

# Vibrational Spectroscopic Investigation of 2-amino-4-methylpyrimidine Tetracyanonickelate Complexes

## 2-amino-4-metilpirimidin Tetrasiyanonikelat Komplekslerinin Titreşim Spektroskopisi ile İncelenmesi

Research Article

**Celal Bayrak**

Hacettepe University, Faculty of Education, Department of Physics Education, 06800, Beytepe, Ankara, Turkey

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### ABSTRACT

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New Hofmann-type complexes in the form of  $M(\text{AMPM})_2\text{Ni}(\text{CN})_4$  (where  $M = \text{Mn}, \text{Co}, \text{Ni}$  or  $\text{Cd}$ ;  $\text{AMPM} = 2\text{-amino-4-methylpyrimidine}$ ) were prepared in powder form and their FT-IR, far-IR, FT-Raman spectra are reported. The complexes are also characterized by thermal gravimetric analysis (TGA), differential thermal analysis (DTA), X-ray diffraction (XRD) and elemental analyses measurements.  $\text{AMPM}$  molecules are found to involve coordination through one of the pyrimidine ring nitrogen atoms. The spectral features suggest that the compounds are similar in structure to the Hofmann type two dimensional coordination polymer compounds, formed with  $\text{Ni}(\text{CN})_4^{2-}$  ions bridged by  $M(\text{AMPM})_2^{2+}$  cations. Vibrational bands originated from both  $\text{AMPM}$  and  $\text{Ni}(\text{CN})_4$  group were assigned.

### Key Words

2-amino-4-methylpyrimidine, far-IR, FT-IR, FT-Raman spectra, XRD, DTA, Hofmann type complexes

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### ÖZET

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İki boyutlu kordinasyon polimer kompleksleri  $M(\text{AMPM})_2\text{Ni}(\text{CN})_4$  (burada  $M = \text{Mn}, \text{Co}, \text{Ni}$  ve  $\text{Cd}$ ;  $\text{AMPM} = 2\text{-amino-4-metilpirimidin}$ ) ilk kez elde edilmiş ve FT-IR, FT-Raman ve far-IR spektroskopi ile incelenmiştir. Ayrıca bu komplekslerin, termal gravimetrik analizi (TGA), taramalı termal analizi (DTA), X-ray saçılması ve elemental analiz ölçümleri yapıldı.  $\text{AMPM}$  molekülleri pirimidin halkasının azot atomlarının biri ile kordinasyon yaptığı bulunmuştur.  $\text{Ni}(\text{CN})_4^{2-}$  iyonları ile  $M(\text{AMPM})_2^{2+}$  katyonlarının koordinasyonu sonucu, Hofmann tipi iki boyutlu kordinasyon polimer bileşikleri oluşturduğu spektral özellikler ile desteklenmiştir.  $\text{AMPM}$  ve  $\text{Ni}(\text{CN})_4$  grubunun her ikisinden kaynaklanan titreşim bandları tanımlanmıştır.

### Anahtar Kelimeler

2-amino-4-metilpirimidin, far-IR, FT-IR, FT-Raman spektrum, XRD, DTA, Hofmann tipi kompleksler

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**Correspondence to:** Celal Bayrak, Hacettepe University, Faculty of Education, Department of Physics Education, Beytepe, Ankara, Turkey

Tel: +90 312 297 86 15

Fax: +90 312 299 86 00

E-Mail: cbayrak@hacettepe.edu.tr

## INTRODUCTION

Pyrimidine is the parent heterocycle of a very important group of compounds that have been studied extensively because of their occurrence in living systems [1,2]. Many pyrimidines, and their derivatives, possess remarkable biological activity, and they have been used widely in fields ranging from medicinal to industrial applications. The pyrimidine ring system provides a potential binding site for metals, and so any information on their coordinating properties is important for understanding the role of metal ions in biological systems. 2-amino-4-methylpyrimidine is of great biological importance.

The well known Hofmann-type two-dimensional complexes,  $\{M(L)_2Ni(CN)_4\}_n$ , are built by stacking the two-dimensional nickel cyanide sheets in layers [3,4]. The two-dimensional sheet is constructed by the alternate linkage between square-planar Ni(II) and octahedral M(II) (M = Mn, Fe, Co, Ni, Cu, Zn or Cd) through the cyanide bridges. The octahedral coordination of M(II) is satisfied by four N-terminals of the cyano groups and two nitrogen atoms of the two N-donor ligands (L) in a trans configuration, protruding above and below the sheet [3,4]. In this study, 2-amino-4-methylpyrimidine tetracyanonickelate,  $M(AMPM)_2Ni(CN)_4$  (where M = Mn, Co, Ni or Cd; AMPM= 2-amino-4-methylpyrimidine, abbreviated hereafter as M-Ni-AMPM), coordination polymer compounds have been prepared for the first time, and their far-IR, FT-IR and FT-Raman spectra are reported. The aims of this study are to examine the coordination sensitive ligand modes and to determine vibrational wavenumbers of modes arising from metal-ligand bonds  $\{(M-N)_{AMPM}, \delta(N-M-N)_{AMPM}\}$  by studying isostructural complexes  $\{M(AMPM)_2Ni(CN)_4\}_n$ .

