Infrared and Raman study of some isonicotinic acid metal(II) halide and tetracyanonickelate complexes

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ABSTRACT

In this study the $M(IN)_2Ni(CN)_4$ [where M: Co, Ni, and Cd, and IN: isonicotinic acid, abbreviated to M–Ni–IN] tetracyanonickelate and some metal halide complexes with the following stoichiometries: $M(IN)_6X_2$ (M: Co; X: Cl and Br, and M: Ni; X: Cl, Br and I) and $Hg(IN)X_2$ (X: Cl, Br, and I) were synthesized for the first time. Certain chemical formulas were determined using elemental analysis results. The FT-IR and Raman spectra of the metal halide complexes were reported in the $4000–0\,cm^{-1}$ region. The FT-IR spectra of tetracyanonickelate complexes were also reported in the $4000–400\,cm^{-1}$ region. Vibrational assignments were given for all the observed bands. For a given series of isomorphous complexes, the sum of the difference between the values of the vibrational modes of the free isonicotinic acid and coordinated ligand was found to increase in the order of the second ionization potentials of metals. The frequency shifts were also found to be depending on the halogen. The proposed structure of tetracyanonickelate complexes consists of polymeric layers of $|M–Ni(CN)_4|_\infty$ with the isonicotinic acid molecules bound directly to the metal atom.

1. Introduction

Isonicotinic acid ($C_6H_5NO_2$, 4-pyridinecarboxylic acid: IN) is a compound that has considerably biological interest. A derivative of IN, the hydrazine, isoniazide possesses tuberculastotic properties, it can be administered to patients. Both IN, and isonicotinylglycine are found in the urine because of their metabolism in human body [1]. IN substituted different atoms or groups shows antibacterial properties [2]. It is also used for the determination of cyanide in water as an effective substance with together pyrazolone [3]. The metal complexes of biologically important ligands are sometimes more effective than free ligands [4]. Therefore, some of the metal halide complexes of IN were synthesized and their spectroscopic features were investigated.

The vibrational analysis of free IN was made by Afifi and Shabana [5]. In that study, the spectroscopic features of some pyridine derivatives such as nicotinamide, nicotinic acid and isonicotinic acid were evaluated for a few bands. The synthesis, spectral and thermal properties of some various complexes $[M(IN)_nH_2O]$ has been reported [6]. The structural properties of Cu(II) and Cu(I) chloride complexes of IN are described in the literature [7–9]. In a recent paper the theoretical vibrational analysis of free IN were made by Koczon et al. for a few bands [10]. There is no plentiful report on the complexes of IN with transition metal(II) salts and tetracyanonickelate complexes studied here.

In our recent papers, the structural and spectroscopic properties of metal(II) halide and tetracyanonickelate complexes of isonicotinamide [11–13] nicotinamide [14–16] were investigated. In addition to these we have also reported the IR spectra of $M(IN)_2Ni(CN)_4$ [M: Cu, Mn, Zn, $Cu(IN)X_2$ (X: Br and I), $Cd(IN)_2X_2$ (X: Cl and Br) and $Zn(IN)_4X_2$ (X: Br and I) [17]. In this study we continue with $M(IN)_2Ni(CN)_4$ [M: Co, Ni and Cd], $M(IN)_6X_2$ (M: Co; X: Cl, Br and M: Ni; X: Cl, Br and I) and $Hg(IN)X_2$ (X: Cl, Br and I) complexes to detect any relation between the free ligand and complex vibrational values in their IR spectral data.

2. Experimental

All the chemicals (Aldrich and Sigma) were reagent grade and were used without further purification. Metal chloride, bromide or iodide (1 mmol) was dissolved in absolute hot ethanol (10 ml). The appropriate quantity of IN was added to the solution. The mixture was stirred magnetically at room temperature for 24 h. The precipitated complexes were filtered, washed with the ether and dried. The potassium tetracyanonickelate was prepared by mixing stoichiometric amounts of nickel(II) chloride with potassium cyanide in

