

**SYNTHESES, SPECTROSCOPIC AND THERMAL ANALYSES OF THE HOFMANN-
TYPE METAL(II) TETRACYANONICKELATE(II) PYRIDAZINE COMPLEXES:
{[M(pdz)Ni(CN)₄]·H₂O}_n (M = Zn(II) or Cd(II))**

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ABSTRACT. Two new Hofmann-type complexes in the form of {[M(pdz)Ni(CN)₄]·H₂O}_n [where pdz = pyridazine; M = Zn(II) and M = Cd(II)] have been synthesized as a powder and their structural properties have been characterized by vibrational (FT-IR and Raman) spectroscopy, thermal and elemental analysis. The spectral and thermal analysis results suggest that these complexes are similar in structure to the Hofmann type complexes and their structures consist of polymeric layers of [M–Ni(CN)₄]_∞ with the pdz bound to the metal (M) atom.

KEY WORDS: Hofmann-type complexes, Vibrational spectra, Pyridazine, Tetracyanonickelate(II), Thermal analysis

INTRODUCTION

Cyano-bridged complexes have been shown to form polymeric structures by studies over the last few decades. These polymeric metal complexes are especially macromolecules formed by metal–metal or metal–ligand–metal bridge connections in one, two or three dimensions. These types of complexes have applications in the fields of chemistry, biology and material science and therefore they have been attracting increasing attention from scientists [1]. Functional polymeric cyanide complexes can be prepared with mono-, di- or polydentate ligands. These types of materials are packed to form crystal structures due to bridging groups and intermolecular interactions. Cyano-bridged polymeric complexes structurally contain chains oriented in one dimension. These structures may be linear, zig-zag, stepwise, lateral and pipe shaped [2]. The well-known Hofmann-type complexes, {M(L)₂Ni(CN)₄}, are built by stacking the two-dimensional nickel cyanide sheets in layers. 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]. The square-planar [Ni(CN)₄]²⁻ moiety may take a number of catenation modes to build up multidimensional structures. Based on this structure, metal(II) tetracyanonickelate(II) complexes have been developed using N-donor ligands such as ammonia [4], pyridine [5], O-donor ligands such as water [6], dioxane [7] and S-donor ligands as N,N-dimethylthioformamide [8].

Diazines are heteroaromatic molecules with the formula C₄H₄N₂. In these molecules, two of benzene's six CH groups are replaced by nitrogen atoms. The diazine rings are important building blocks of both natural and synthetic compounds, e.g., mononucleotides. This is why, the simplest diazines: pyrazine, pyrimidine and pyridazine, have early attracted attention of chemists [9]. Pyridazine is a heteroaromatic organic compound. It contains a six-membered ring with two adjacent nitrogen atoms, and is a bidentate ligand. Pyridazine systems have attracted considerable attention because of their biological activities as antimicrobial agents, antiplatelet agents and inhibitors of glycogen synthase kinase [10].

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In previous studies, FT-IR, Raman and thermal studies of Hofmann-type host complexes and Hofmann-type clathrates of 2-methylpyrazine (2mpz) were reported [11, 12]. The vibrational spectra [12–14] and tetracyanometallate clathrates [15–17] of pyrazines have been extensively studied by several authors; however, to the best knowledge, neither crystallographic nor spectroscopic data have been so far would explicitly tell the structural analyses of the pyridazine (pdz) complexes of tetracyanonickelate(II) ions. In this study, we have now prepared for the first time the cyanide complexes of the form $\{[M(\text{pdz})\text{Ni}(\text{CN})_4]\cdot\text{H}_2\text{O}\}_n$ {where $M = \text{Zn}(\text{II})$ or $\text{Cd}(\text{II})$; $\text{pdz} = \text{pyridazine}$, abbreviated hereafter as $M\text{-Ni-pdz}$ } and characterized by spectral (FT-IR and Raman), thermal and elemental analyses. 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 $\{(M\text{-N})_{\text{pdz}}, \delta(\text{N-M-N})_{\text{pdz}}\}$ by studying isostructural complexes $\{M(\text{pdz})\text{Ni}(\text{CN})_4\}_n$.

