

# Synthesis and Vibrational Spectroscopic Study of Some Metal(II) Halide and Tetracyanonickelate Complexes of Isonicotinic Acid

Ahmet ATAÇ<sup>1\*</sup>, Fehmi BARDAK<sup>2</sup>

<sup>1</sup>*Department of Physics, Faculty of Arts and Science, Celal Bayar University,  
45043, Muradiye, Manisa-TURKEY  
e-mail: ahmet.atac@bayar.edu.tr*

<sup>2</sup>*Department of Physics, Faculty of Arts and Science, Gazi University,  
06500, Teknikokullar, Ankara-TURKEY*

Received 10.03.2006

The  $M(IN)_2Ni(CN)_4$  [where M: Cu, Mn, Zn, IN: Isonicotinic acid, abbreviated to M-Ni-IN] tetracyanonickelate and some metal halide complexes with the following stoichiometries:  $Cu(IN)X_2$  (X:Br,I),  $Cd(IN)_2X_2$ , (X:Cl,Br), and  $Zn(IN)_4X_2$  (X:Br,I) were synthesized for the first time. Their FT-IR spectra were reported in the 4000-400  $cm^{-1}$  region. Vibrational assignments were given for all the observed bands. The analysis of the vibrational spectra indicates that there are some structure-spectrum correlations. For a given series of isomorphous complexes, the sum of the difference between the values of the vibrational modes of uncoordinated isonicotinic acid that were coordinated to the metal ion isonicotinic acid was investigated and found to depend on the halogen for a given metal. 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 (M) atoms. Certain chemical formulae were determined using the elemental analysis results.

**Key Words:** Infrared spectra, isonicotinic acid, metal halide complexes, tetracyanonickelate complexes.

## Introduction

Isonicotinic acid (IN) is a compound of considerable biological interest. A derivative of IN, the hydrazine isoniazide, possesses tuberculostatic properties and can be administered to patients. Both IN and isonicotinylglycine are found in urine because of their metabolism in the human body.<sup>1</sup> IN shows antibacterial properties with different atomic groups.<sup>2</sup> It is also used for the determination of cyanide in water as an effective substance with pyrazolone.<sup>3</sup> The metal complexes of biologically important ligands are sometimes more effective than free ligands;<sup>4</sup> therefore, the metal halide complexes of IN were synthesized and their spectroscopic features were investigated.

---

\*Corresponding author

The vibrational analysis of free IN was performed by Affi.<sup>5</sup> 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 various complexes  $[M (IN)_nH_2O]$  have been reported.<sup>6</sup> The structural properties of Cu (II) and Cu (I) chloride complexes of IN are described in the literature.<sup>7-9</sup> In a recent paper, the theoretical vibrational analysis of free IN was performed by Koczon for a few bands.<sup>10</sup> To the best of our knowledge, no complete vibrational studies have been reported for the transition metal(II) halide and tetracyanonickelate complexes of IN.

In our previous studies, the spectroscopic and structural properties of metal halide and tetracyanonickelate complexes of isonicotinamide<sup>11-13</sup> nicotinamide<sup>14-16</sup> were investigated. In the present work, we prepared and reported the IR spectra of some metal(II) halide and tetracyanonickelate complexes of IN for detecting any possible relationship between the ligand vibrational values and the metal, and presented their IR spectral data.

## Experimental

### Synthesis

All the chemicals were reagent grade and were used without further purification. Metal chloride, bromide, or iodide (1 mmol) was dissolved in hot (about 78 °C) absolute ethanol (10 mL). The appropriate quantity of IN (1 mmol for  $Cu(IN)X_2$ , 2 mmol for  $Cd(IN)_2X_2$ , and 4 mmol for  $Zn(IN)_4X_2$ ) was added to the solution. The mixture was stirred magnetically at room temperature for 24 h. The precipitated complexes were filtered, washed with ether, and dried. Potassium tetracyanonickelate was prepared by mixing stoichiometric amounts of nickel(II) chloride with potassium cyanide in water solution.  $M (IN)_2Ni (CN)_4$  was prepared by dissolving 1 mmol of  $K_2Ni (CN)_4$  in water. To this solution, 2 mmol of ligand (IN) and 1 mmol of the metal halide dissolved in ethanol were added consecutively. The reaction mixture was stirred for 24 h at room temperature. The product obtained was filtered and washed with ethanol and dried in vacuum desiccators.