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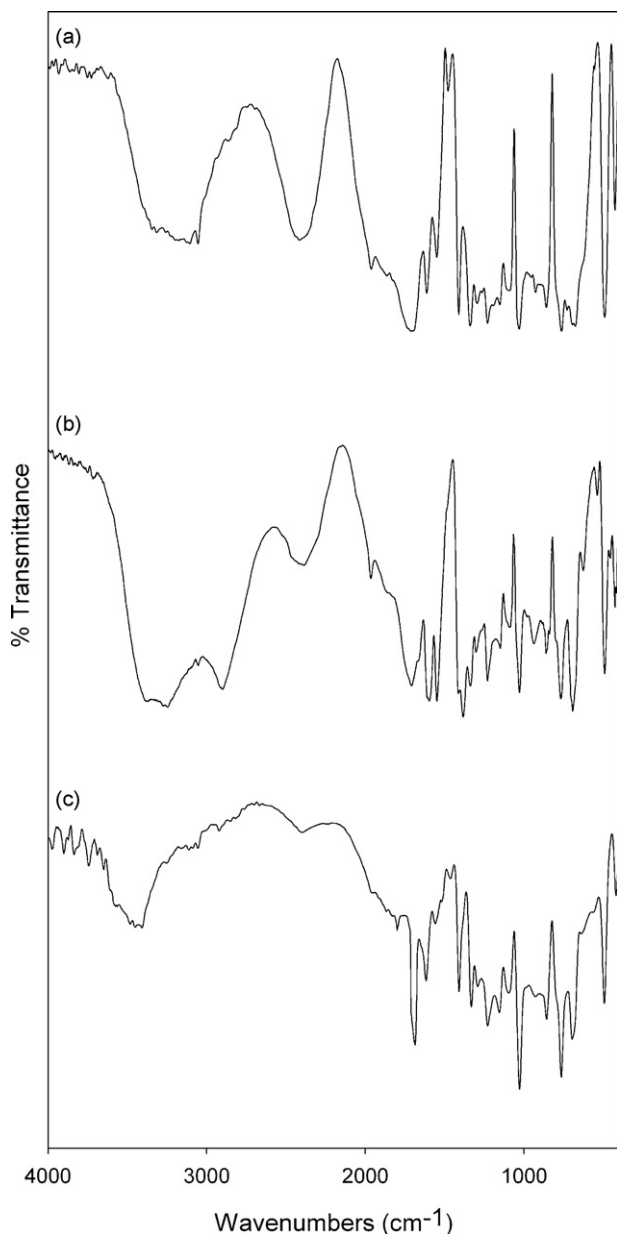 E-mail address: fbardak@gmail.com (F. Bardak).

Fig. 1. The FT-IR spectra of Co(IN)$_6$Cl$_2$ (a), Ni(IN)$_6$Cl$_2$ (b) and Hg(IN)I$_2$ (c) complexes.

water solution. M(IN)$_2$Ni(CN)$_4$ was prepared by dissolving 1 mmol of K$_2$Ni(CN)$_4$ in water. To this solution 2 mmol of ligand (IN) and 1 mmol of the metal halide dissolved in ethanol was added. The reaction mixture was stirred for few days at room temperature. The product obtained was filtered and washed with ethanol and dried in vacuum desiccators.

The prepared samples were analyzed for C, H and N with a LECO CHN-932 analyzer. The middle and far infrared spectra of discs (KBr) of fresh samples were recorded on Mattson 1000 FT-IR (4000–400 cm^{-1}) and IFS/66(400–0 cm^{-1}). The Raman spectra of complexes were recorded on FRA6106/S (3500–80 cm^{-1}).

3. Results and discussion

IN has substitution in *para*-position of the pyridine. If we assume the carboxyl group (−COOH) had a single mass point all the molecules under consideration would belong to C_{2v} point group. It has 27 normal vibrations of which 19 ($10A_1 + 9B_2$) are planar and

8 ($3A_2 + 5B_1$) are non-planar. In addition to these 27 ring vibrations there would be 9 vibrations due to the substitute carboxyl group.

Although most metal halide pyridine complexes have been characterized crystallographically, there is a distinct lack of structural data for isonicotinic acid halide and tetracyanonickelate complexes studied here. However, since isostructural complexes are known to exhibit similar band patterns in their vibrational spectra [18–20] in the absence of structural data on a given complex, it has been classified depending on its spectroscopic features.

