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ORIGINAL ARTICLE

Vibrational spectroscopic studies of some dimethylpyrazine cadmium (II) tetracyanonickelate benzene clathrates: $[Cd(C_6H_8N_2)Ni(CN)_4]\cdot C_6H_6$

Güneş Süheyla Kürkçüoğlu

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Abstract Two new cadmium dimethylpyrazine (2,3-dimethylpyrazine or 2,5-dimethylpyrazine) tetracyanonickelate benzene clathrates, $[Cd(C_6H_8N_2)Ni(CN)_4]\cdot C_6H_6$, have been prepared in powder form and characterized by FT-IR spectroscopy, Raman spectroscopy, X-ray diffraction, thermal analyses and elemental analyses. Vibrational assignments are proposed for the bands of the host lattice and guest molecule. It is shown that the spectra are consistent with a proposed crystal structure for these compounds derived from X-ray diffraction measurements. The C, H, N, Cd and Ni analyses were carried out for all the compounds. Thermal behaviors of these compounds are followed using TG and DTA techniques. The FT-IR, Raman spectroscopic, XRD, thermal and elemental analyses results propose that these compounds are similar in structure to the Hofmann-type clathrates. Their structure consists of planar polymeric layers, $\{M–Ni(CN)_4\}_\infty$, formed from $Ni(CN)_4$ anions coordinated to the bridging 2,3- or 2,5-dimethylpyrazine molecules bound directly to the cadmium. The cadmium atoms are bound to four N atoms of the CN ions and, the Ni atoms are surrounded by four C atoms of the CN groups in a square-planar layer.

Keywords 2, 3-dimethylpyrazine · 2, 5-dimethylpyrazine · Benzene · Inclusion compounds · Tetracyanonickelate · FT-IR and Raman spectra

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Introduction

The crystal structures of 2,3-dimethylpyrazine (2,3-dmpz) and 2,5-dimethylpyrazine (2,5-dmpz) were studied by X-ray diffraction [1]. Only a few articles were found in the literature that dealt with the determination and calculation of their geometric parameters and vibrational frequencies [2, 3]. In our previous work [4], we reported that the infrared, Raman spectra, thermal property and crystal structure results of cyano-bridged heteronuclear polymeric complex with a 2-methypyrazine ligand, $[Cd(H_2O)(2mpz)Ni(CN)_4]_n$. Several polynuclear $Ni(CN)_4^{2-}$complexes have been reported [4–18], however, to the best our knowledge, neither crystallographic, nor spectroscopic data have been so far that would explicitly tell the structural analyses of the 2,3-dmpz and 2,5-dmpz tetracyanonickelate metal(II) complexes and clathrates.

In various studies, the host–guest compounds named Hofmann-type clathrates, given by the formula $[ML_2Ni(CN)_4]\cdot nG$, were produced. Here M is a transition metal atom, L is a ligand molecule or half of a bidentate ligand molecule, and G is a guest molecule. In these structures, the guest molecules are enclosed in a cavity formed by the host lattice [19]. The clathrates are of interest because of their inclusion behaviors and use as catalysts, anti-oxidants and stabilizing agents [20]. Based on this structure, metal(II) tetracyanonickelate complexes have been developed using mono-, bi-, three- and tetradentate ligands such as ammonia [11, 21–23], ethylenediamine [24, 25], piperazine [26, 27], pyridine [28], diethylenetriamine [29], triethylenetetramine [14, 15], pyrazine [17, 18]. In the present study, we report the syntheses, spectral (FT-IR and Raman), X-ray diffraction, thermal and elemental analyses of these compounds. The complexing ability of 2,3-dmpz and 2,5-dmpz with cadmium ion is of great interest, since 2,3-dmpz and 2,5-dmpz can coordinate

through the pyrazine ring nitrogens and two methyl groups. The thermal decomposition behaviors of the clathrates were followed up to 600 °C in static air atmosphere.

Experimental

Materials and instrumental

Cd(II) chloride, Ni(II) chloride, potassium cyanide (KCN), 2,3-dimethylpyrazine, 2,5-dimethylpyrazine and benzene were purchased from commercial sources and used without further purification. Elemental analyses for C, H, N (LECO CHNS-932 analyzer) and metal content (Perkin Elmer Analyst 800 Model AAS) were carried out at the TÜBİTAK Ankara Test and Analysis Laboratory. The FT-IR spectra of the compounds were recorded using ATR attachment in the range 4000–250 cm^{-1} on a Perkin Elmer 100 FT-IR spectrometer which was calibrated using polystyrene and CO_2 bands. The Raman spectra of the powdered samples were recorded in the range 4000–250 cm^{-1} and were excited using the 488.0 nm line of an Ar + laser, recorded on a Cary 81 spectrometer with resolution of 3.2 cm^{-1}, with the use of a spinning cell. The XRD patterns of the powder products were obtained on a Rigaku Rint 2200 diffractometer using Cu-Kα radiation. The samples were loaded in a 0.3 mm glass capillary, which were rotated during the data collection. Perkin Elmer Diamond TG/DTA thermal analyzer was used to record simultaneous TG, DTG and DTA curves in the static air atmosphere at a heating rate of 10 $Kmin^{-1}$ in the temperature range 18–600 °C using platinum crucibles.

