SPECTROSCOPIC STUDY OF CYANO-BRIDGED HETERO-METALLIC POLYMERIC COMPLEXES WITH 2-METHYLPYRAZINE: $[M(NH_3)(2mpz)Ni(CN)_4]\cdot nH_2O$ (M(II) = Cu or Zn)

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We have synthesized new cyano-bridged hetero-metallic polymeric complexes $[M(NH_3)(2mpz)Ni(CN)_4]\cdot nH_2O$ in the powder form for the first time. Their structures were determined by elemental and spectral (infrared and Raman) analyses. In the complexes, the center of the nickel atom binds with four cyano ligands and shows a square planar geometry. In addition, the metal atoms (Cu(II) or Zn(II)) are linked to the ring nitrogen atom of one 2mpz ligand, one ammonia ligand, and four bridging cyano groups and show a distorted octahedral geometry. The spectral features suggest that these complexes are similar to each other and their structures consist of $|M – Ni(CN)_4|_\infty$ type polymeric layers with the ligands (2mpz and ammonia) bound to the metal atom (M).

Keywords: *tetracyano nickelate(II), 2-methylpyrazine, cyano-bridged complex, vibration spectra.*

СПЕКТРОСКОПИЧЕСКОЕ ИССЛЕДОВАНИЕ ЦИАНОМОСТИКОВЫХ ГЕТЕРОМЕТАЛЛИЧЕСКИХ ПОЛИМЕРНЫХ КОМПЛЕКСОВ С 2-МЕТИЛПИРАЗИНОМ: $[M(NH_3)(2mpz)Ni(CN)_4]\cdot nH_2O$ (M(II) = Cu или Zn)

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Синтезированы новые цианомостиковые гетерометаллические полимерные комплексы $[M(NH_3)(2mpz)Ni(CN)_4]\cdot nH_2O$ в порошковой форме. Их структура определена элементным и спектроскопическими (ИК и КР) методами. В комплексах центр атома никеля связывается с четырьмя цианолигандами и имеет плоскую квадратную геометрию. Атомы металла (Cu(II) или Zn(II)) связаны с кольцевым атомом азота одного лиганда 2mpz, одного аммиачного лиганда и четырех мостиковых цианогрупп и демонстрируют искаженную октаэдрическую геометрию. Спектральные особенности позволяют предположить, что эти комплексы схожи, а их структура состоит из полимерных слоев типа $|M – Ni(CN)_4|_\infty$ с лигандами (2mpz и аммиак), связанными с атомом металла (M).

Ключевые слова: *тетрацианоникелат(II), 2-метилпиразин, цианомостиковый комплекс, колебательный спектр.*

Introduction. The ability of cyano metal complexes to build polynuclear architectures that include appropriately designed ligands and transition metal ions has attracted the attention of scientists because of its applications in chemistry, biology, and materials sciences [1]. These applications mainly focus on catalysts [2], host-guest systems [3], molecular magnets [4], molecular sieves [5], and ion exchangers [1, 6].

The cyano ligand is extensively used to prepare 1D, 2D, or 3D structures because it acts as a σ-donor and a π-acceptor and possesses negative charges and an ambidentate character. The cyano ligand can be coordinated to the metal as monodentate (C-) or bidentate (C-, N-) and thus exhibit bridging properties. Due to its bridging properties, it is used to obtain cyano-bridged polymeric complexes and Hofmann type complexes $[M(L)_2Ni(CN)_4]_n$, where M is a transition metal atom, such as Cu(II), Zn(II), or Cd(II), and L is either a bidentate or two monodentate ligand, such as ammonia [7], pyrazine [8], cyclohexanethiol [9], 1-phenylpiperazine [10], or pyridine [11]. In addition, cyano-bridged hetero-metallic polymeric crystals have recently

been obtained using transition metals, bridging a cyano ligand and neutral ligands. Their structures have been investigated extensively by the X-ray diffraction method [12–15].