The FT-IR spectra of Co(IN)$_6$Cl$_2$, Ni(IN)$_6$Cl$_2$, and Hg(IN)I$_2$ complexes was given in Fig. 1. The vibrational assignments of IN taken from our previous paper Ref. [17] were given together with the observed bands of the Co(IN)$_6$Cl$_2$, Co(IN)$_6$Br$_2$, Ni(IN)$_6$Cl$_2$, Ni(IN)$_6$Br$_2$, Ni(IN)$_6$I$_2$, Hg(IN)Cl$_2$, Hg(IN)Br$_2$, and Hg(IN)I$_2$ complexes in Table 1.

IN has different coordination form it is coordinated not only through the carboxyl group but also through the nitrogen atom of
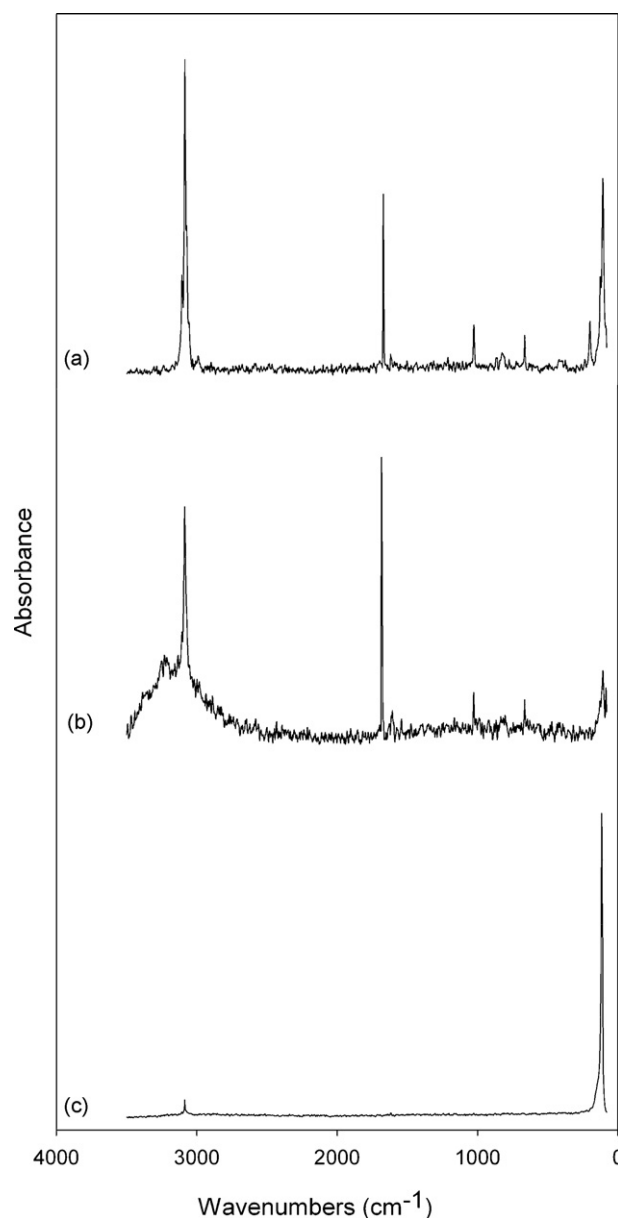

Fig. 2. The Raman spectra of Co(IN)$_6$Cl$_2$ (a), Ni(IN)$_6$Cl$_2$ (b) and Hg(IN)I$_2$ (c) complexes.

Table 1
The infrared wave numbers (cm^{-1}) of free IN and metal halide complexes