## EXPERIMENTAL

All chemicals used were reagent grade (Aldrich) and they were used without further purification. The complexes M-Ni-AMPM (M= Mn, Co, Ni or Cd) were prepared as following: at first 1 mmol of  $MCl_2$  was dissolved in the distilled water, then to this solution 1 mmol of  $K_2Ni(CN)_4$  dissolved in distilled water was added under stirring. After a short time slightly more than 2 mmol of the

2-amino-4-methylpyrimidine solution in alcohol were added to the mixture prepared drop wise, again under stirring. The final mixture was left for stirring around a week at room temperature. The obtained product was filtered and washed with water, ethanol and ether successively and dried in a desiccator which included  $P_2O_5$ .

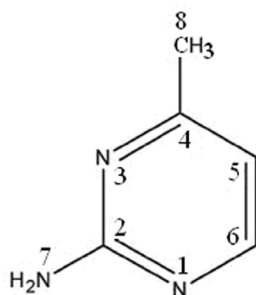
The freshly prepared compounds were analyzed for C, H and N by a LECO CHNS-932 analyzer with the following results (found %/calculated %). The analytical results were agreement with the proposed formula.

$Mn(C_4H_7N_3)_2Ni(CN)_4$ :  
C= 38.43/38.57, H= 3.32/3.23, N= 32.06/32.12  
 $Co(C_4H_7N_3)_2Ni(CN)_4$ :  
C= 38.15/38.21, H= 3.16/3.20, N= 31.57/ 31.83  
 $Ni(C_4H_7N_3)_2Ni(CN)_4$ :  
C= 38.13/38.23, H= 3.17/3.20, N= 31.53/31.85  
 $Cd(C_4H_7N_3)_2Ni(CN)_4$ :  
C= 33.85/34.07, H= 2.94/2.85, N= 28.22/28.38

The FT-IR (400-4000  $cm^{-1}$ ) spectra between KBr windows as Nujol or hexachloro-1,3-butadiene mulls and far-infrared (20-400  $cm^{-1}$ ) spectra between polyethylene plates as Nujol mulls of the compounds were recorded via a Bruker Optics IFS66v/s FT-IR spectrometer with 2  $cm^{-1}$  resolution in vacuum. FT-Raman spectra (70-4000  $cm^{-1}$ ) of the compounds were recorded using a Bruker Senterra Dispersive Raman microscope spectrometer with 532 or 633 nm excitations from a 3B diode laser having 3  $cm^{-1}$  resolution in the region of 3700 and 60  $cm^{-1}$ . Far-IR spectra of the nujol mulls between polyethylene windows of the samples were recorded on a Perkin-Elmer System 2000 FT-IR Interferometer resolution (4  $cm^{-1}$  resolution).

## RESULTS AND DISCUSSION

The structural formula of AMPM is given Figure 1. The FT-IR, FT-Raman and far-IR spectra of  $M(AMPM)_2Ni(CN)_4$  (where M= Mn, Co, Ni and Cd) are found to be very similar, suggesting that they have isomorphous crystal structures. The FT-IR, FT-Raman and far-IR spectra of the  $M(AMPM)_2Ni(CN)_4$  (where M= Mn, Co, Ni and Cd) complexes are given in Figures 2, 3 and 4, respectively. The assignments were divided