### Instrumental measurement

The prepared samples were analyzed for C, H, and N with a LECO CHN-932 analyzer and the results are presented in Table 1. The IR spectra of discs (KBr) of fresh samples were recorded on a Mattson 1000 FT-IR instrument that was calibrated using polystyrene bands.

**Table 1.** Elemental analysis results related to complexes.

Complex	C (%)		H (%)		N (%)	
	Found	Calculated	Found	Calculated	Found	Calculated
$Cu(IN)I_2$	16.80	16.36	1.07	1.135	3.43	3.17
$Cd(IN)_2Br_2$	28.05	27.77	1.61	1.91	5.46	5.4
$Zn(IN)_4I_2$	33.15	33.51	2.16	2.46	6.37	6.89
$Mn(IN)_2Ni(CN)_4$	40.81	41.39	1.87	2.15	17.48	18.1
$Cu(IN)_2Ni(CN)_4$	40.07	40.63	1.83	2.11	16.96	17.7
$Zn(IN)_2Ni(CN)_4$	39.75	40.48	1.98	2.11	17.15	17.71

## Results and Discussion

IN has substitution in the para-position of the pyridine. If we assumed that the carboxyl group (-COOH) had a single mass point, all the molecules under consideration would belong to the  $C_{2v}$  point group. It has 27 normal vibrations, of which 19 are planar and 8 are non-planar. In addition to these 27 ring vibrations, there are 9 vibrations due to the substitute carboxyl group.

The vibrational assignments for a few bands of free IN were made by Affi<sup>5</sup> and compared with those of some pyridine derivatives, such as nicotinamide and nicotinic acid. The spectroscopic features of free IN were investigated theoretically by using ab initio calculation methods by means of the B3PW91 level and 6-311++G\*\* basis set by Koczon et al.<sup>10</sup> In that study, some selected bands (3450-3050, 1717-1597, and 1455-1370  $\text{cm}^{-1}$ ) were assigned and the influence of the nitrogen atom position with respect to the carboxyl group on the vibrational structure of the molecule was investigated. They also interpreted the calculated spectra in terms of potential energy distributions and made the assignment of selected experimental bands from PED analysis results.<sup>10</sup>

Although most metal halide pyridine complexes have been characterized crystallographically, there is a distinct lack of structural data for the isonicotinic acid halide and tetracyanonickelate complexes studied here. However, since isostructural complexes are known to exhibit similar band patterns in their vibrational spectra<sup>17-19</sup> in the absence of structural data on a given complex, they have been classified based on their spectroscopic features.