Co(IN)$_6$Cl$_2$	Co(IN)$_6$Br$_2$	Ni(IN)$_6$Cl$_2$	Ni(IN)$_6$Br$_2$	Ni(IN)$_6$I$_2$	Hg(IN)Cl$_2$	Hg(IN)Br$_2$	Hg(IN)I$_2$	IN	Assignments[a]
3343m	3369m	3370s	3374s	3374s	3404w	3403w	3407w	3440w	i.p.ν(OH)
3314m	3332m	3376s							
3105m	3107m	3245s	3249s	3246s	3103m	3101m		3102vw	i.p.ν(CH)
3053m	3053m	3052m			3053m	3052m		3052vw	i.p.ν(CH)
1711vs	1713s	1706m	1707m	1730w	1692vs	1690vs	1685s	1711s	ν(C=O)
			1662sh	1661m	1658m				
1613s	1611s	1596s	1595vs	1597s	1615m	1615m	1617m	1616m	Py(CC+CN)str
1549m	1547s	1548s	1550vs	1551s	1567m	1566m	1559w	1563w	Py(CC+CN)str
1479vw	1484w				1470vw	1474w	1464vw	1472vw	CH bend
1411s	1410vs	1414vs	1416s	1420m	1411s	1411s	1410m	1411s	CH bend
	1382vs	1384vs	1384vs	1384vs					
1339vs	1339vs	1337s	1341sh		1334vs	1340vs	1332m	1338s	ν(C—O)
1295s	1302s	1302m	1301m		1302vs	1304s	1292m	1302m	COO tr
1229vs	1229s	1229s	1230m	1233m		1229s	1229s	1231s	COH tr
					1219sh	1193sh		1216sh	CH rock+COH tr
1152s	1149s	1149m	1149m	1153w	1147s	1161s	1155m	1146m	ν(C$_{py}$C$_{COOH}$)
1090m	1087s	1086m	1092w	1089w	1100s	1101m	1097m	1094m	C—O str
			1052sh	1056m	1085m			1081m	Ring CC str+C—Ostr
1030vs	1027vs	1029s	1027m	1024m	1031vs	1029vs	1032vs	1027vs	Ring def.
954sh		978sh	980sh	984vw	981sh			972sh	Ring breath
926s	929s	936m	938m	940m	911m	926s	927m	921m	o.p.CH bend
			862m	868m	882m			881sh	o.p.CH bend
859s	855s	861m	854m	854m	855s	861vs	854m	857s	o.p.CH rock
763vs	761vs	768s	771s	776s	761s	751vs	765vs	762vs	Ring def.
695vs	693vs	693vs	692vs	690vs	695vs	692vs	697s	697vs	o.p.COOH def.
676sh		626w	623w	621m	678sh	673sh		674sh	Ring def.
553vw		539vw	539w	539m	559vw		565w	549vw	o.p. OH bend
491s	488s	492m	492m		486s	495s	494m	492s	γOCO
		457sh	458vw	458m					
426m	418s	427m	422w	423m	423m	427m	419vw	418w	o.p.ring def.+COOH def
95	93	83	81	51	51	30	28	Sum shift	

Py: pyridine, rock: rocking, tr: torsion, str: stretching, i.p.: in plane, bend: bending, o.p.: out of plane, def.: deformation, vs: very strong, s: strong, m: medium, w: weak, vw: very weak, and sh: shoulder.

[a] Taken from Ref. [17].

the pyridine ring. The most important vibrational modes are ν(C=O) and pyridine ring vibrations to interpret the coordination of the metal atom to the IN ligand molecule. Because, it is known that if the coordination takes place through carboxyl oxygen it is expected that the ν(C=O) vibration shifts strongly to below region as shown in the spectra of isonicotinic acid N-oxide metal complexes [21,22]. On the other hand similar negative shifts are expected in vibrational modes of pyridine ring nitrogen when the coordination takes place through pyridine ring nitrogen.

The ν(C=O) bands of pyridine derivatives containing carboxyl group were expected around the usually higher than $1650\,cm^{-1}$ [23]. A strong band was appeared at $1711\,cm^{-1}$ in the infrared spectrum of free IN and assigned ν(C=O). Pyridine has four ring vibrations in the region of $1615–1410\,cm^{-1}$ [23]. These bands observed at $1616\,cm^{-1}$, $1563\,cm^{-1}$, $1472\,cm^{-1}$, and $1411\,cm^{-1}$ in the spectrum of free IN and assigned Py(CC+CN)strength, Py(CC+CN)strength, CH bending, CH bending, respectively.

The ν(C=O) band was observed at $1692\,cm^{-1}$, $1690\,cm^{-1}$ and $1685\,cm^{-1}$ in the spectra of Hg(IN)Cl$_2$, Hg(IN)Br$_2$ and Hg(IN)I$_2$ complexes, respectively. This significant shift was a result of coordination taken place through the carboxyl oxygen to the Hg atom. Pyridine ring vibration bands observed at $1616\,cm^{-1}$ and $1563\,cm^{-1}$ in the spectrum of free IN are not shift in the spectra of Hg(IN)X$_2$ (X: Cl, Br, I) complexes. This situation clearly indicates that the coordination of IN take place via only the carboxyl oxygen to the Hg atom with a monomer structure.