EXPERIMENTAL

All the chemicals used were reagent grade and used without further purification. $\text{NiCl}_2\cdot 6\text{H}_2\text{O}$ (1.25 g, 5 mmol) was dissolved in 25 mL water and added to a 20 mL solution of KCN (1.30 g, 20 mmol) in water. The mixture was stirred at 50 °C during three hours. To this solution was added a solution of ZnCl_2 (0.136 g, 1 mmol) or $\text{CdCl}_2\cdot\text{H}_2\text{O}$ (0.201 g, 1 mmol) one by one. These mixtures were refluxed with stirring for 3 h at 50 °C in a temperature-controlled bath and then the solutions were filtered and slowly evaporated in air. A solution of pdz (0.160 g, 2 mmol) in ethanol was added dropwise upon stirring to these suspensions. The solutions were refluxed with stirring for 3 h at 50 °C and then cooled to room temperature. The complexes were filtered and washed with 10 ml of water and acetone and dried in air.

The FT-IR spectra of the complexes were recorded as KBr pellets in the range of 4000–400 cm^{-1} (2 cm^{-1} resolution) on a Perkin Elmer Spectrum 100 FT-IR spectrometer. The Raman spectra were recorded in the range of 4000–250 cm^{-1} on a Bruker Senterra Dispersive Raman instrument using laser excitation of 785 nm.

A Perkin Elmer Diamond TG/DTA thermal analyzer was used to record simultaneous TG, DTG and DTA curves in the static air atmosphere in the temperature range 30–700 °C using platinum crucibles.

The freshly prepared complexes were analyzed for C, H, and N by a LECO CHNS-932 analyzer with the following results (calculated % / found %): $[\text{Zn}(\text{C}_4\text{H}_4\text{N}_2)\text{Ni}(\text{CN})_4]\cdot\text{H}_2\text{O}$ (1) $M_w = 326.26$ g/mol: C = 29.45/29.58., H = 1.85/1.98, N = 25.76/25.83; $[\text{Cd}(\text{C}_4\text{H}_4\text{N}_2)\text{Ni}(\text{CN})_4]\cdot\text{H}_2\text{O}$ (2) $M_w = 373.28$ g/mol : C = 25.74/25.61, H = 1.62/1.94, N = 22.51/22.95.

RESULTS AND DISCUSSION

Vibrational spectra

Water vibrations. The vibrational spectra of Zn–Ni–pdz and Cd–Ni–pdz complexes are shown in Figures 1 and 2, respectively. The assignments and the wavenumbers of the vibrational bands of pdz observed in the spectra of the complexes studied are listed in Table 1, together with free pdz wavenumbers for comparison [9, 18]. The absorption bands of the complexes are observed in the region from 3700 cm^{-1} to 3300 cm^{-1} because of symmetric and asymmetric $\nu(\text{OH})$ stretching vibrations of the coordinated water molecules. The absorption band at about 3420 cm^{-1} may be attributed to the symmetric $\nu(\text{OH})$ stretching mode of crystal water molecules. Moreover, the absorption bands are observed in the region from 1650 cm^{-1} to 1600 cm^{-1} due to $\delta(\text{OH})$ deformation vibrations of the water molecule in the complexes. The shift to lower frequencies of $\nu(\text{OH})$ stretching modes and the shift to higher frequencies of $\delta(\text{OH})$ bending modes (1620–1650 cm^{-1}) may be attributed to hydrogen bonding in the complexes. In our

previous study [19], the available of water molecules in the structures of the complexes were identified by the vibrational analysis and was supported by X-ray diffraction.