Synthesis

$[Cd(C_6H_8N_2)Ni(CN)_4]\cdot C_6H_6$ ($C_6H_8N_2$ = 2,3-dmpz or 2,5-dmpz) compounds were prepared by adding slightly in excess of 2 mmol of 2,3- or 2,5-dimethylpyrazine dissolved in benzene, and this solution, together with an aqueous solution of 1 mmol of $[K_2Ni(CN)_4]\cdot H_2O$, were added to an aqueous solution of the cadmium (II) chloride, with constant stirring. The precipitate was filtered and washed with water and acetone, successively, and kept in a desiccator containing molecular sieves and saturated benzene vapour. The freshly prepared compounds were analyzed for C, H, N, Cd and Ni and the following results (found %/calculated %) were obtained: $[Cd(C_6H_8N_2)Ni(CN)_4]\cdot C_6H_6$ ($C_6H_8N_2$ = 2,3-dmpz); C = 36.74/36.96, H = 2.266/2.624; N = 19.65/19.89; Cd = 26.32/26.612; Ni = 13.49/13.899. $[Cd(C_6H_8N_2)Ni(CN)_4]\cdot C_6H_6$ ($C_6H_8N_2$ = 2,5-dmpz), C = 40.95/41.65, H = 3,51/3.06, N = 18.41/18.21; Cd = 24.74/24.36; Ni = 12.938/12.72. These analytical results are poor for the samples obtainable in powder form because of partial decomposition. Such instabilities have been reported for clathrates having low boiling guest molecules [9].

Results and discussion

The FT-IR (a) and Raman spectra (b) of the $[Cd(C_6H_8N_2)Ni(CN)_4]\cdot C_6H_6$ ($C_6H_8N_2$ = 2,3-dmpz or 2,5-dmpz) benzene clathrates are given in Figs. 1 and 2, respectively. The spectra of the clathrates are very similar to each other, suggesting that they have similar structural features. The assignments were divided into three groups arising from the $Ni(CN)_4$ units, from the dimethylpyrazine ligands and from the benzene moieties. The vibrational wavenumbers of the bands in the spectra of these species are tabulated in Tables 1, 2, 3, together with some relevant spectral data for comparison.

The XRD patterns of benzene enclathrated the 2,3-dmpz and 2,5-dmpz tetracyanonickelate cadmium(II) compounds were recorded. These patterns suggest that benzene molecules enclathrated into the interlayers of compounds. The XRD pattern of benzene enclathrated Cd-Ni-2,3dmpz is given in Fig. 3. The powder diffraction data have suggested that the dimethylpyrazine molecules in these compounds bridge cadmium and nickel atoms, as a result of which a polymeric three-dimensional network is formed. There is no direct chemical bond between the guest molecules and the host lattice [30].

Vibrations of ligands

In 2,3-dmpz, the geometry belongs to C_{2v} point group, each methyl groups has a hydrogen atom in the aromatic plane in a *cis* conformation with respect to the closest nitrogen atom [31]. In 2,5-dmpz, the geometry belongs to C_{2h} point group given that the hydrogen atom of each methyl group lying in the aromatic plane shows a *trans* conformation with respect to the closest nitrogen atom [32]. The assignments and the wavenumbers of the vibrational bands of 2,3-dmpz or 2,5-dmpz observed in the spectra of the compounds studied are listed in Table 1, together with the wavenumbers of 2,3-dmpz and 2,5-dmpz in liquid [31, 32] on which the assignments are based. In order to determine the coordination mode of 2,3-dmpz and 2,5-dmpz in clathrates, the wavenumbers of ligands in clathrates are compared with those of free ligands. All of the vibrational modes of the ligands are observed in the infrared and Raman spectra of the compounds studied. A glance at Table 1 shows that the vibrational wavenumbers of the ligand modes of the host complexes exhibit coordination properties, namely, several modes of the ligand molecule have upward shifts in frequency when compared with the free molecule and the shifts are metal dependent.