The Py(CC+CN)strength vibration frequencies shift to the negative region in the spectra of M(IN)$_6$X$_2$ (M: Co; X: Cl, Br and M: Ni; X: Cl, Br and I) complexes are studied here. As seen from Table 1 the ν(C=O) vibration modes did not shift remarkable to the below region with respect to free mode. Therefore, it was suggested that

only the pyridine ring nitrogen is involved in complex formations in these complexes. On the other hand, a strong band was observed due to ν(C=O) vibration in the higher region in the spectrum of the Ni(IN)$_6$I$_2$ complex. It is commonly known that if the ring nitrogen is involved in complex formation, it affects the ν(C=O) and pyridine ring vibrations and they shift to the higher region in the complexes of pyridine and pyridine derivatives [11–13]. The positive shift in the spectrum of Ni(IN)$_6$I$_2$ complex is explained that the carboxyl group does not involved in coordination with nickel atom.

Since isostructural complexes are known to exhibit similar band patterns in their vibrational spectra, [18,19] the Co(IN)$_6$X$_2$ (X: Cl and Br) and Ni(IN)$_6$X$_2$ (X: Cl, Br and I) complexes are assumed to have the same structure due to mentioned reason. The proposed geometric structure of the M(IN)$_6$X$_2$ (where M: Ni and Co) according to vibrational frequency and elemental analysis results; the metal atoms surrounded by six ligand molecules binding coordinate covalent bonds with an octahedral environment in this structure. The metal atoms keep their valance electrons in this kind of bindings. The halogen atoms hold onto metal atoms with ionic bindings by using these valance electrons.

The Raman spectra of the Co(IN)$_6$Cl$_2$, Ni(IN)$_6$Cl$_2$ and Hg(IN)I$_2$ complexes were given in Fig. 2. It is known that CH stretching band is observed between the ranges of $3090–3010\,cm^{-1}$ [23]. A similar band was observed in the Koczon's [10] and Park's [24] papers at $3086\,cm^{-1}$ and $3081\,cm^{-1}$ in the Raman spectra of the free IN, respectively. A very strong band was observed in $3084\,cm^{-1}$ in the Raman spectra of the cobalt, nickel complexes and a weak band mercury complex studied here and assigned ν(C—H) as in literature [23]. The ν(C=O) vibration band was observed at $1671\,cm^{-1}$, and $1682\,cm^{-1}$ in the spectra of cobalt and nickel complexes, respectively. These bands were observed at $1687\,cm^{-1}$ in Koczon's [10]
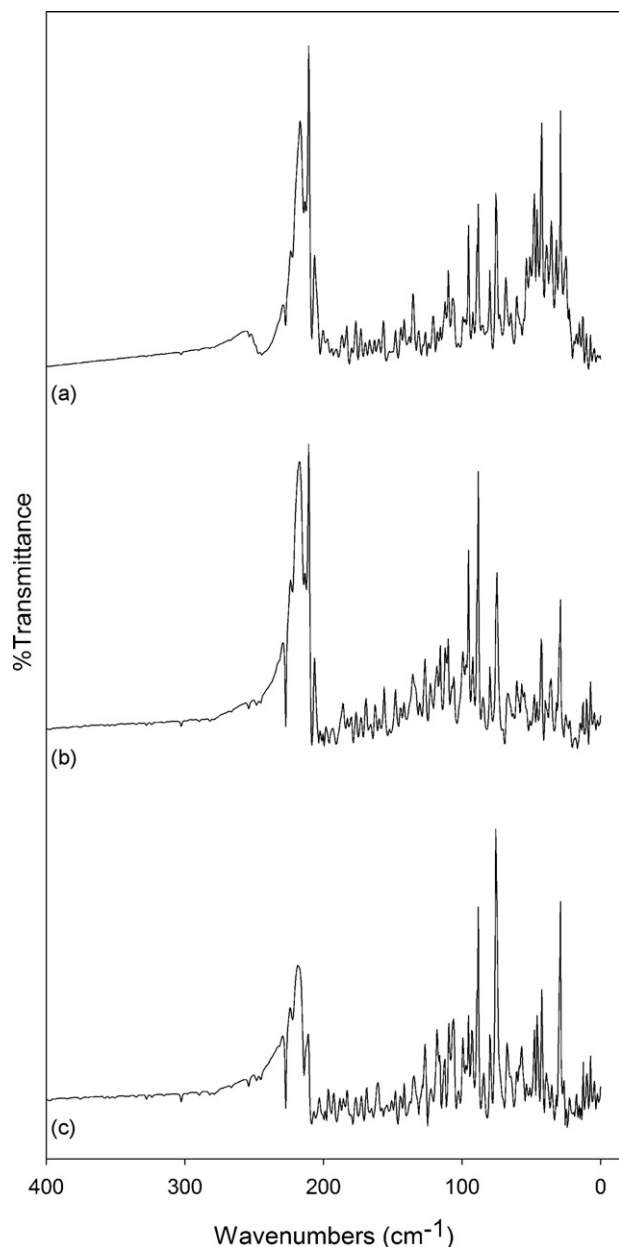
Fig. 3. The far-IR spectra of Co(IN)$_6$Cl$_2$ (a), Ni(IN)$_6$Cl$_2$ (b) and Hg(IN)I$_2$ (c) complexes.