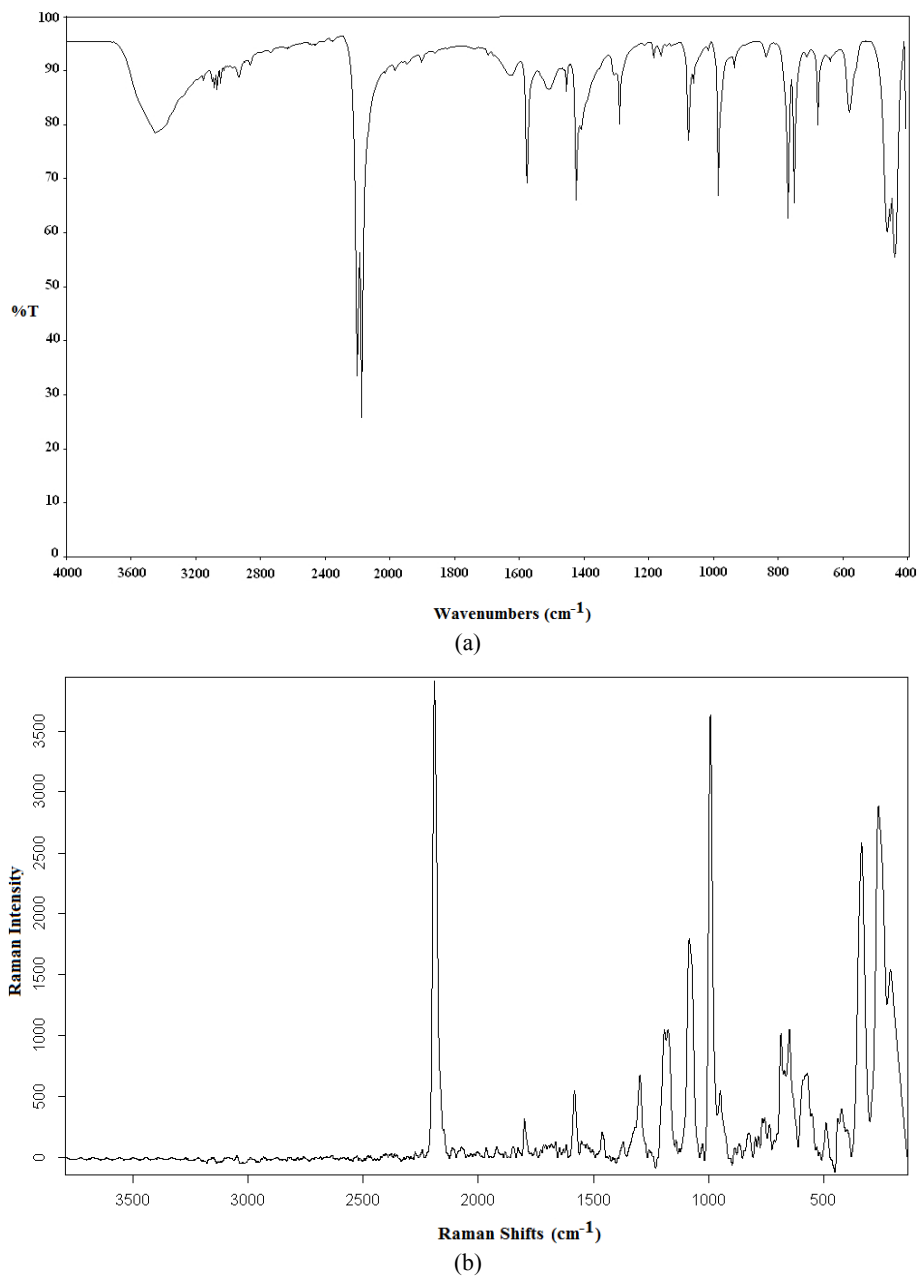


Figure 1. (a) FT-IR and (b) Raman spectra of Zn-Ni-pdz.