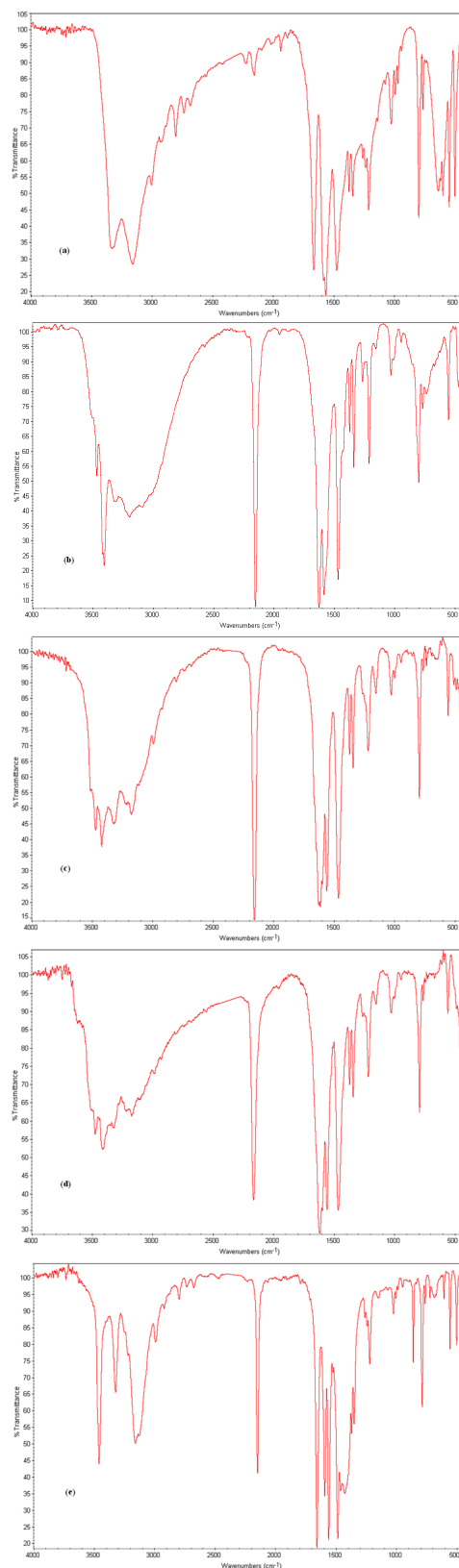
**Figure 1.** Structural formula of 2-amino-4-methylpyrimidine.

into two groups arising from the 2-amino-4-methylpyrimidine and the  $\text{Ni}(\text{CN})_4$  ions.

### 2-Amino-4-methylpyrimidine vibrations

2-amino-4-methylpyrimidine has amino and imino tautomers. The amino form is the most stable tautomer of 2-aminopyrimidine [5]. It is, therefore, not expected that any trace of the rare imino forms should be seen in the vibrational spectra of AMPM complexes. The vibrational spectroscopic investigation of M-Ni-AMPM complexes also indicates that the molecule is in the amino form. The complexing ability of AMPM with transition metal ions is of great interest, since AMPM has endo- and exo-cyclic nitrogen donors for coordination. The FT-IR, FT-Raman and far-IR spectra of microcrystalline AMPM and M-Ni-AMPM (M= Mn, Co, Ni or Cd) are given in Figures 2, 3 and 4. The vibrational wavenumbers of AMPM in M-Ni-AMPM compounds are tabulated in Table 1 in comparison with those of microcrystalline AMPM. The amino group vibrational wavenumbers of 2-amino-4-methylpyrimidine as a solid and in M-Ni-AMPM complexes are tabulated in Table 1.

As is clearly seen in Figures 2 and 3, Table 1, the  $\nu_a\text{NH}_2$  and  $\nu_s\text{NH}_2$  modes of AMPM in M-Ni-AMPM complexes are found to have higher wavenumbers than those of microcrystalline AMPM. The absence of large systematic shifts to lower wavenumbers for the  $\nu_a\text{NH}_2$  and  $\nu_s\text{NH}_2$  modes in the spectra of all the complexes implies that the amino nitrogen of AMPM does not take part in coordination. Similarly, the  $\nu(\text{C-NH}_2)$  mode of aniline and aniline derivatives shows a negative shift around 50-60  $\text{cm}^{-1}$ , upon coordination [6, 7, 8], but we do not observe such



**Figure 2.** The FT-IR spectra of Hofmann-AMPM compounds in KBr: (a) AMPM (ligand), (b) Mn-Ni-AMPM, (c) Co-Ni-AMPM, (d) Ni-Ni-AMPM and (e) Cd-Ni-AMPM.