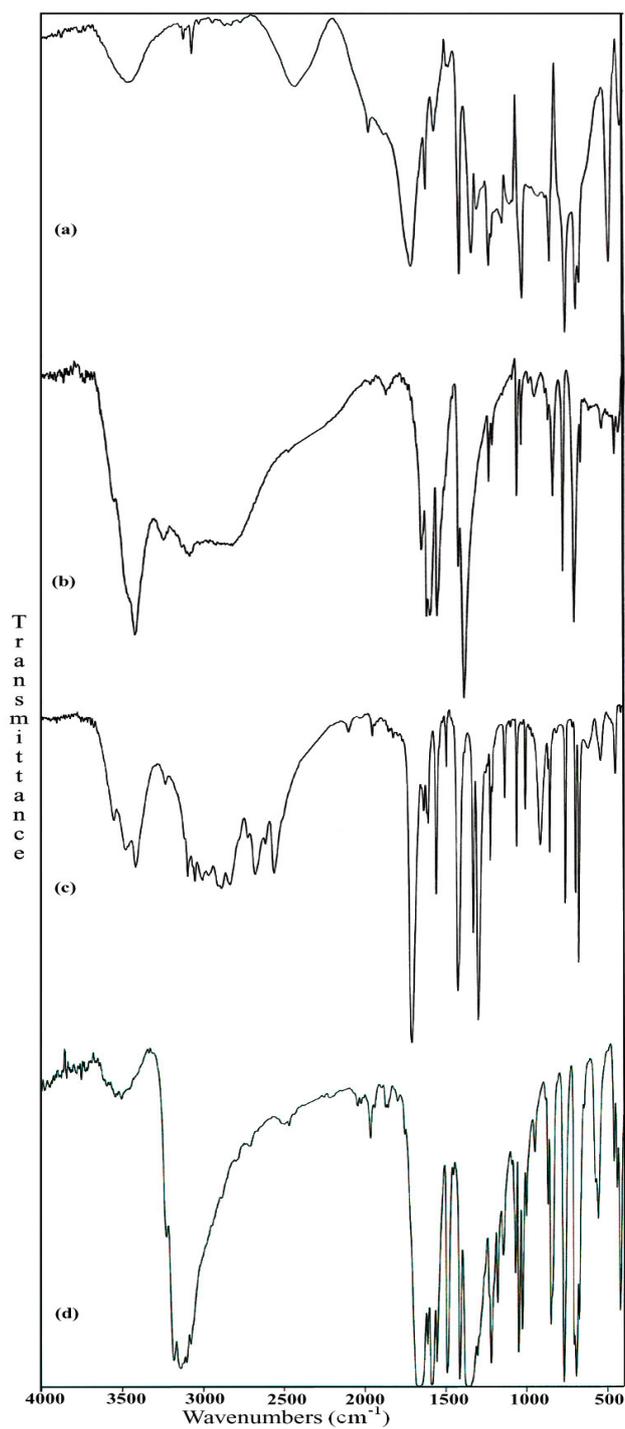
The FT-IR spectra of free IN,  $\text{Cu}(\text{IN})\text{Br}_2$ ,  $\text{Cd}(\text{IN})_2\text{Br}_2$ , and  $\text{Zn}(\text{IN})_4\text{I}_2$  complexes are given in Figures 1a-d, respectively. The vibrational assignments of free IN were made by comparison with the assignments of pyridine,<sup>20,21</sup> isonicotinamide,<sup>11-13</sup> and isonicotinic acid N-oxide.<sup>22</sup> The vibrational wavenumbers of IN for the  $\text{Cu}(\text{IN})\text{Br}_2$ ,  $\text{Cu}(\text{IN})\text{I}_2$ ,  $\text{Cd}(\text{IN})_2\text{Cl}_2$ ,  $\text{Cd}(\text{IN})_2\text{Br}_2$ ,  $\text{Zn}(\text{IN})_4\text{Br}_2$ , and  $\text{Zn}(\text{IN})_4\text{I}_2$  complexes are listed along with the results reported by Affi and Koczon in Table 2.

IN has a different coordination form and it is coordinated not only through the carboxylate group but also through the nitrogen atom of the pyridine ring. This property leads to different constructions in the metal complexes, such as tri-nuclear,<sup>8</sup> 3-dimensional supranuclear network<sup>23</sup>, and square pyramidal<sup>24</sup>. Similar structure variations were observed in the complexes studied here, for different transition metal atoms.

The most important vibrational modes implying the coordination of the metal atom to the IN ligand molecule were  $\nu(\text{C}=\text{O})$  and pyridine ring vibrations. Because it is known that if the coordination takes place through ring nitrogen, the  $\nu(\text{C}=\text{O})$  and pyridine ring vibrations shift to the higher region in the complexes of pyridine and pyridine derivatives.<sup>11,13</sup> Nevertheless, an opposite situation was observed in the IR spectra of these complexes studied here, and if the coordination takes place through carboxyl oxygen, it is expected that the  $\nu(\text{C}=\text{O})$  vibrations strongly shift to a lower region, as in isonicotinic acid N-oxide metal complexes.<sup>22,25</sup>

The  $\nu(\text{C}=\text{O})$  bands of pyridine derivatives containing the carboxyl group were expected at higher than 1650  $\text{cm}^{-1}$ .<sup>20</sup> A strong band appeared at 1711  $\text{cm}^{-1}$  in the IR spectrum of free IN and it was assigned to  $\nu(\text{C}=\text{O})$ . This band was observed at 1661 and 1662  $\text{cm}^{-1}$  in the spectra of  $\text{Zn}(\text{IN})_4\text{Br}_2$  and  $\text{Zn}(\text{IN})_4\text{I}_2$  complexes. This significant shift was a result of coordination that took place through the carboxyl oxygen to the zinc atom. On the other hand, this band underwent a slight negative shift in the spectra of  $\text{Cu}(\text{IN})\text{X}_2$  and  $\text{Cd}(\text{IN})_2\text{X}_2$  complexes, which explained the influence of the hydrogen bindings that led to the formation of hydrogen-bonded frameworks and a polymeric network structure.<sup>26</sup>

Pyridine has 4 ring vibrations in the region of 1615-1410  $\text{cm}^{-1}$ .<sup>20</sup> These bands were observed at 1616,



**Figure 1.** The FT-IR spectra of free IN(a), Cu(IN)Br<sub>2</sub>(b), Cd(IN)<sub>2</sub>Br<sub>2</sub>(c), and Zn(IN)<sub>4</sub>I<sub>2</sub>(d) complexes.

