PZA complexes (Table 1), which are known to be very sensitive to complex formation through the ring nitrogen [14–17].

The IR spectra of the M–Ni–PZA compounds show negative shifts of $\nu(C{=}O)$. The $\nu(C{=}O)$ mode was observed at 1714 cm^{-1} in the FT-IR spectrum of the KBr disk of PZA and was observed at 1716 cm^{-1} in the Raman spectrum of solid PZA [7]. In the IR spectra of M–Ni–PZA compounds the $\nu(C{-}O)$ mode is observed in the range of 1686–1704 cm^{-1} ($\Delta = \nu_{solid} - \nu_{compl.} = 14-10\ cm^{-1}$). Since in solid PZA, a intra molecular H-bond, between the carbonyl oxygen and adjacent amide hydrogen, exists [7], the $\nu(C{=}O)$ mode of the free molecule is expected at higher wavenumber than in the solid, thus the real shift on the $\nu(C{=}O)$ vibration should be higher. We may conclude that coordination through the >C=O groups in the M–Ni–PZA complexes is implied by the FT-IR spectra. A similar coordination mode of PZA was observed in lanthanide complexes [9–10] and in adsorbed species on metal surfaces [8].

The vibrational wavenumbers of the $Ni(CN)_4$ group for the complexes studied are given in Table 2 together with those of $Na_2Ni(CN)_4$ crystal [23], Hofmann-type clathrates [24] and pyridine complexes [14] for comparison. The CN stretching mode, $\nu(CN)$, is observed at 2080 cm^{-1} in the IR spectrum of solid KCN, whereas the IR active $\nu(CN)$ mode (E_u) of free $Ni(CN)_4^{-2}$ group is observed at 2130 cm^{-1} in the IR spectrum of solid $K_2Ni(CN)_4$. The upward shift of 50 cm^{-1}on going from CN^{-1} to $Ni(CN)_4^{-2}$ was explained as the mechanical coupling of the Ni–C(CN) stretching mode with the $\nu(CN)$ [14]. In Hofmann-type hosts $\{M(L)_2Ni(CN)_4\}$, the $Ni(CN)_4^{-2}$ group is further coordinated to the metals (M) through the nitrogen atoms. In this case the IR active $\nu(CN)$ (E_u) mode was observed around 2148–2170 cm^{-1} (e.g. for Hofmann-type pyridine complexes and benzene or aniline clathrates [14,24]). The further shift which is around 18–40 cm^{-1} compared to the free $Ni(CN)_4^{-2}$ ion is explained to be the result of the coupling of the M–N(NC) stretching mode with $\nu(CN)$ [14,24]. In Hofmann-type host lattices, $\{M(L)_2Ni(CN)_4\}$, the CN stretching wavenumber was also known to be very sensitive to the coordination state of the M(II) atom; in the case of decomposed host lattices, where the metal–ligand (L)

Table 2
The IR spectral wavenumbers of the $Ni(CN)_4$ group vibrations in sodium crystal, Hofmann-type pyridine complexes and benzene clathrates and in M–Ni–PZA complexes

Assignment	Na[a]	Pyridine[b]		Clathrate[c]		Mn	Fe	Co	Ni	Cd	Rel. Int.
		Mn	Ni	Mn	Ni						Int.
$E_u\ \nu(CN)$	2132	2155	2170	2152	2161	2149	2151	2152	2160	2150	vs
	2128										vs
$\nu(^{13}CN)$	2087	2114	2129	2112	2120	2110	2110	–	2133	2113	vw
$E_u\ \nu(NiC)$	543	545	550	–	554	547	548	551	554	548	vw
$A_{2u}\ \pi(NiCN)$	448	–	453	448	460	456	456	456	458	456	sh
$E_u\ \delta(NiCN)$	433	432	441	428	436	431	432	434	442	429	vs
	421										

[a] $^{a}Na_2Ni(CN)_4$ crystal taken from Ref. [23].

[b] $^{b}M(pyridine)_2Ni(CN)_4$ complexes (M = Mn or Ni) taken from Ref. [14].

[c] $^{c}M(NH_3)_2Ni(CN)_4{\cdot}C_6H_6$ clathrates (M = Mn or Ni) taken from Ref. [24].

bonds were broken, the ν(CN) shifted to ca. 2190 cm^{-1} [24,25], indicating the contribution of an electronic component in the up-shift of the bridging CN-groups. In our complexes studied, this mode is observed in 2148–2160 cm^{-1}, similar to those of non-decomposed Hofmann-type hosts and this confirms the coordination of PZA to the M(II) cation. It is concluded that M–Ni–PZA compounds are similar in structure to the Hofmann type two dimensional coordination polymer compounds, formed with $Ni(CN)_4^{-2}$ ions bridged by $M(PZA)_2^{+2}$ cations. The ν(CN) E_u and δ(NiCN) E_u modes are both observed as strong and sharp bands in the IR spectra of the complexes showing that $Ni(CN)_4$ groups have a local D_{4h} symmetry.

4. Conclusion

The IR spectroscopic study of five new complexes has shown that they have similar structures with linkage between the square planar $Ni(CN)_4^{2-}$ and the octahedral M(II) through cyano bridges. The six coordination of M(II) is satisfied by four terminal N of the cyano groups and two PZA molecules. IR spectra reveal coordination of the PZA through carbonyl oxygen.

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