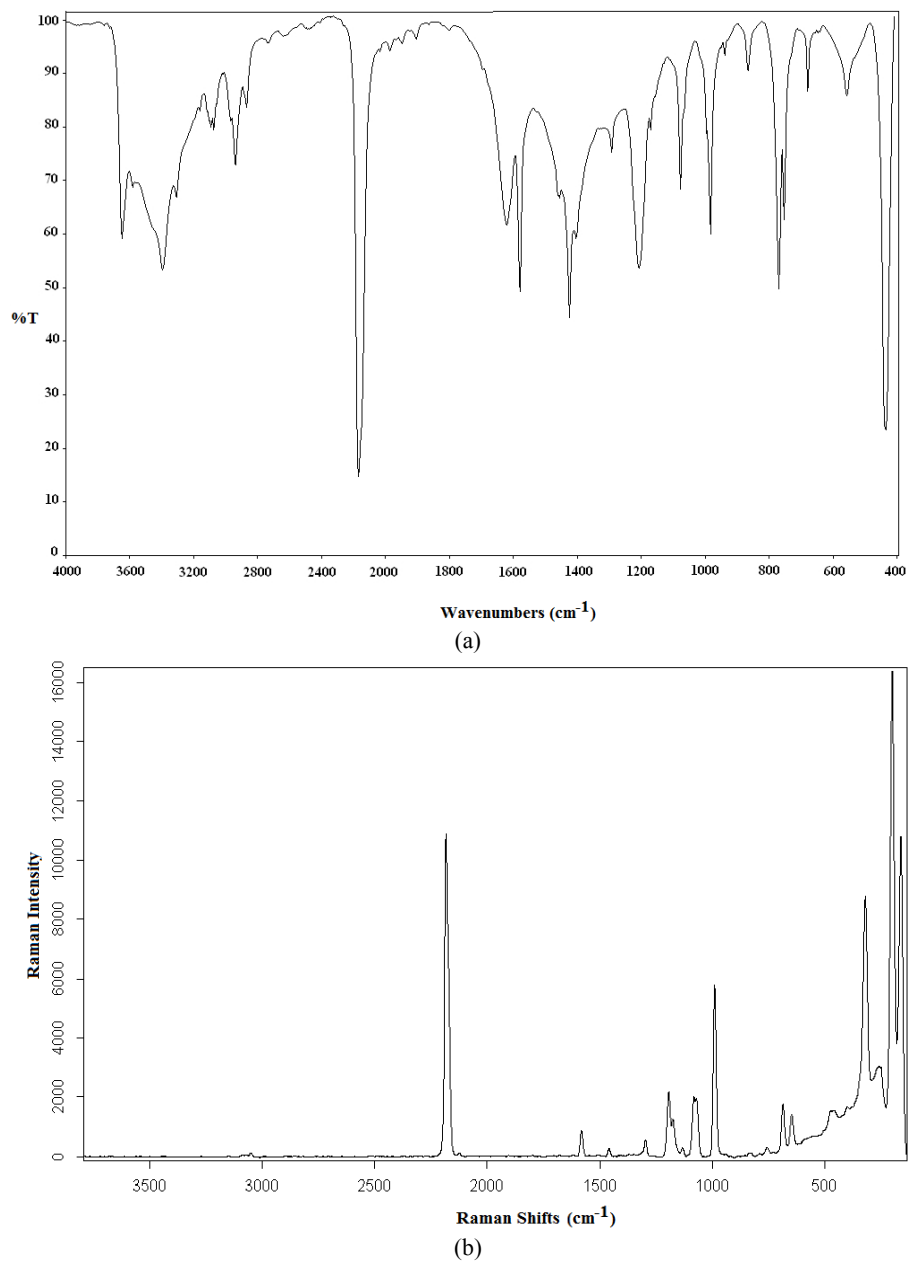


Figure 2. (a) FT-IR and (b) Raman spectra of Cd-Ni-pdz.

Pyridazine vibrations. The wavenumbers of pdz in the complexes are compared with those of free pdz. A glance at Table 1 shows that the vibrational wavenumbers of the pdz modes in the complexes exhibit coordination properties. Vibration modes of the pdz molecule have upward and downward shifts in wavenumber when compared with the free pdz molecule. Analogous shifts on coordination were observed in pyridine [5], 4,4'-bipyridyl [20] and 2-methylpyrazine [11, 12] complexes. These shifts were explained as the coupling of the internal modes of the aromatic molecule with the M–N vibrations [5, 20–22]. The C–H stretching bands of pdz were observed in the 3100–3000 cm⁻¹ region. The ring $\nu(\text{CH})$ modes of the pdz were found downward and upward shifts in wavenumbers when compared with the free pdz molecule. The C–H in-plane bending vibrational modes of the pdz can be observed in the 1600–1000 cm⁻¹ region of the spectra, but several other internal coordinates are mixed with them, e.g. the ν_{ring} modes. The ring-stretching modes appear in the spectra of the pdz in the 1600–1000 cm⁻¹ region. When the aromatic ring nitrogen involves in complex formation, certain ring modes, particularly modes 1400–1600 cm⁻¹ increase in value both due to the coupling with M–N_{pdz} (Zn(II) or Cd(II)) bond vibrations [23, 24] and due to alterations of the ring force field [21].

Table 1. The vibrational wavenumbers of pdz in M–Ni–pdz (M = Zn(II) and Cd(II)) (cm⁻¹).