**Table 1.** The vibrational wavenumbers (cm<sup>-1</sup>) of 2-amino-4-methylpyrimidine M-Ni-AMPM complexes.

Tentative assignment	AMPM		Mn-Ni-AMPM		Co-Ni-AMPM		Ni-Ni-AMPM		Cd-Ni-AMPM	
	IR	Raman	IR	Raman	IR	Raman	IR	Raman	IR	Raman
$\nu_a(\text{NH}_2)$	3331vs	3341vw	3470m 3410s 3320s	3421w 3349vw	3474m 3425s 3326s	3426w 3352vw	3479m 3415s 3327m	3472w 3434vw	3463s 3327m	3372vw 3362vw
$\nu_s(\text{NH}_2)$	3161vs	3280vw	3198m	3204vw	3180s 3116w		3180m 3114w		3161s 3131s	3169w
$\nu(\text{CH})$	3081vw	3124w	3094m	3099w	3094m	3085w	3079m	3095w		3085w
$\nu(\text{CH})$	3008s	3024w	3020m,sh	3025m		3025m				
$\nu(\text{CH})$			2998w	2984vw	2998w	2984vw	2988w		2993vw	
$\nu_s(\text{CH}_3)$	2962sh		2954m		2954m					
$\nu_s(\text{CH}_3)$	2929s	2925w	2922w	2933vw	2922w	2933vw	2932w	2924w	2925w	2935w
$\delta(\text{NH}_2)$	1668vs	1698vw	1626vs		1630vs 1614vs		1621vs	1607w	1657vs	
$\nu_{\text{ring}}$	1586s	1604vw	1587vs	1595vw	1600s	1591vw	1599vs	1569w	1594s	1608w
$\nu_{\text{ring}}$	1567vs		1470vs		1560vs		1561vs		1561vs	1564w
$\delta(\text{CH})+\nu_{\text{ring}}$	1476vs	1485w		1480vw	1467vs	1477vw	1466vs	1468vw	1486vs	1506m
									1463s	
$\delta_a(\text{CH}_3)$									1429s	
$\delta_s(\text{CH}_3)$	1375s	1388m	1374m	1386w	1375m	1382w	1373m	1385vw	1371m	1385m
$\nu_{\text{ring}}+\delta(\text{CH})$	1346m	1356w	1339s	1348vw	1345m	1344w	1344m	1355w	1351m	
$\nu_{\text{ring}}$	1262vw	1280m	1267w	1281w	1267vw	1271w	1267vw	1280w	1263vw	1278w
$\nu(\text{C-NH}_2)$	1238m	1232m		1226vw	1245vw	1236vw	1247vw		1244vw	1240w
$\nu_{\text{ring}}$	1213m		1212s		1220m		1217m	1228vw	1223w	
$\delta(\text{CH})$	1138m	1167w	1155w	1156vw	1155w	1151w	1153w	1149vw	1147vw	1167w
$\nu_{\text{ring}}$ (ring breath)	1076w	1094w		1100vw		1100vw	1073vw	1089w	1074vw	1099w
$(\text{CH}_3)$ rock	1025m		1032m		1028 m		1029m		1026m	
$(\text{CH}_3)$ rock	993m	1006m	1008w,sh	1018vw	999 vw	1011vw	1001w	1011w	1006vw	1015vw
$\delta_{\text{ring}}$	970m	959vw	983vw	962w		958w				
$\gamma_{\text{CH}}$	941vw	891vw	947w	913vw	947 vw	911vw	946vw		951vw	951vw
$\gamma_{\text{CH}}$	800vs	783vs	801s		794 s		796s		861m	844vw
$\gamma_{\text{ring}}+\gamma_{\text{C-NH}_2}$	765m	673vw	769m	780vw	765vw	785w	764w	776m	787s	781s
$\text{NH}_2$ wag.	636s	648s	669w	680w	693vw		670w		763w	717vw
$\gamma_{\text{CH}}$	619s		621vw	615vw	656vw	613vw	633vw	613vw	689w	612w
$\tau_{\text{ring}}$	600s	609w		570vw	611vw	572vw	591vw	571vw	605w	
$\delta_{\text{ring}}$	548vs	562vw	553m		557m		560m		557m	571m
$\tau_{\text{ring}}$	500vs	507w	504vw	485m	510w	481m	503w,sh	502w	503m	511m
$\gamma_{\text{ring}}$	441m		*		*		*		*	
$\tau(\text{CN})$	333m	281vs		333m		329m		353w	425m	324w
$\tau(\text{NH}_2)+\text{NH}_2$ wag.	182w 174w	205m	206m 199m	229m	208w 199w	225m	200w 193w	278m	200m	
$\tau_{\text{ring}}$	118w	124vs		133m		132m		120m		131m

<sup>a</sup>Coordination sensitive bands are marked in bold. Overlapped with the strong Ni(CN)<sub>4</sub> band.

a low-wavenumber shift of this mode in the M-Ni-AMPM complexes, which is further evidence of non-coordination through the amino nitrogen.

In solid AMPM, the amino group hydrogens are involved in H-bonding interactions [6]. In the case of M-Ni-AMPM complexes, the  $\nu_a\text{NH}_2$  and  $\nu_s\text{NH}_2$  modes of AMPM are found to be higher in value than those of microcrystalline AMPM, indicating that the amino group hydrogens are not involved in hydrogen bonding interaction as strongly as in the solid AMPM. On the other hand, the  $\text{NH}_2$  scissoring mode wavenumber of M-Ni-AMPM, is lower than in solid AMPM, indicating that the amino group hydrogens may be involved in a weak hydrogen bonding interaction, probably between AMPM molecules protruding above and below the  $\{\text{M-Ni}(\text{CN})_4\}$  sheets, but the H-bonding interaction must be weaker than in the solid. In the case of  $\text{M}(\text{2-aminopyrimidine})_2\text{M}'(\text{CN})_4$  (where M = Mn, Co, Ni or Cd and M' = Ni; M = Mn or Cd and M' = Pt) complexes [9,10], similar low-frequency shifts of the  $\nu_a\text{NH}_2$  and  $\nu_s\text{NH}_2$  modes in comparison with those of 2-aminopyrimidine in a  $\text{CCl}_4$  solution [6] were also observed.