Spectroscopic studies of pyrazine and 2-methylpyrazine have been carried out in the literature [16–18], and their various metal complexes have been obtained and their structures described [19–21]. However, only one paper deals with the crystal structure of heteronuclear aqua 2mpz-metal (II) complexes of the $[Ni(CN)_4]^{2-}$ anion [22]. We have prepared $[M(NH_3)(2mpz)Ni(CN)_4]\cdot nH_2O$ [where 2mpz = 2-methylpyrazine; M(II) = Cu or Zn, n = 1 or 2; hereafter abbreviated as Cu–Ni–2mpz and Zn–Ni–2mpz] for the first time and investigated their structures by spectroscopic and elemental analysis techniques. The spectroscopic features of these complexes have been studied in the 400–4000 cm^{-1} region for FT-IR and the 250–4000 cm^{-1} region for Raman spectroscopy.

Experimental. Metal(II) chloride [($CuCl_2\cdot 2H_2O$, 99%), ($ZnCl_2$, 96%), and ($NiCl_2\cdot 6H_2O$, 97%)], potassium cyanide (KCN, 96%), and 2-methylpyrazine ($C_5H_6N_2$, 98%) were purchased and used without further purification.

Synthesis of the complexes. One millimole of $NiCl_2\cdot 6H_2O$ (0.238 g) was dissolved in 80 mL of distilled water. Four millimoles of KCN (0.260 g) dissolved in 80 mL of distilled water was added dropwise to this solution. The prepared solution was stirred with a magnetic stirrer for 4 h and then allowed to stand by filtration. Within a few weeks, the tetracyanonickelate ($K_2[Ni(CN)_4]\cdot H_2O$) compound was obtained. One millimole of the tetracyanonickelate (0.259 g) complex was mixed with a magnetic stirrer with distilled water for 4–5 min and dissolved. The aqueous solution of 1 mmol metal (II) chloride [$CuCl_2\cdot 2H_2O$ (0.170 g) or $ZnCl_2$ (0.136 g)] salt prepared was added dropwise to the tetracyanonickelate solution in a separate beaker. The solution was stirred in the magnetic stirrer at room temperature for 3 h, and then $M[Ni(CN)_4]\cdot H_2O$ [M(II) = = Cu or Zn] was obtained. One millimole of $M[Ni(CN)_4]\cdot H_2O$ [$Cu[Ni(CN)_4]\cdot H_2O$ = 0.244 g or $Zn[Ni(CN)_4]\cdot H_2O$ = 0.246 g] was completely dissolved in 25 mL of distilled water. Into this solution, 2 mmol of the 2mpz dissolved in ethanol (10 mL) and ammonia (5 mL) was added dropwise. The resulting solution was stirred in the magnetic stirrer at 40ºC for 3 h, and then the resulting complexes were filtered and washed with distilled water and ethanol, and dried in the air. These compounds were analyzed for C, H, and N, with the following results obtained: anal. found (calc.) (%) for $C_9H_{11}N_7O_1CuNi$ (M_w = 355.47 g/mol): C 30.21 (30.41), H 2.69 (3.12), N 28.41 (27.58), for $C_9H_{13}N_7O_2ZnNi$ (M_w = 375.33 g/mol): C 28.36 (28.80), H 2.49 (3.49), N 25.85 (26.12).

Measurements. The resulting complexes were analyzed for C, H, and N with a LECO CHN-932 analyzer at the Middle East Technical University Central Laboratory in Ankara, Turkey. Infrared spectra were recorded using a Perkin Elmer 100 FT-IR spectrometer with KBr pellets in the 400–4000 cm^{-1} (2 cm^{-1} resolution) region. The Raman spectrum of the compound obtained was carried out with a Bruker Senterra dispersive Raman apparatus between 4000 and 250 cm^{-1} using 785 nm laser excitation.