^a Assignments (PED %)*	^b Pyridazine (Gas)	^b Pyridazine (CCl ₄)	Pyridazine (Liquid)	Zn–Ni–pdz		Cd–Ni–pdz	
				FT-IR	Raman	FT-IR	Raman
A ₁ $\nu(\text{CH})_s(79.5)+\nu(\text{CH})_s(19.6)$	3086 s	-	-	3090 vw	-	3088 w	-
B ₂ $\nu(\text{CH})_{\text{as}}(97.0)$	3071 s	3068 m	-	3076 w	-	3077 w	-
A ₁ $\nu(\text{CH})'_s(80.0)+\nu(\text{CH})_s(19.7)$	3056 s	3056 m	3057 m	3059 w	-	3059 w	3050 vw
A ₁ $\nu(\text{C4C5})(46.8)+\delta(\text{CH})_s(18.9)$	1567 m	1570 vs	1570 m	1572 m	1582 w	1571 s	1581 vw
B ₂ $\nu(\text{CC})_{\text{as}}(44.3)+\delta(\text{CH})'_{\text{as}}(24.4)+\nu(\text{NC})_{\text{as}}(22.7)$	-	1563 vs	1563 s	1570 m	-	-	-
A ₁ $\delta(\text{CH})_s(39.2)+\delta(\text{CH})'_s(24.0)+\nu(\text{CC})_s(19.3)+\nu(\text{NN})(13.7)$	1455 w	1443 s	1444 m	1449 w	1463 vw	1454 sh	1459 vw
B ₂ $\delta(\text{CH})_{\text{as}}(62.3)+\nu(\text{CH})'_{\text{as}}(23.5)$	1413 s	1412 vs	1413 vs	1419 m	1431 vw	1417 s	-
B ₂ $\delta(\text{CH})_{\text{as}}(34.9)+\nu(\text{NC})_{\text{as}}(32.7)+\delta(\text{CH})'_{\text{as}}(30.5)$	1281 m	1281 m	1281 m	1285 w	1298 w	1285 m	1297 vw
A ₁ $\nu(\text{NC})_s(62.1)+\nu(\text{CC})_s(21.0)+\delta(\text{CH})'_s(10.4)$	-	1156 w	1159 vw	1157 vw	1176 w	1163 w	1175 vw
A ₁ $\nu(\text{CH})'_s(59.2)+\delta(\text{CH})_s(16.4)+\nu(\text{NN})'_s(10.4)+\nu(\text{NC})_s(10.5)$	1121 sh	1129 w	1131 vw	1125 vw	1141 vw	1121 w	1132 vw
A ₁ $\nu(\text{C4C5})_s(41.0)+\delta(\text{CH})_s(22.6)+\nu(\text{NN})_s(22.1)+\nu(\text{CC})'_s(12.2)$	1068 s	-	-	1072 w	1084 m	1070 m	1082 w
B ₂ $\nu(\text{CC})_{\text{as}}(42.3)+\delta(\text{CH})_{\text{as}}(29.5)+\nu(\text{NC})_{\text{as}}(12.7)+\delta \text{ ring 1}(10.4)$	1061 s	1062 vs	1062 m	1056 w	-	1062 w	-
B ₂ $\delta \text{ ring 1}(87.1)$	1027 w	-	982 vw	1011 vw	992 vs	988 w	990 m
A ₁ $\nu(\text{NN})(45.5)+\nu(\text{CC})_s(34.4)+\nu(\text{NC})_s(15.6)$	968 m	963 vs	962 s	980 m	-	976 m	-
B ₁ $\gamma(\text{CH})'_s(106.4)$	959 m	-	-	931 vw	949 w	931 vw	940 vw
B ₁ $\gamma(\text{CH})'_s(97.0)$	760 s	-	758 vs	764 m	767 w	762 s	756 vw
A ₂ $\tau \text{ ring 1}(114.2)$	745 s	757 s	753 s	746 m	756 w	745 m	-
A ₂ $\delta \text{ ring 2}(90.0)$	665 w	665 s	665 w	672 w	686 w	672 w	686 w
B ₂ $\delta \text{ ring 3}(92.7)$	622 vw	622 w	622 vw	634 vw	649 w	639 vw	647 vw

*Taken from Ref. [9]. ^bTaken from Ref. [18]. ^cThe symbols: ν stretching, δ deformation, β in plane of bending, w wagging, γ out plane of bending, t twisting, r rocking. Abbreviations used; s strong, m medium, w weak, sh shoulder; v very, br broad. PEDs lower than 10% are not included.