Table 2. The IR wavenumbers ( $\text{cm}^{-1}$ ) of free IN and metal halide complexes.

	Cu(IN)Br <sub>2</sub>	Cu(IN)I <sub>2</sub>	Cd(IN) <sub>2</sub> Cl <sub>2</sub>	Cd(IN) <sub>2</sub> Br <sub>2</sub>	Zn(IN) <sub>4</sub> Br <sub>2</sub>	Zn(IN) <sub>4</sub> I <sub>2</sub>	IN NEW	Affi [5]	Koczon [10]	Assignments
3423s		3418m	3446w	3440w			3440vw	3405m.br	3436m	i.p.OH str.
3090s		3083m	3103w	3097m	3103s	3101m	3102vw	3118v.w	3104w	i.p.CH str.
3066s		3060m	3053w	3052m	3077s	3077m	3052vw	3060w	3084w	i.p.CH str.
1698s		1699vs	1696s,1692sh	1703vs	1661vs	1662vs	1711s	1720s.br	1712vs	C=O str.
1597vs		1597m	1608m	1609m	1613m	1612m	1616m	1620m-s	1616w	Py.(CC + CN)str.
					1586vs	1586vs				
1551vs		1554s	1560vw	1555m	1555s	1555m	1563w	1567m	1597w	Py.(CC + CN)str.
			1461w		1492s	1491s	1472vw	1471m-w	1478w	CH bend.
1418s		1419s	1414s	1412vs	1414s	1414s	1411s	1415v.s	1412vs	CH bend.
1382vs		1383vs								
		1327m	1331s	1332m	1355vs	1350vs	1338s	1374w.sh	1370vw	(C-O)str.
		1294m	1294m	1297m	1305m	1305m	1302m	1333s		COO tr.
1233m		1236w	1227m	1227m	1221m	1219m	1231s	1233m-s		COH tr.
1213sh		1214w	1214sh	1214sh	1181m	1179m	1216sh	1215m		CH rock. + COH tr.
1142sh		1135vw	1137m	1130m	1146m	1145m	1146m	1102m.sh		C <sub>py</sub> C <sub>COOH</sub> str.
		1095vw			1095vw	1094m	1094m	1084m.sh		C-O str.
1060m		1061w	1068w	1065m	1071m	1068m	1081m	1052m.sh		Ring CC str. + C-O str.
1032w		1035vw	1025vs	1010m	1051s, 1029m	1052s, 1028m	1027vs	1033v.s		Ring def.
986vw		986vw	971sh		1005w	1007sh	972sh	975w.br		Ring breath.
922w		924w	916vw	917m	953w	954vw	921m	941w.br		o.p.CH bend.
885sh			882vw	868sh	872w	871w	881sh			o.p.CH bend.
864sh		868sh	858m	860m	850m	852m	857s	859s		o.p.CH rock.
837m,776s		838w, 776m	761s	761s	769vs	768s	762vs	783v.w		Ring def.
704vs		702m	698m	699s	693vs	694s	697vs	701s		o.p. COOH def.
670sh		677m	674m	679vs	676m	676m	674sh	677s		Ring def.
553m		541w	545w	543m	577sh, 559m	577w, 557m	549vw			o.p. OH bend.
458m		457w	492m	452m	462w, 443w	460vw, 443w	492s	497s		$\gamma$ OCO
434m		422vw	419w	422m	422m	420m	418w	416m		o.p. ring def. +COOH def.

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; sh: shoulder

1563, 1472, and 1411  $\text{cm}^{-1}$  in the spectrum of free IN and assigned Py(CC + CN)strength, Py(CC + CN)strength, CH bending, and CH bending, respectively. The bands observed at 1616 and 1563  $\text{cm}^{-1}$  in the spectrum of free IN undergo a slight negative shift in the metal halide complexes studied here. These variations clearly indicate that the other coordination of IN takes place via the pyridine ring nitrogen to the metal atoms (Cu, Cd, and Zn). It is also known that the donor power of pyridine ring nitrogen is strong.<sup>27</sup>

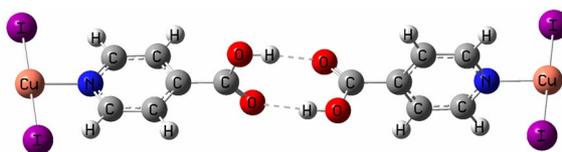


Figure 2. The hydrogen-bonded  $\text{Cu}(\text{IN})\text{X}_2$  complexes.