Results and discussion. *Spectroscopic studies of the complexes. Vibrations of 2-methylpyrazine.* The vibration spectra of Cu–Ni–2mpz and Zn–Ni–2mpz are shown in Fig. 1. The assignments of the 2mpz and the vibration frequencies of the 2mpz in the complexes are given in Table 1, together with the frequencies of 2mpz in liquid [16]. Table 1 shows the changes in the vibration frequencies of a coordinated ligand to the metal atom. The C–H stretching vibrations of the 2mpz molecule were observed around 2900–3100 cm^{-1}. The ν(CH) stretching vibration frequencies of the 2mpz molecule were generally shifted upwards in the vibration spectra of the complexes, but the $\nu(CH_3)$ stretching vibration frequencies of the 2mpz molecule were shifted downwards. The δ(CH) and γ(CH) modes of the 2mpz molecule, along with other modes, were found in the range 700–1350 cm^{-1}. It was observed that these modes are shifted upward or downward in the vibration spectra of the complexes. The $\delta(CH_3)$ modes of the methyl group appear between the ring stretching modes and have upward shifts in frequency when compared with the free 2mpz. The ring stretching vibration modes ν_{ring} in the spectra of the 2mpz are observed in the range 1000–1600 cm^{-1}. Ring stretching modes in this range are generally shifted to the up frequency region. In particular, the ring stretching mode at 1059 cm^{-1} shifts approximately around 20–30 cm^{-1} in the spectrum of the complexes. When the coordination takes place via the aromatic ring nitrogen of the 2mpz ligand, certain ring modes increase in value due to the coupling of M–N (ligand) bond vibrations with vibrations of the internal modes of the ligand [11, 23]. The δ_{ring} and γ_{ring} modes were observed at 977, 636, 559, and 404 cm^{-1} in the infrared spectra of the 2mpz. These modes are from 417 to 980 cm^{-1} in the vibration spectra of the complexes. Other significant bands of the 2mpz are ν(CC) at 1249 cm^{-1} and γ(CC) at 465 cm^{-1}. The C–C vibrational modes appear in the 1249–1263 and 435–490 cm^{-1}, regions in the vibration spectra of the 2mpz in the complexes. Consequently, these shifts suggest that the ring nitrogen of the 2mpz for both complexes is involved in the complex formation.