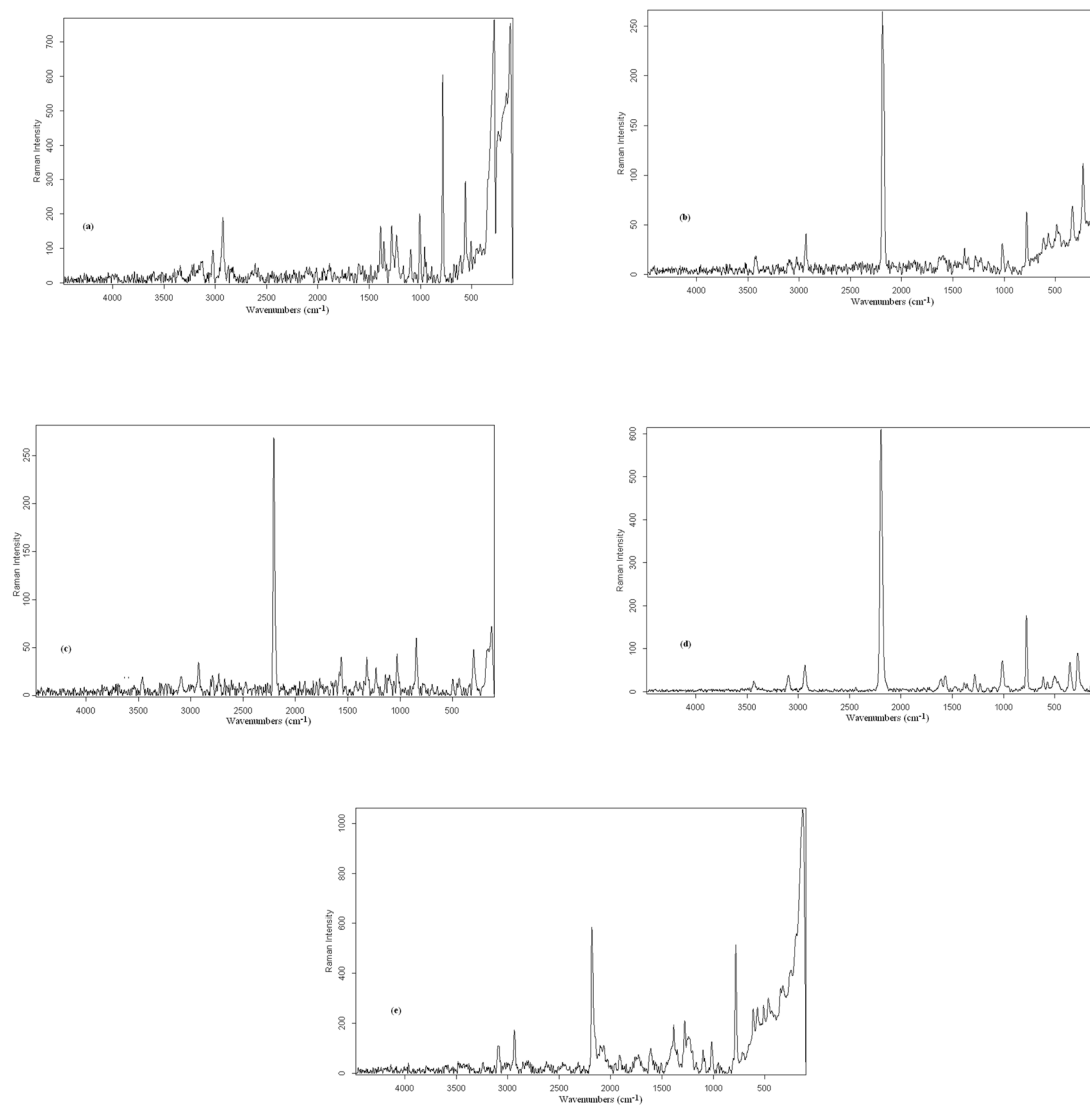
In the case of pyridine-metal complexes, a shift to higher wavenumber in the ring breathing mode is used as a guide to metal coordination [11,12]. The increase in value in certain ring modes was found to be due both to coupling with M-N (pyridine) bond vibrations and alterations of the ring force field. Similar effects were also observed in 2-aminopyrimidine complexes [9, 13]. In the case of AMPM complexes, we clearly observed an upward frequency shift of the ring breathing mode ( $988\text{ cm}^{-1}$ ), the ring stretching modes around  $1400\text{-}1600\text{ cm}^{-1}$  and the other coordination sensitive modes of AMPM. Based on the spectral results, it is concluded that the ring nitrogen and not the amino nitrogen is involved in complex formation.