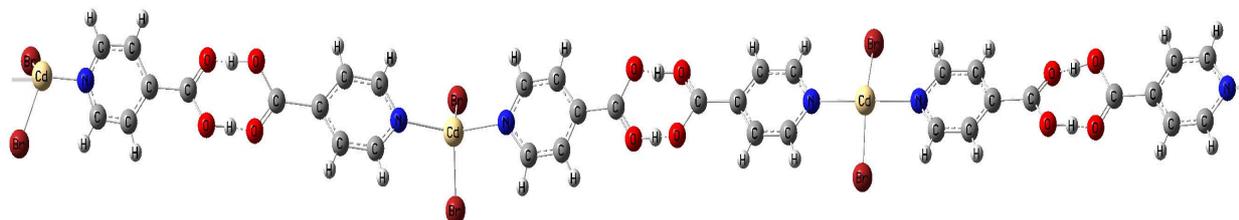


Figure 3. The hydrogen-bonded linear infinite network of  $\text{Cd}(\text{IN})_2\text{X}_2$  complexes.

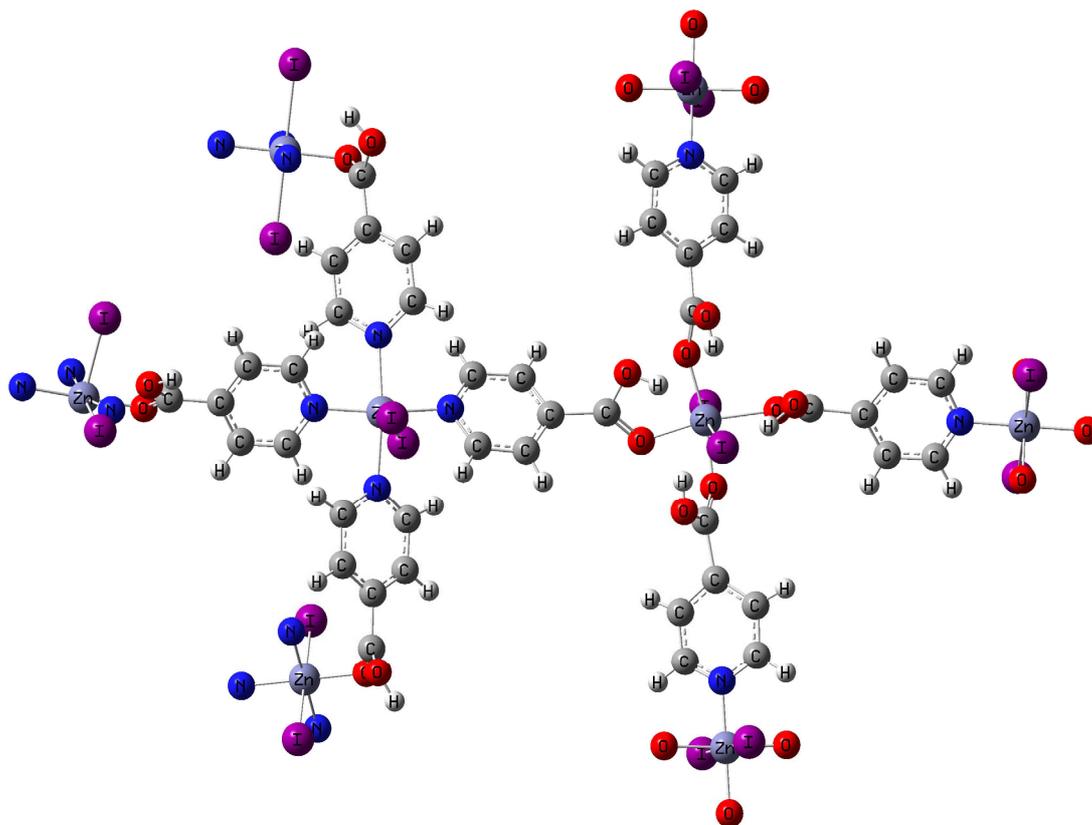


Figure 4. The polynuclear network structure of  $\text{Zn}(\text{IN})_4\text{X}_2$  complexes.