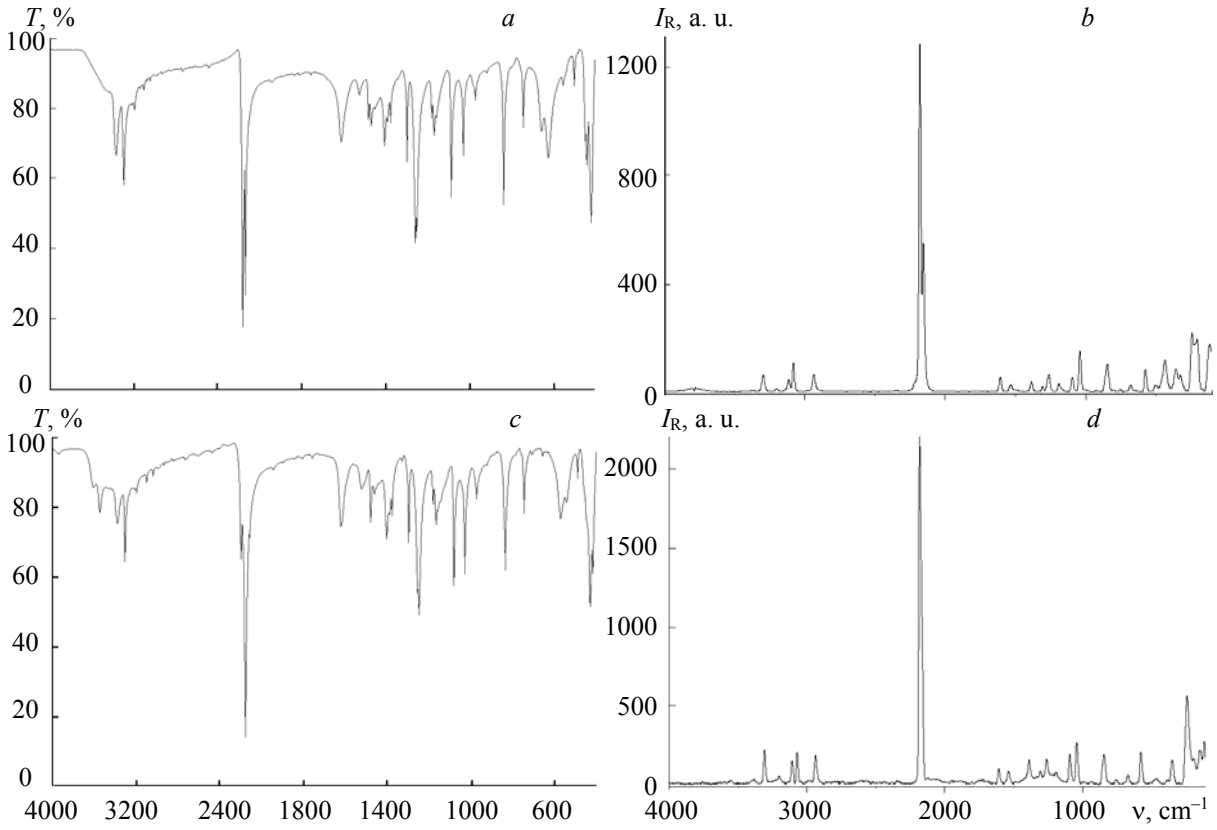

Fig. 1. The infrared (a, c) and Raman (b, d) spectrum of the Cu–Ni–2mpz (a, b), and Zn–Ni–2mpz (c, d).

TABLE 1. The Vibrational Wavenumbers (cm^{-1}) of the 2mpz in the Complexes

Assignment [16]	2mpz [16] (liquid)		Cu–Ni–2mpz		Zn–Ni–2mpz	
	FT-IR	Raman	FT-IR	Raman	FT-IR	Raman
ν(CH)	3053 s	3056 s	3098 w	3079 w	3093 w	3071 w
ν(CH)	3037 sh	3039 s	3040 w	–	3032 w	–
$\nu(CH_3)$	3007 m	–	–	–	–	–
$\nu_{as}(CH_3)$	2965 sh	2966 w	2925 vw	2934 w	2928 vw	2937 w
ν_{ring}	1579 m	1582 m	1609 m	1608 w	1619 m	1609 w
ν_{ring}	1526 s	1528 vw	1523 w	1533 vw	1521 w	1537 w
ν_{ring}	1477 vs	–	1480 w	–	1477 w	–
$\delta_{as}(CH_3)$	1445 s	1446 vw	1467 w	–	1459 w	–
$\delta_{as}(CH_3)$	1419 sh	1437 vw	1448 vw	–	–	–
ν_{ring}	1400 vs	1397 vw	1403 m	–	1400 m	–
$\delta(CH_3)$	1375 sh	1377 w	1390 w	1386 w	1376 w	1388 w
δ(CH)	1303 s	1304 w	1296 m	1307 vw	1295 m	1308 vw
ν(CC)	1249 s	1249 m	1256 s	1263 w	1249 m	1261 w
ν_{ring}	1195 sh	1183 sh	1179 w	1190 vw	1180 w	1192 vw
δ(CH)	1176 s	1179 w	1167 m	–	1165 w	–
ν_{ring}	1059 s	1060 s	1086 s	1096 w	1080 m	1092 w
$r(CH_3)$	1040 sh	1036 sh	–	1041 w	–	1042 w
δ (CH)	1019 vs	1021 s	1029 m	–	1028 m	–
δ_{ring}	977 m	979 vw	971 w	–	972 w	–
γ(CH)	943 sh	–		–		–
r(CH)	–	931 vw	917 vw	–	923 vw	–
γ(CH)	830 vs	829 m	837 m	846 w	835 m	843 w