Table 2
The vibrational wave numbers of cyanide group for the M–Ni compounds

Complexes	Vibrational modes		
	ν(C–N)(E$_u$)	ν(NiCN)	δ(Ni–CN)
Co(IN)$_2$Ni(CN)$_4$	2153vs	536m	432vs
Ni(IN)$_2$Ni(CN)$_4$	2160vs	538m	432s
Cd(IN)$_2$Ni(CN)$_4$	2155vs	526m	424vs

vs: very strong, s: strong, and m: medium.

the ν(M–X) vibrations are observed in the higher region than the ν(M–L) vibrations. Two sharp and strongly bands were observed at 216 cm^{-1}, and 210 cm^{-1} for cobalt complex and at 217 cm^{-1}, and 210 cm^{-1} for nickel complex and at 218 cm^{-1}, and 211 cm^{-1} for mercury complex in their far infrared spectra. They were assigned ν(M–X) and ν(M–L). The other bands were observed in the lower frequency (below the 200 cm^{-1}) regions are suggested lattice vibrations.
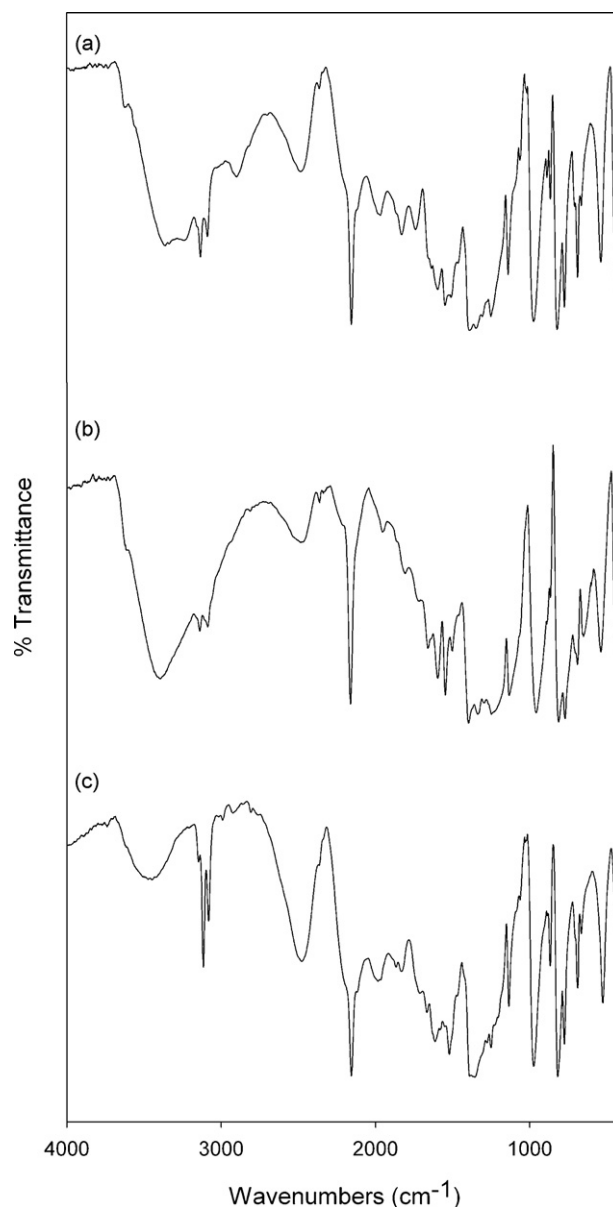