Similar bindings were also seen in different isonicotinic acid metal complexes.<sup>7,23,26</sup> Based on frequency analysis, the coordination of IN takes place through the pyridine ring nitrogen to the metal atoms (Cd and Cu), as illustrated in Figures 2 and 3, for the Cu(IN)X<sub>2</sub> and Cd(IN)<sub>2</sub>X<sub>2</sub> complexes. The coordination of zinc atoms to ligand molecules formed both the carboxyl oxygen and pyridine ring nitrogen in the Zn (IN)<sub>4</sub>X<sub>2</sub> complexes illustrated in Figure 4. These geometric conformations were confirmed by shift values and elemental analysis results. As shown in Figure 2, the Cu atom coordinated with a pair of halogens and a pyridine ring nitrogen, and an interesting bonding took place between the carboxyl groups of ligand molecules. A similar coordination was assumed for the Cd(IN)<sub>2</sub>X<sub>2</sub> complexes because of the exhibition of a similar band pattern in its IR spectrum; this structure has linear infinitive networks as seen in Figure 3. On the other hand, the zinc atom surrounded by the 4 ligand molecules coordinated from the ring nitrogen and a pair of halogens with a distorted octahedral environment at the first center of the polynuclear network structure, which is surrounded by 4 carboxyl groups and the other pairs of halogens at the second center of the structure in the Zn(IN)<sub>4</sub>X<sub>2</sub> complexes, as shown in Figure 4.

### The Ni(CN)<sub>4</sub> group vibrations of the M(IN)<sub>2</sub>Ni(CN)<sub>4</sub> complexes

The wavenumbers of the Ni(CN)<sub>4</sub> group vibrations of the compounds studied are given in Table 3. In the IR spectrum of NaNi(CN)<sub>4</sub>, the CN stretching vibration mode was observed at 2132 cm<sup>-1</sup>,<sup>28</sup> and, for the corresponding modes of M(IN)<sub>2</sub>Ni(CN)<sub>4</sub> complexes, an upward shift was observed. The spectra of Cu(IN)<sub>2</sub>Ni(CN)<sub>4</sub> and Mn(IN)<sub>2</sub>Ni(CN)<sub>4</sub> are given in Figure 5a and b. The  $\nu(\text{CN})$  and  $\delta(\text{NiCN})$  vibrational frequencies were also found to be similar to the Hoffmann-type clatrates<sup>29</sup> aniline and isonicotinamide complexes,<sup>13,30</sup> indicating that the  $[\text{M-Ni(CN)}_4]_\infty$  polymeric layers were preserved. If the cyanide group around the nickel atoms has a local D<sub>4h</sub> environment, only one  $\nu(\text{CN})(E_u)$  band is expected in the IR spectrum. A strong band was observed at 2148, 2169, and 2159 cm<sup>-1</sup> in the spectrum of Mn, Cu, and Zn complexes, respectively, belonging to  $\nu(\text{C-N})(E_u)$ . The other 2 strong bands that were observed belonging to  $\nu(\text{NiCN})$  and  $\delta(\text{Ni-CN})$  are given in Table 3. These frequency variations were found to be slightly dependent upon the metal atoms (M) and it was probably due to changes in 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.<sup>21</sup>

**Table 3.** The IR wavenumbers of the Ni(CN)<sub>4</sub> group vibrations of the M(IN)<sub>2</sub>Ni(CN)<sub>4</sub> complexes.

Complexes	Vibrational modes		
	$\nu(\text{C-N})(E_u)$	$\nu(\text{NiCN})$	$\delta(\text{NiCN})$
Mn(IN) <sub>2</sub> Ni(CN) <sub>4</sub>	2148vs	532m	430s
Cu(IN) <sub>2</sub> Ni(CN) <sub>4</sub>	2169vs	576s	443s
Zn(IN) <sub>2</sub> Ni(CN) <sub>4</sub>	2156vs	535m	430vs