Ni(CN)₄ group vibrations. The vibrational wavenumbers of the [Ni(CN)₄]²⁻ group of M–Ni–pdz complexes are given in Table 2. In order to assign the bands attributable to the [Ni(CN)₄]²⁻ ion in the spectra, we refer to the work of McCullough *et al.* who presented vibrational data for the salt

$\text{Na}_2\text{Ni}(\text{CN})_4$ in the solid state [25]. In this salt, $[\text{Ni}(\text{CN})_4]^{2-}$ anion is not coordinated to Na^+ cation; therefore, it can be treated as an isolated unit with D_{4h} symmetry and thus used as a reference to comment on vibrational changes when M–NC bonding takes place. The assigned wavenumbers of the $[\text{Ni}(\text{CN})_4]^{2-}$ units of the complexes appear to be much higher than those for isolated $[\text{Ni}(\text{CN})_4]^{2-}$ ion. Such wavenumber shifts have been observed for Hofmann-type complexes [5, 24, 26, 27]. It is known that cyanide stretching modes shift to higher wavenumbers in the case of the complexes having the $[\text{M}-\text{Ni}(\text{CN})_4]_\infty$ polymeric layers. This case are explained as the mechanical coupling of the internal modes of $[\text{Ni}(\text{CN})_4]^{2-}$ with the metal M–NC vibrations. It follows that the nitrogen ends of the $[\text{Ni}(\text{CN})_4]^{2-}$ units are bound to M (M = Zn(II) or Cd(II)) atom in the complexes.

Table 2. Vibrational wavenumbers of the $[\text{Ni}(\text{CN})_4]^{2-}$ group in M–Ni–pdz (M = Zn(II) and Cd(II)) (cm^{-1}).

^a Assignments*	^a $\text{Na}_2[\text{Ni}(\text{CN})_4]$	$\text{K}_2[\text{Ni}(\text{CN})_4] \cdot \text{H}_2\text{O}$	Zn–Ni–pdz	Cd–Ni–pdz
$A_{1g}, \nu(\text{CN})$	(2149)	(2160) vs	(2191) vs	(2183) s
$B_{1g}, \nu(\text{CN})$	(2141)	(2137) m	(2112) vw	(2124) vw
$E_u, \nu(\text{CN})$	2132	2122 vs	2192 m, 2165 vs	2154 vs
$\nu(^1\text{CN})$	2128	2084 m	2124 sh	2136 sh
$E_u, \nu(\text{NiC})$	543	540 w	575 w	549 w
$A_{2u}, \pi(\text{NiCN})$	448	443 w	448 m, 457 m	-
$E_u, \delta(\text{NiCN})$	433	417 s	436 m	428 vs

^aTaken from Ref. [25]. ^{*}Abbreviations used; s strong, m medium, w weak, sh shoulder; v very. The symbols; ν , δ and π refer to valence, in-plane and out-of-plane vibrations, respectively. Raman spectra are given in parentheses.

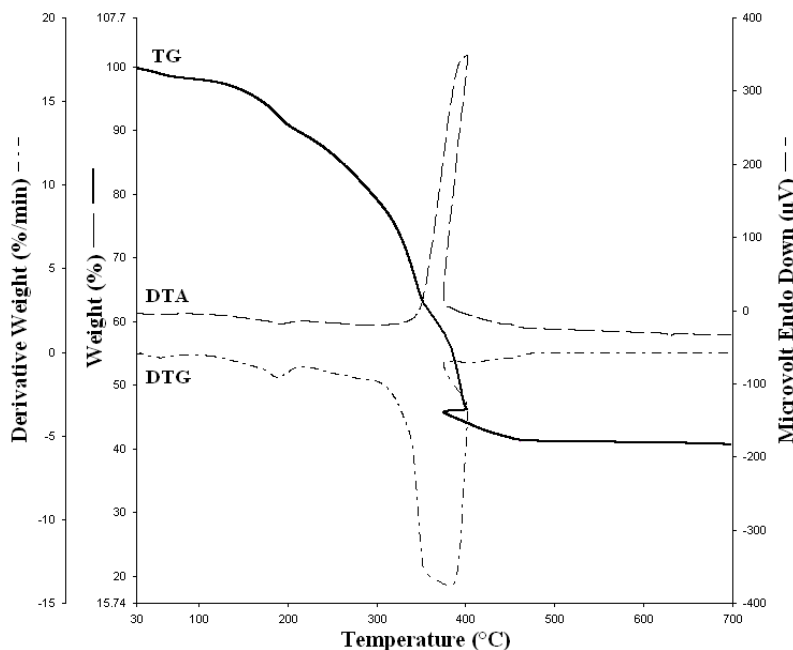


Figure 3. The TG, DTG and DTA curves of Zn–Ni–pdz complex.