### Vibrations of the polymeric sheet

The CN stretching vibrational mode  $\{\nu(\text{CN})\}$  is observed at  $2080\text{ cm}^{-1}$  in the IR spectrum of solid KCN, whereas the IR active  $\nu(\text{CN})$  mode ( $E_u$ ) of the free  $\text{Ni}(\text{CN})_4^{2-}$  group is observed at  $2124\text{ cm}^{-1}$  in the IR spectrum of solid  $\text{K}_2\text{Ni}(\text{CN})_4$  [12]. The upward shift of  $44\text{ cm}^{-1}$  on going from  $\text{CN}^{-1}$  to  $\text{Ni}(\text{CN})_4^{2-}$  has been explained as arising from the coupling

of the Ni-C(CN) vibrational modes with  $\text{C}\equiv\text{N}$  vibrations [14]. In tetracyanonickelate complexes  $\{\text{M}(\text{L})_2\text{Ni}(\text{CN})_4\}$  the  $\text{Ni}(\text{CN})_4^{2-}$  group is further complexed through the nitrogen atoms to the metal (M). The further rise of around  $20\text{-}30\text{ cm}^{-1}$  compared to the free  $\text{Ni}(\text{CN})_4^{2-}$  ion, observed in the IR spectrum of  $\text{M}(\text{L})_2\text{Ni}(\text{CN})_4$ , has been explained as the coupling of the M-N(NC) vibrational modes with  $\text{C}\equiv\text{N}$  vibrations [14]. The vibrational wavenumbers of the  $\text{Ni}(\text{CN})_4$  group vibrations of the M-Ni-AMPM complexes are tabulated in Table 2 together with those of Hofmann-type clathrate complexes and  $\text{K}_2\text{Ni}(\text{CN})_4$ . The CN vibrational mode of the M-Ni-AMPM complexes studied are found to be closer to those of Hofmann-type complexes than that of the free  $\text{Ni}(\text{CN})_4$  group. It is thus concluded that the polymeric sheet structure of a two-dimensional network of M-NCNi units is preserved in all of the M-Ni-AMPM complexes. If a local  $\text{C}_{4h}$  environment for the Ni is assumed, one IR active ( $E_u$ ) and two Raman active ( $A_g$  and  $B_g$ ) CN stretching vibrations are expected (Figure 4).

The IR active ( $E_u$ ) cyanide stretching mode is observed as one single band in the case of M = Mn, Co, Ni and Cd complexes. The IR active CN stretching mode of M-Ni-AMPM complexes for M = Mn, Co, Ni and Cd are shown in Figure 2. FT-Raman spectra of the cyanide stretching region of Mn, Co, Ni and Cd complexes are shown in Figure 3. X-ray single crystal studies on Hofmann-type pyridine [15] and 3- and 4-methyl pyridine complexes [16,17] proved that the square-planar environment around the tetracyano tetracyanonickelate ion is slightly distorted when compared with the Hofmann-type clathrates, which have tetragonal symmetry [3]. The structure of Hofmann-type pyridine and methyl pyridine complexes also consists of two-dimensional networks made up of tetracyanonickelate ions coordinated to metal (M), but the M-Ni(CN)<sub>4</sub> layers are not planar like Hofmann's benzene clathrate [3], they are undulated [15-17]. The effect of a slight distortion from a square-planar environment was not apparent in the vibrational spectra of the M-Ni-pyridine complexes. Moreover, the IR active  $\nu(\text{CN})$  and  $\delta(\text{NiCN})$  vibrations, which are doubly degenerate ( $E_u$ ) in clathrates that have tetragonal symmetry, were also found to be doubly degenerate in Hofmann-type pyridine complexes [14]. However,



**Figure 3.** The FT-Raman spectra of Hofmann-AMPM compounds in KBr: (a) AMPM (ligand), (b) Mn-AMPM-Ni, (c) Co-AMPM-Ni, (d) Ni-AMPM-Ni and (e) Cd-AMPM-Ni.

such distortion could be inferred from the vibrational spectra of  $M(L)_2Ni(CN)_4$  complexes where (L = aniline or 2-amino-4-methylpyridine) [7,18].