Continue Table 1

Assignment [16]	2mpz [16] (liquid)		Cu–Ni–2mpz		Zn–Ni–2mpz	
	FT-IR	Raman	FT-IR	Raman	FT-IR	Raman
γ(CH)	–	814 sh	–	–	–	–
γ(CH)	749 m	749 vw	743 m	753 vw	746 w	755 w
δ_{ring}	636 w	637 w	657 w	680 vw	657 vw	670 vw
δ_{ring}	559 vw	559 w	554 w	576 w	571 w	577 w
γ(CC)	465 m	465 vw	449 vw	435 w	490 w	463 vw
γ_{ring}	404 vs	408 vw	–	–	417 w	–

N o t e. ν – stretching, δ – deformation, γ – out-of-plane bend, r – rocking, s – strong, m – medium, w – weak, sh – shoulder, v – very.

Ammonia vibrations. We expect ν(NH), δ(HNH), and $\rho_r(NH_3)$ vibration modes for an ammonia molecule attached to a metal atom. Asymmetric and symmetric $\nu(NH_3)$ stretching, NH_3 degenerate deformation, NH_3 symmetric deformation, $\delta(NH_3)$ bending, and NH_3 rocking vibrations in the ammonia ligand are found in the ranges 3400–3000, 1650–1550, 1370–1000, and 950–590 cm^{-1}, respectively [24].

Asymmetric and symmetrical stretching and bending vibrations of free ammonia molecules are observed at 3390 and 3328 cm^{-1} for $\nu(NH_3)$ and at 1626 and 1113 cm^{-1} for $\delta(NH_3)$, respectively. In addition, $\delta_r(NH_3)$ rocking vibrations appear at 682 and 515 cm^{-1} (Table 2). Asymmetric and symmetric stretching vibrations of the ammonia molecule in the infrared spectrum of Cu–Ni–2mpz and Zn–Ni–2mpz are found at 3359 and 3288 cm^{-1} for Cu–Ni–2mpz, and at 3372 and 3301 cm^{-1} for Zn–Ni–2mpz, respectively. The $\nu(NH_3)$ stretching vibrations in the Raman spectrum of the complexes are observed at 3296 and 3201 cm^{-1} for Cu–Ni–2mpz and at 3308 and 3201 cm^{-1} for Zn–Ni–2mpz. Asymmetric and symmetric $\nu(NH_3)$ stretching vibrations show downward shifts in frequencies compared to the free ammonia molecule. In the vibration spectra the modes of the 2mpz with the $\delta(NH_3)$ bending modes of the ammonia molecule are found to be overlapping. Besides, the $\rho_r(NH_3)$ rocking modes of the NH_3 molecule in the complexes have upward or downward shifts in frequency when compared with the free NH_3 molecule.

TABLE 2. The Vibrational Wavenumbers (cm^{-1}) of Ammonia in the Complexes

Assignment [24]	Ammonia	$[Zn(NH_3)_6]Cl_2$ [24]	$Ni(NH_3)_2Pd(CN)_4 \cdot 2C_6H_6$ [25]	Cu–Ni–2mpz		Zn–Ni–2mpz	
	FT-IR	FT-IR	FT-IR	FT-IR	Raman	FT-IR	Raman
$\nu_a(NH_3)$	3390 m	3350	3390 m	3359 m	3296 w	3372 w	3308 w
$\nu_s(NH_3)$	3328 m	3220	3305 m	3288 s	3201 vw	3301 w	3201 vw
δ_a(HNH)	1626 m	1596	1603 m	1609 m	1608 w	1620 m	1609 w
δ_s(HNH)	1113 m	1145	1160 s	1157 sh	–	–	1135 vw
$\rho_r(NH_3)$	682 m	645	604 s	625 m	–	706 vw	–
$\rho_r(NH_3)$	515 w	–	495 vw	501 w	504 vw	–	–

N o t e. Abbreviations used; s – strong, m – medium, w – weak, sh – shoulder, v – very. The symbols ν, δ, and ρ refer to valence, deformation, and rocking vibrations, respectively.