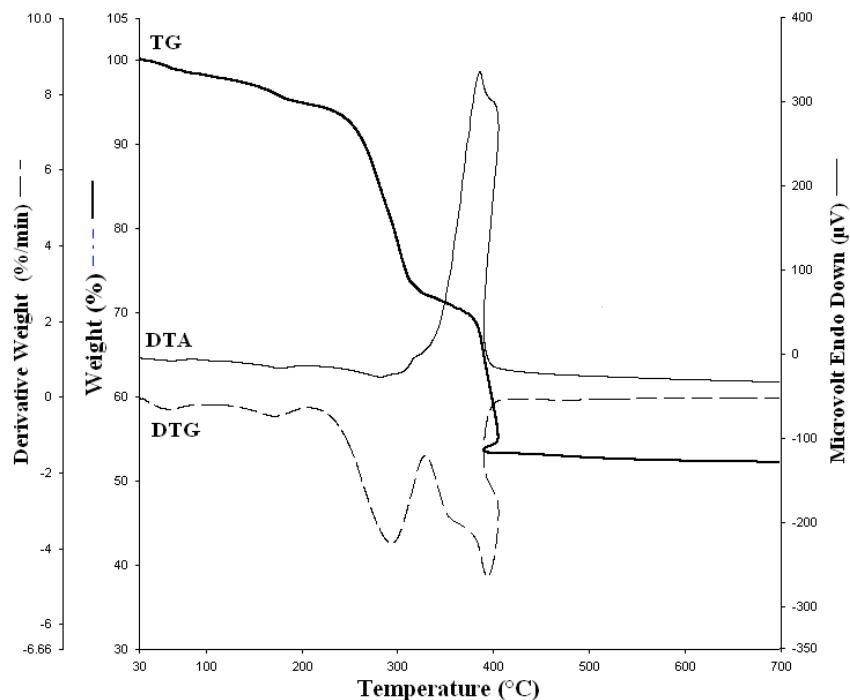


Figure 4. The TG, DTG and DTA curves of Cd-Ni-pdz complex.

Thermal analysis

The thermal decomposition behaviors of Zn-Ni-pdz and Cd-Ni-pdz complexes were studied in the temperature range 30-700 °C in static air atmosphere. The thermal analysis curves of Zn-Ni-pdz and Cd-Ni-pdz complexes are similar (Figures 3 and 4). Thermal decomposition of the complexes proceeds in three stages. In the first stage, Zn-Ni-pdz complex starts to lose one water molecule between 30 and 150 °C whereas Cd-Ni-pdz complex are related to release of one water molecule between 30 and 210 °C (found 4.77%, calcd. 4.90% for Zn-Ni-pdz and found 5.29%, calcd. 4.82% for Cd-Ni-pdz). In second stage of the complexes, one pdz ligand for Zn-Ni-pdz (found 25.11%, calcd. 24.57%) and one pdz ligand for Cd-Ni-pdz (found 22.63%, calcd. 21.45%) are released. The following stage remaining four cyano groups in Zn-Ni-pdz and Cd-Ni-pdz complexes decompose between 303 and 397 °C for Zn-Ni-pdz, 330 and 410 °C for Cd-Ni-pdz (DTA_{max}: 398°C for Zn-Ni-pdz and 386 °C for Cd-Ni-pdz). The final solid product of the thermal decomposition was identified as MO + NiO metal oxides found (calcd.) % = 46.96 (47.78) for Zn-Ni-pdz and found (calcd.) % = 53.30 (54.40) for Cd-Ni-pdz.

CONCLUSIONS

In this study, two new Hofmann-type complexes were synthesized and investigated by vibrational (FT-IR and Raman) spectroscopy, thermal and elemental analyses. On the basis of the vibrational spectroscopic results, we propose that pdz molecule are coordinated to metal (Zn(II) or (Cd(II)) ions of the adjacent layers of $[M-Ni(CN)_4]_{\infty}$ in the complexes.