Relative to the high wavenumber region, the assignment of vibrational bands below the 300

$cm^{-1}$  region is more complex because of the lack of far IR and Raman data, but we made a comparison with isostructural compounds. The assignment reported here is based on a comparison with the Raman spectra of Hofmann-type clathrates and tetracyanonickelate complexes [10,12,19,

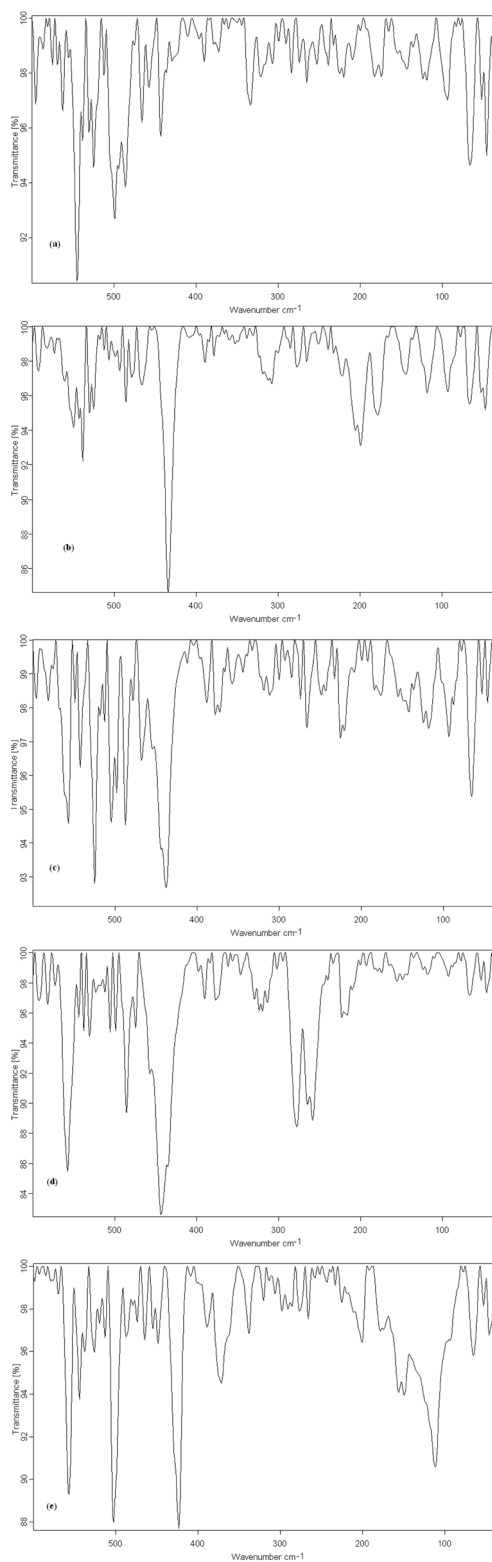
**Table 2.** Vibrational wavenumbers of tetracyanonickelate group and metal-AMPM vibrations.

Assignment	K <sub>2</sub> Ni(CN) <sub>4</sub> <sup>a</sup>		M(NH <sub>2</sub> ) <sub>2</sub> Ni(CN) <sub>4</sub> ·2Bz		M-Ni-AMPM				
	M= Ni	M= Cd	Mn	Cd	Mn	Co	Ni	Cd	
$\nu_3(\text{CN}) E_u$	2124 <sup>b</sup>	2156	2157	2136	2154vs	2158vs	2166vs	2149vs	
$\nu(\text{Ni-CN}) E_u$	538	554	553		553m	557m		557m	
$\otimes(\text{NiCN}) A_g$	444	446	456	442	470m	470sh	487sh	472w	
$\delta(\text{NiCN}) E_u$	419	425	436	423	435vs	439vs	444vs	449s	
$\nu(\text{CN}) A_g$		2175	2177	2159vs	2187vs	2194vs	2194vs	2177vs	
$\nu(\text{CN}) B_g$		2164	2165s	2144s		2164s		2159s	
$\nu(\text{Ni-CN}) A_g$	405	445-450	452w	451m	442m	450w	458w	465m	
$\delta(\text{NiCN}) E_g$	302	305-307	318m		333m	320vw	353w	324m	
$\nu(\text{M-L})_L$	200	190-192	219	190s	229s		277w	191m,sh	
$\delta(\text{MNM})_L$	176 <sup>b</sup>	160 <sup>b</sup>		144w	133m		120m	131s	

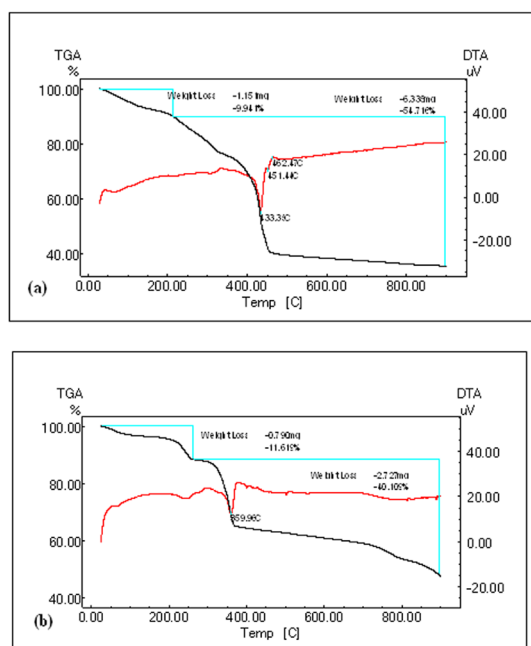
<sup>a</sup>Hofmann type clathrates M(NH<sub>2</sub>)<sub>2</sub>Ni(CN)<sub>4</sub>·2C where G is either zero (host lattice) or the guest molecule benzene taken from Ref.[22].