Water vibrations. Water molecules have three fundamental vibrations, asymmetric and symmetric ν(OH) stretching and δ(HOH) bending. In the infrared spectra of the free water molecule, ν(OH) stretching and ν(HOH) bending vibrations appear around 3700–3400 and 1630–1600 cm^{-1}, respectively [24]. In the infrared spectra of Zn–Ni–2mpz, asymmetric and symmetric ν(OH) stretching vibrations are also found at 3604 and 3540 cm^{-1}, respectively, but they are observed as broad bands in the range 3650–3400 cm^{-1} for Cu–Ni–2mpz. In addition, δ(HOH) bending vibrations belonging to water molecules were found to be overlapping at about 1630–1600 cm^{-1}.

Vibrations of tetracyanonickelate. The vibration bands of the tetracyanonickelate group in the obtained complexes are assigned to the vibrational data of the tetracyanonickelate ion of the $Na_2[Ni(CN)_4]$ salt in the solid form [26]. The assignments of the tetracyanonickelate anion and the vibration frequencies of the complexes obtained are given in Table 3. The tetracyanonickelate anion possesses a square planar structure and shows D_{4h} symmetry. This structure has 16 vibration modes ($2A_{1g}$, $1A_{2g}$, $2B_{1g}$, $2B_{2g}$, $1E_g$, $2A_{2u}$, $2B_{2u}$,

TABLE 3. The Wavenumbers of the $[Ni(CN)_4]^{2-}$ Vibrations in the Complexes (cm^{-1})

Assignment [26]	$K_2[Ni(CN)_4] \cdot H_2O$	Cu–Ni–2mpz	Zn–Ni–2mpz
A_{1g}, ν(CN)	(2160) vs	(2179) vs	(2182) vs
B_{1g}, ν(CN)	(2137) m	(2155) m	–
E_u, ν(CN)	2120 vs	2156 vs, 2130 s	2193 m, 2150 s
ν(^{13}CN)	2084 vw	–	2111 vw
E_u, ν(NiC)	542 w	555 w	544 w
A_{2u}, π(NiCN)	443 w	441 w	448 sh
E_u, δ(NiCN)	414 vs	421 s	430 s

N o t e. ν – valence, δ – in-plane, π – out-of-plane, s – strong, m – medium, w – weak, sh – shoulder, v – very. The vibrational frequencies in the Raman spectrum are enclosed in parentheses.

and $4E_u$) [24], and from them, A_{2u} and E_u are infrared active while A_{1g}, B_{1g}, B_{2g}, and E_g are Raman active. The A_{2g} and B_{2u} are inactive. The ν(CN) stretching frequency of the cyano group exhibits a strong and sharp peak in the 2200–2000 cm^{-1} region and can be easily determined in the infrared and Raman spectrum of the complexes. The ν(CN) stretching frequency of CN^- in aqueous solution is seen at 2080 cm^{-1}, but when cyano ligand binds to a metal, the ν(CN) shifts to higher frequencies due to the coupling of the Ni–C(CN) vibrational modes with the ν(CN) vibrations [11, 24]. The ν(CN) stretching vibration frequency of the synthesized tetracyanonickelate was observed at 2120 cm^{-1} in the infrared spectra. If the Ni–C≡N group in the cyano complexes forms a Ni–C≡N–M type bridge, due to the formation of the cyanide-bridge the ν(CN) stretching frequency shifts to a higher frequency. In the infrared spectrum of the cyano-bridged metal complexes, the ν(CN) stretching vibration frequency appears at 2156 and 2130 cm^{-1} (for Cu–Ni–2mpz) and 2193 and 2150 cm^{-1} (for Zn–Ni–2mpz). The appearance of two absorption bands shows deviation from the ideal D_{4h} geometry. According to this, the ν(CN) frequencies in the infrared spectra of Cu–Ni–2mpz and Zn–Ni–2mpz are higher about 10–73 cm^{-1} than in $K_2[Ni(CN)_4]\cdot H_2O$ salt. Such frequency shifts are explained as the mechanical coupling of the internal modes of the tetracyanonickelate anion with the M–NC vibrations [27]. These cyano stretching peaks suggest that all cyano groups in the complexes act as bridged ligands. The shifts in the ν(C≡N) stretching vibration frequencies indicate that the tetracyanonickelate anion bound to M metals from nitrogen ends form $|M–Ni(CN)_4|_\infty$ type polymeric layers. Furthermore, these shifts are observed in Hofmann type complexes [28, 29]. In the resulting complexes, the A_{1g} and B_{1g} cyano stretching modes are observed at 2179 and 2155 cm^{-1} for Cu–Ni–2mpz) and at 2182 cm^{-1} for Zn–Ni–2mpz. These data show