Furthermore, M (Zn(II) or (Cd(II)) atoms are bound to four N atoms of the CN ions and, the Ni(II) atoms are surrounded by four C atoms of the CN groups in a square-planar layer. Thermal analyses of the complexes also support the spectroscopic conclusions.

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REFERENCES

1. Mukherjee, P.S.; Maji, T.K.; Mallah, T.; Zangrando, E.; Randaccio, L.; Chaudhuri, N.R. *Inorg. Chim. Acta* **2001**, 315, 249.
2. Cernak, J.; Orendac, M.; Potocnak, I.; Chomic, J.; Orendacova, A.; Skorsepa, J.; Feher, A. *Coord. Chem. Rev.* **2002**, 224, 51.
3. Iwamoto, T. *J. Incl. Phenom.* **1996**, 24, 61.
4. Rayner, H.; Powell, H.M. *J. Chem. Soc.* **1952**, 67, 319.
5. Akyüz, S.; Dempster, A.B.; Morehouse, R.L.; Suzuki, S. *J. Mol. Struct.* **1973**, 17, 105.
6. Yuge, H.; Kim, C.H.; Iwamoto, T.; Kitazawa, T. *Inorg. Chim. Acta* **1997**, 257, 217.
7. Dempster, A.B.; Uslu, H. *Spectrochim. Acta* **1978**, 34, 71.
8. Şenel, M.; Kürkçüoğlu, G.S. *J. Appl. Spect.* **2001**, 68, 862.
9. Breda, S.; Reva, I.D.; Lapinski, L.; Nowak, M.J.; Fausto, R. *J. Mol. Struct.* **2006**, 786, 193.
10. Ünal, D.; Sarıpınar, E.; Akçamur, Y. *Turk. J. Chem.* **2006**, 30, 691.
11. Kürkçüoğlu, G.S.; Yeşilel, O.Z.; Kavlak, İ.; Büyüküngör, O. *Struct. Chem.* **2008**, 19, 879.
12. Kürkçüoğlu, G.S.; Kavlak, İ.; Çaylı, İ. *Spectr. Lett.* **2010**, 42, 5.
13. Endredi, H.; Billes, F.; Keresztury, G. *J. Mol. Struct.* **2004**, 677, 211.
14. Arenas, J.F.; Centeno, S.P.; Lopez-Tocon, I.; Otero, J.C. *J. Mol. Struct.* **2005**, 744, 289.
15. Kantarcı, Z.; Davarcıoğlu, B.; Bayrak, C. *J. Incl. Phenom.* **2001**, 39, 115.
16. Ekici, N.; Kantarcı, Z.; Akyüz, S. *J. Incl. Phenom.* **1991**, 10, 9.
17. Akyüz, T.; Akyüz, S.; Davies, J.E.D. *J. Incl. Phenom.* **1990**, 9, 349.
18. Vazquez, J.; Jesus, J.; Gonzalez, L.; Marquez, F.; E. Boggs, J. *J. Raman Spectrosc.* **1998**, 29, 547.
19. Kürkçüoğlu, G.S.; Hökelek, T.; Yeşilel, O.Z.; Aksay, S. *Struct. Chem.* **2008**, 19, 493.
20. Sungur, A.; Akyüz, S.; Davies, J.E.D. *J. Incl. Phenom.* **1987**, 5, 491.
21. Suzuki, S.; Orville-Thomas, W.J. *J. Mol. Struct.* **1977**, 37, 321.
22. Parlak, C. *Bull. Chem. Soc. Ethiop.* **2010**, 24, 375.
23. Kantarcı, Z.; Davarcıoğlu, B.; Bayrak, C. *J. Incl. Phenom.* **2001**, 39, 115.
24. Ekici, N.; Kantarcı, Z.; Akyüz, S. *J. Incl. Phenom.* **1991**, 10, 9.
25. McCullough, R.L.; Jones, L.H.; Crosby, G.A. *Spectrochim. Acta* **1960**, 16, 929.
26. Kantarcı, Z.; Bülbül, M.M. *J. Incl. Phenom.* **2001**, 40, 105.
27. Kantarcı, Z.; Bayrak, C. *J. Incl. Phenom.* **2003**, 45, 59.