<sup>b</sup>s: Taken from Refs.[12,9,10], respectively.

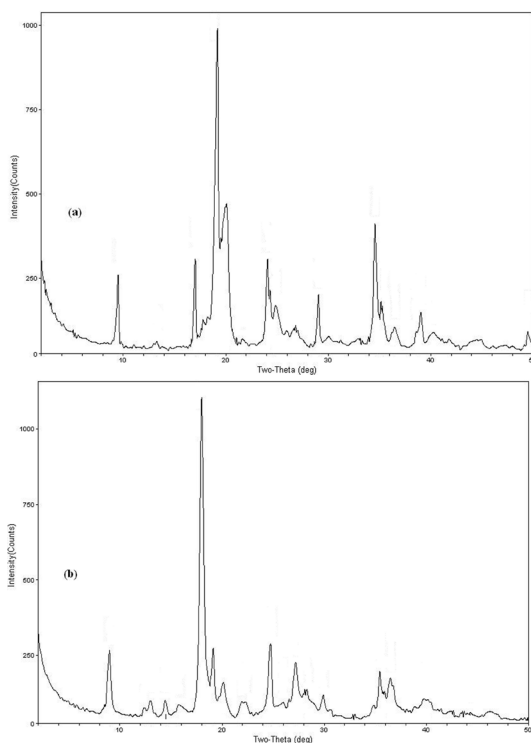
vs: very strong, s: strong, m: medium, w: weak, vw: very weak and sh: shoulder.



**Figure 4.** The far-IR spectra of Hofmann AMPM compounds (a) AMPM (ligand), (b) Mn-AMPM-Ni, (c) Co-AMPM-Ni, (d) Ni-AMPM-Ni and (e) Cd-AMPM-Ni.



**Figure 5.** The DTA and DTG curves of the Co-AMPM-Ni (a) and Cd-AMPM-Ni (b) complexes.



**Figure 6.** X-Ray powder diffraction (XRD) pattern of Co-Ni-AMPM (a) and Cd-Ni-AMPM (b) complexes.

20,21] where available. The wavenumbers of the tetracyanonickelate group vibrations together with  $\nu(\text{M-L})_{\text{AMPM}}$  and  $\delta(\text{NMN})_{\text{AMPM}}$  modes are given in Table 2 in comparison with relevant data.

### Thermal behaviour

The TGA and DTA curves of the compounds are given in Figure 5. The TGA and DTA results indicate that samples are stable at room temperature. By heating, however, both of them gradually lose two ligand molecules in a single step between about 50 and 320 °C. DTA curves show two endothermic transitions for present compounds. The first decomposition stage about 301 °C indicates that the AMPM ligand molecule leaves host structure. The second decomposition stage about 460 °C is decomposition of cyanide to yield the respective metals. The decomposition temperatures of M-AMPM-Ni (M= Co, Cd) complexes are given in Table 3. Such decomposition stages have been observed for other Hofmann type complexes [22,23] and clathrates [24].

### CONCLUSIONS

From this spectroscopic study it is concluded that 2-amino-4-methylpyrimidine acts as a monodentate ligand and bonds through endocyclic nitrogen in the five new complexes prepared (M-Ni-AMPM). Comparison of the vibrational wavenumbers of the tetracyanonickelate sheet of the isostructural compounds allowed us to provide a tentative assignment for the  $\nu(\text{M-N})_{\text{AMPM}}$  and  $\delta(\text{NMN})_{\text{AMPM}}$  vibrations. However, more data for the low wavenumber region of the tetracyanonickelate compounds are needed to be sure of the assignment.

**Table 3.** The decomposition temperatures (OC) of the M-AMPM-Ni (M= Mn, Co, Ni and Cd) complexes.

Sample	Decomposition	
	First	Second
$\text{Mn}(\text{AMPM})_2\text{Ni}(\text{CN})_4$	301.3	449.8
$\text{Co}(\text{AMPM})_2\text{Ni}(\text{CN})_4$	310.2	433.3
$\text{Ni}(\text{AMPM})_2\text{Ni}(\text{CN})_4$	301.3	443.5
$\text{Cd}(\text{AMPM})_2\text{Ni}(\text{CN})_4$	252.5	359.9



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