Fig. 4. The FT-IR spectra of Co(IN)$_2$Ni(CN)$_4$ (a), Ni(IN)$_2$Ni(CN)$_4$ (b) and Cd(IN)$_2$Ni(CN)$_4$ complexes.

and at 1690 cm^{-1} in Park's [24] paper in the Raman spectrum of free IN. The bands observed at 1027 cm^{-1} and 664 cm^{-1} in the Raman spectrum of cobalt and nickel complexes were assigned ν(C=C) and ν(C–COOH), respectively as in Ref. [10,24]. On the other hand these bands were not observed in the Raman spectrum of the Hg(IN)I$_2$ complex. This situation definitely supports that the coordination of the Hg atom to the ligand molecule from the carboxyl group in the mercury complexes studied here. It is known that the δ(X–M–X) vibrations occur below the 200 cm^{-1} [25]. A middle band was observed at 107 cm^{-1}, 107 cm^{-1} and 114 cm^{-1} in the Raman spectrum of the cobalt, nickel and mercury complexes. So they were assigned δ(Cl–Co–Cl), δ(Cl–Ni–Cl) and δ(I–Hg–I).

The far infrared spectra of the Co(IN)$_6$Cl$_2$, Ni(IN)$_6$Cl$_2$ and Hg(IN)I$_2$ complexes were given in Fig. 3. The metal–pyridine (or pyridine derivatives) and metal halide vibrations have been located in the region of 400–200 cm^{-1} [5]. In addition to these,

3.1. The Ni(CN)$_4$ group vibrations of the M(IN)$_2$Ni(CN)$_4$ complexes

The wave numbers of the Ni(CN)$_4$ group vibrations of the compounds studied were tabulated in Table 2. In the IR spectrum of NaNi(CN)$_4$ the CN stretching vibration mode was observed at 2132 cm^{-1} [26] for the corresponding modes of M(IN)$_2$Ni(CN)$_4$ complexes an upward shift was observed. The spectrum of Co(IN)$_2$Ni(CN)$_4$, Ni(IN)$_2$Ni(CN)$_4$ complexes and Cd(IN)$_2$Ni(CN)$_4$ were given in Fig. 4. The ν(CN) and δ(NiCN) vibrational frequencies were also found to be similar to the Hoffmann-type clatrates [27] aniline and isonicotinamide complexes [13,28] indicating that the |M–Ni(CN)$_4$|$_\infty$ polymeric layers were preserved. If the cyanide group around the nickel atom has a local D$_{4h}$ environment, one ν(CN)(E$_u$) band is only expected in the IR spectrum. A strong band was observed at 2153 cm^{-1}, 2160 cm^{-1}, and 2155 cm^{-1} in the spectrum of Co, Ni, Cd complexes, respectively belongs to ν(C—N)(E$_u$). The other two strong bands are observed which belongs to ν(NiCN) and δ(Ni–CN) and they were given in Table 2. These frequency variations were found to be slightly depend on the metal atom (M) and its probably due to changes of the strength of the M–NC bonds, since it is known that there is a mechanical coupling between the M–N and C≡N stretching modes [29].

4. Conclusion

The analysis of IR spectra of metal halide complexes of IN indicates that there are some structure–spectra correlations. It is concluded that the ring nitrogen of IN is only involved in M(IN)$_6$X$_2$ and the carboxyl oxygen of IN is only involved in M(IN)X$_2$ in complex formations. The ν(M–X), ν(M–L) and ν(X–M–X) vibrations were observed in the far IR and Raman spectra.

It was found that the frequency shift values depend on the metal in order second ionization potentials and it is noted that for the isomorphous complexes the shift values depend on the halogen for a given metal it decreases in the order Cl > Br > I. In addition, the analysis of the IR spectra of three new Hofmann-type complexes has shown that they have structures consisting of polymeric layers of |M–Ni(CN)$_4$|$_\infty$ with the IN molecules bound directly to metal (M).

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