



## 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  $4000\text{--}0\text{ cm}^{-1}$  region. The FT-IR spectra of tetracyanonickelate complexes were also reported in the  $4000\text{--}400\text{ cm}^{-1}$  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.

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## 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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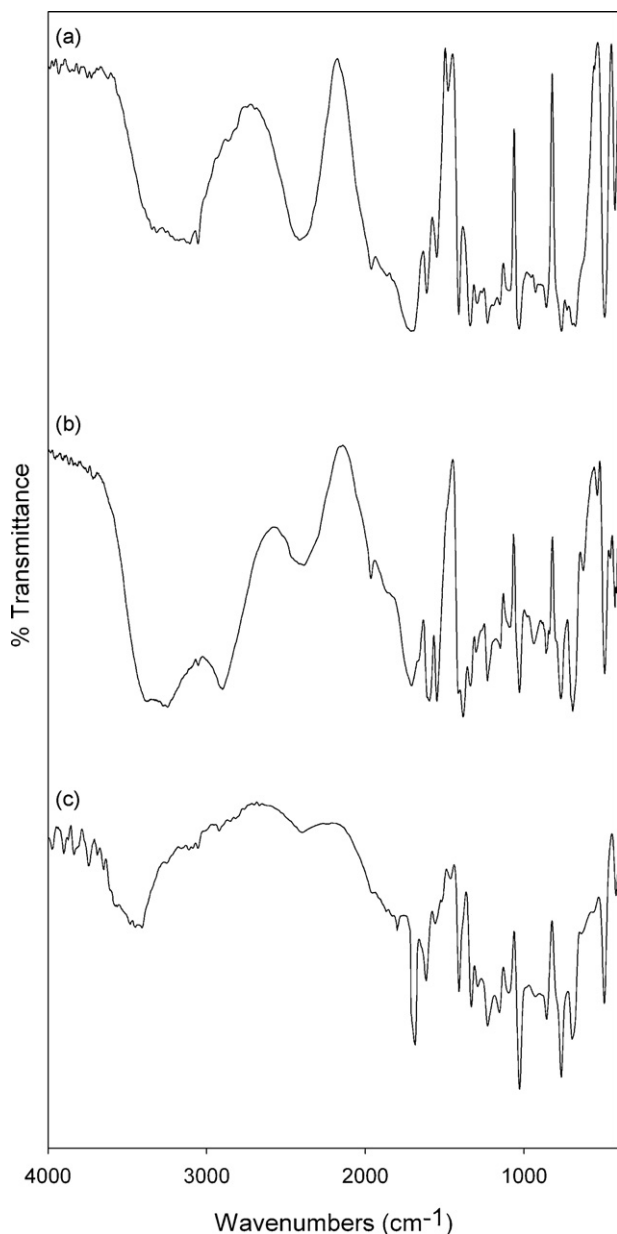


Fig. 1. The FT-IR spectra of  $\text{Co}(\text{IN})_6\text{Cl}_2$  (a),  $\text{Ni}(\text{IN})_6\text{Cl}_2$  (b) and  $\text{Hg}(\text{IN})\text{I}_2$  (c) complexes.

water solution.  $\text{M}(\text{IN})_2\text{Ni}(\text{CN})_4$  was prepared by dissolving 1 mmol of  $\text{K}_2\text{Ni}(\text{CN})_4$  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 ( $4000\text{--}400\text{ cm}^{-1}$ ) and IFS/66( $400\text{--}0\text{ cm}^{-1}$ ). The Raman spectra of complexes were recorded on FRA6106/S ( $3500\text{--}80\text{ cm}^{-1}$ ).

### 3. Results and discussion

IN has substitution in *para*-position of the pyridine. If we assume the carboxyl group ( $-\text{COOH}$ ) had a single mass point all the molecules under consideration would belong to  $\text{C}_{2v}$  point group. It has 27 normal vibrations of which 19 ( $10\text{A}_1 + 9\text{B}_2$ ) are planar and

8 ( $3\text{A}_2 + 5\text{B}_1$ ) 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  $\text{Co}(\text{IN})_6\text{Cl}_2$ ,  $\text{Ni}(\text{IN})_6\text{Cl}_2$ , and  $\text{Hg}(\text{IN})\text{I}_2$  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  $\text{Co}(\text{IN})_6\text{Cl}_2$ ,  $\text{Co}(\text{IN})_6\text{Br}_2$ ,  $\text{Ni}(\text{IN})_6\text{Cl}_2$ ,  $\text{Ni}(\text{IN})_6\text{Br}_2$ ,  $\text{Ni}(\text{IN})_6\text{I}_2$ ,  $\text{Hg}(\text{IN})\text{Cl}_2$ ,  $\text{Hg}(\text{IN})\text{Br}_2$ , and  $\text{Hg}(\text{IN})\text{I}_2$  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

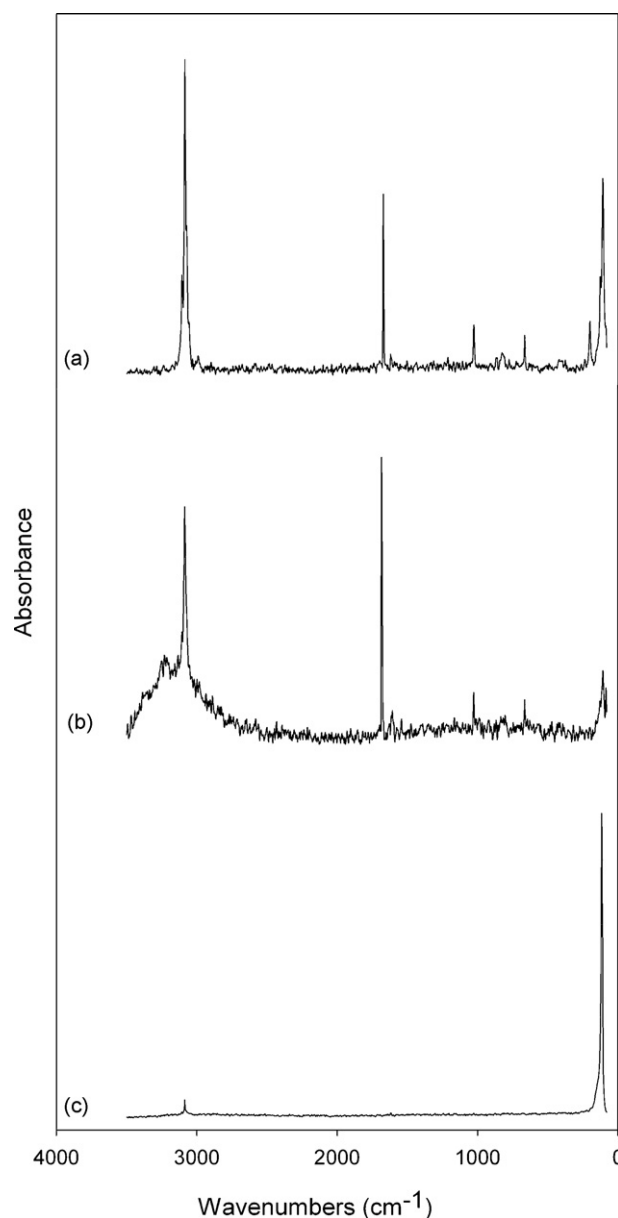


Fig. 2. The Raman spectra of  $\text{Co}(\text{IN})_6\text{Cl}_2$  (a),  $\text{Ni}(\text{IN})_6\text{Cl}_2$  (b) and  $\text{Hg}(\text{IN})\text{I}_2$  (c) complexes.

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