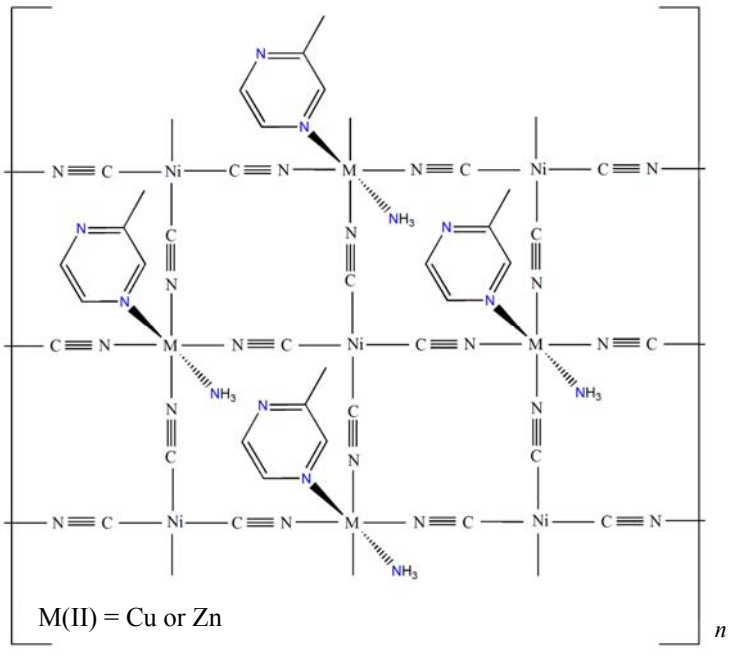

Fig. 2. Representation of molecular structures of the complexes.
The water molecule is not shown in the complexes.

that the A_{1g} and B_{1g} modes are observed at higher frequencies at around 18–22 cm^{-1} in the cyano-bridged metal complexes. In addition to the ν(CN) band, ν(NiC), π(NiCN), and δ(NiCN) bands appear in the low-frequency region in the infrared spectra of the complexes. These bands appear in the region 560–420 cm^{-1} in the infrared spectra of the complexes. In particular, in-plane bending vibration frequencies [δ(NiCN)] shift to a higher frequency by supporting the ν(CN) stretching vibration frequencies.

As a result, 2mpz and ammonia molecules act as a monodentate ligand, while the cyano ligand acts as a bridging ligand between metal (M) and Ni(II) atoms. In this case the structures of the complexes are as shown in Fig. 2.

Conclusions. We have prepared and reported two new cyano bridged hetero-metallic polymeric complexes with the chemical formula $[M(NH_3)(2mpz)Ni(CN)_4] \cdot nH_2O$ [2mpz = 2-methylpyrazine, M(II) = Cu or Zn, n = 1 or 2]. The M(II) atom is octahedrally surrounded by the ring nitrogen of the 2mpz molecule, the nitrogen of the ammonia molecule, and the four nitrogens of the cyano groups, while the nickel atom is square-planarly linked by the carbon atom of the four cyano groups. Infrared and Raman spectral analyses show that the complexes are similar and the 2mpz and ammonia molecules are coordinated to the metal atom (M) as a monodentate ligand. According to this, the structure of Cu–Ni–2mpz and Zn–Ni–2mpz consists of polymeric layers of $|M–Ni(CN)_4|_\infty$ with the ligands (2mpz and ammonia) bound to the metal atom (M).

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