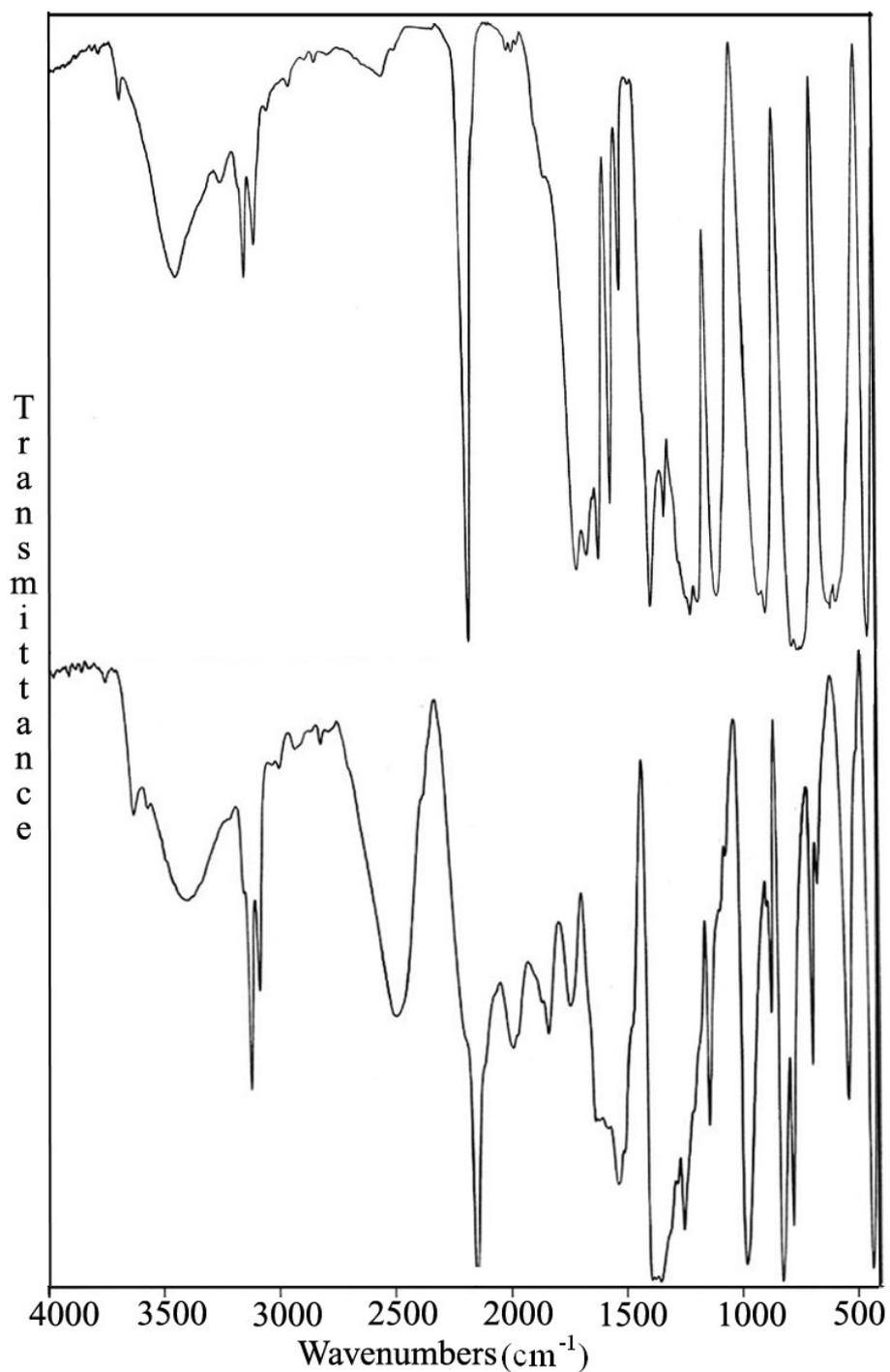


Figure 5. The FT-IR spectra of  $\text{Cu}(\text{IN})_2\text{Ni}(\text{CN})_4$  and  $\text{Mn}(\text{IN})_2\text{Ni}(\text{CN})_4$  complexes.

## Conclusion

The analysis of the IR spectra of 3 new Hofmann-type complexes showed that they have structures consisting of polymeric layers of  $\text{M-Ni}(\text{CN})_{4\infty}$  with the IN molecules bound directly to metal (M) and metal halide complexes of IN, indicating that there were some structure-spectrum correlations. It is concluded that the

ring nitrogen and carboxyl group of IN are involved in a complex formation. In addition, it is found that the shift values depend on the halogen for a given metal and it decreases in the following order: Cl > Br > I.

## Acknowledgments

This study was funded by the Celal Bayar University Research Fund through research grant no: FEF-2005/65

## References

1. W.F.I. Cuthbenstone, D.M. Ireland and W. Wolff, **J. Biochem.** **55**, 669-71 (1953).
2. H. Zhang "Standard Methods of Analysis for Hygienic Chemists Authorized by the Pharmaceutical Society of Japan", HW Press, Beijing, pp 80-81, 1995.
3. J.R.J. Sorensen, "Metal Ions in Biological Systems", H. Sigel (Ed.) vol. 14, pp 77, Marcel Decker, New York, 1982.
4. Y. Jiang, N. Lu, F. Yu, Q. Li and H. Xu, **Fresenius J. Anal. Chem.** **364**, 786-87 (1999).
5. M.S. Affi and A.A. Shabana, **Analysis** **10**, 239-44 (1982).
6. A. Kleinstein and G.A. Webb, **J. Inorg. Chem.** **33**, 405-12 (1971).
7. M. Palicova, P. Segl'a, D. Miklos, M. Kopcova, M. Melnik, B. Dudova, D. Hudecova, and T. Glowiak, **Polyhedron** **19**, 2689-95 (2000).
8. M. Melnik and L. Macaskova, **Coordin.Chem.Rev.** **126**, 71-92 (1993).
9. M.A.S. Goher and T.C.W. Mak, **Inorg. Chim. Acta** **101**, L27-L30 (1985).
10. P. Koczon, J.Cz. Dobrowolski, W. Lewandowski and A.P. Mazurek, **J. Mol. Struct.** **655**, 89-95 (2003).
11. S. Yurdakul, A. Atac, E. Sahin and S. Ide, **Vib. Spectrosc.** **31**, 41-49 (2003).
12. A. Atac, S. Yurdakul and S. Ide, **J. Mol. Struct.** **788**, 79-87 (2006).
13. S. Yurdakul and A. Atac, **Spectrosc. Lett.** **37**, 33-42 (2004).
14. S. Bayari, A. Atac and S. Yurdakul, **J. Mol. Struct.** **655**, 163-70 (2003).
15. S. Ide, A. Atac and S. Yurdakul, **J. Mol. Struct.** **605**, 103-07 (2002).
16. E. Sahin, S. Ide, A. Atac and S. Yurdakul, **J. Mol. Struct.** **616**, 253-58 (2002).
17. S. Akyuz, A.B. Dempster and J.E.D. Davies, **J. Chem. Soc. Dalton** **1746**, (1976).
18. S. Akyuz, J.E.D. Davies and K.T. Holmes, **J. Mol. Struct.** **42**, 59 (1977).
19. S.Yurdakul, S.Akyuz and J.E.D. Davies, **Spectrosc. Lett.** **29**, 175 (1996).
20. L.J. Bellamy, "The Infrared Spectra of Complex Molecules" Third Ed. Chapman and Hall, London, 1975.
21. S. Akyuz, J.B. Dempster and R.L. Morehouse, **J. Mol. Struct.** **17**, 105 (1973).
22. N. Can, A. Atac, F. Bardak and S.E.S. Can, **Turk. J. Chem.** **29**, 1-7 (2005).
23. J.H. Yu and J.Q. Xu et al, **Inorg. Chem. Commun.** **5**, 972-76 (2002).
24. J.Y. Lu and A.M. Babb, **Chem. Commun.** 821-22 (2001).

25. K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds", 2nd Edition, Wiley-Interscience, New York, 1970.
26. J.K. Bera, T.T. Vo, R.A. Walton and K.R. Dunbar, **Polyhedron** **22**, 3009-14 (2003).
27. M. Sandstrom and I. Persson, **Acta Chem. Scand.** **44**, 653 (1990).
28. R.L. McCullough, L.H. Jones and G.A. Crosby, **Spectrochim. Acta** **16**, 929-44 (1960).
29. T. Iwamoto, T. Nakano, M. Morita, T. Miyoshi, T. Miyamoto and Y. Sasaki, **Inorg. Chim. Acta** **2**, 313-17 (1968).
30. S. Akyuz, J.E.D. Davies and K.T. Holmes, **J. Mol. Struct.** **38**, 43-50 (1977).