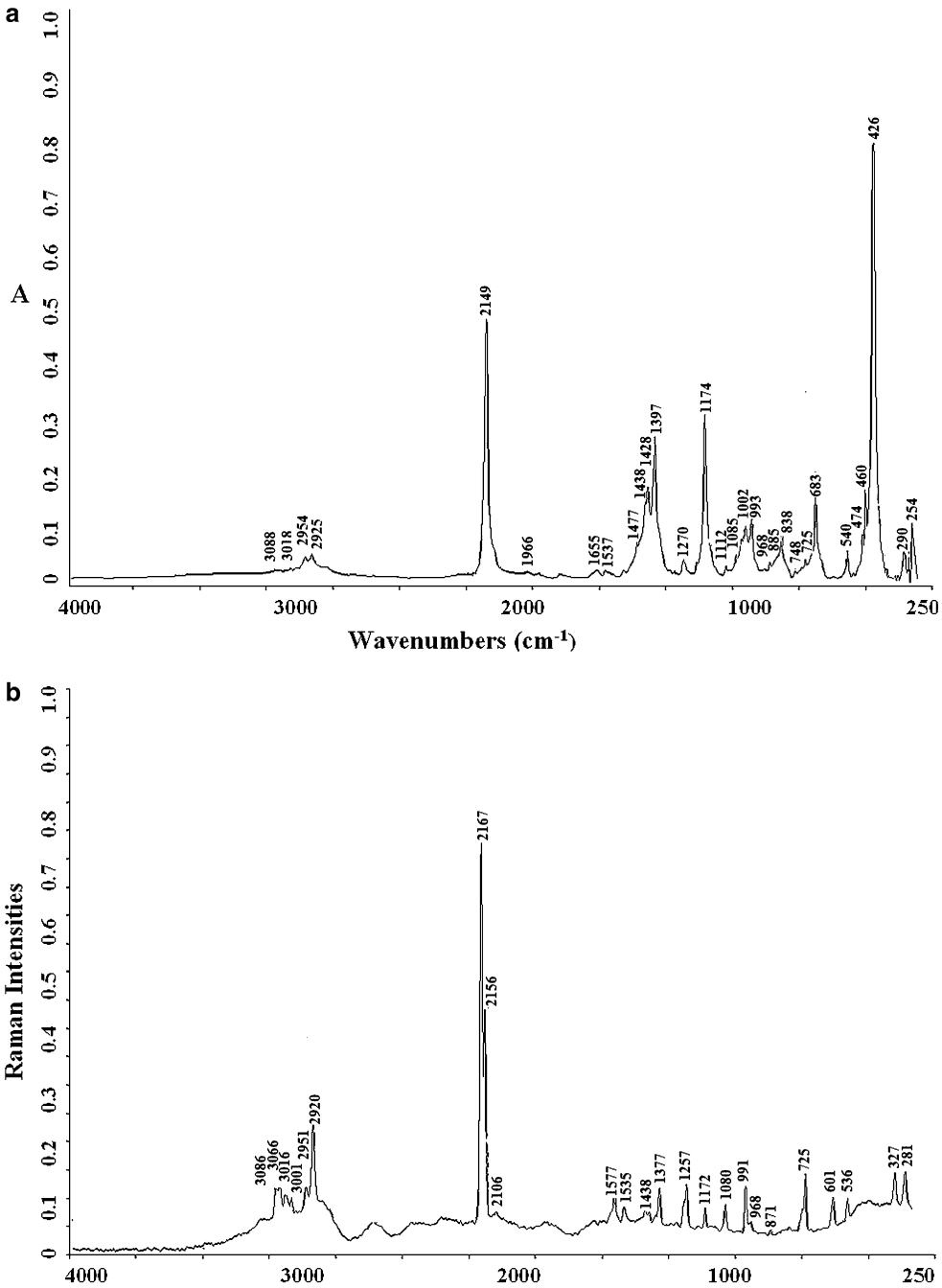


Fig. 1 FT-IR (**a**) and Raman (**b**) spectra of Cd-Ni-2,3-dmpz-Bz

Analogous shifts on coordination were observed in pyridine [13], 4,4′-bipridyl [33] and pyrazine [17, 18] complexes and explained as the coupling of the internal modes of the aromatic molecule with the M–N vibrations [33–35]. The C–H stretching bands of 2,3-dmpz were observed in the 3048–2900 cm^{-1} region. It has been shown that the methyl substitution of the hydrogen atom in any aromatic ring affects to the vibrational frequencies of several normal modes. The wavenumbers of some fundamentals in methyl derivatives appear at lower frequencies than those corresponding to the unsubstituted molecule [31, 32]. In the FT-IR and Raman spectra of clathrates, the observed bands at about 3075 and 2970 cm^{-1} can be assigned to C–H stretching modes. The C–H in-plane bending vibrational modes of the 2,3-dmpz and 2,5-dmpz can be observed in the 1600-1000 cm^{-1} region of the spectrum, 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 methylpyrazines in the 1500–1000 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

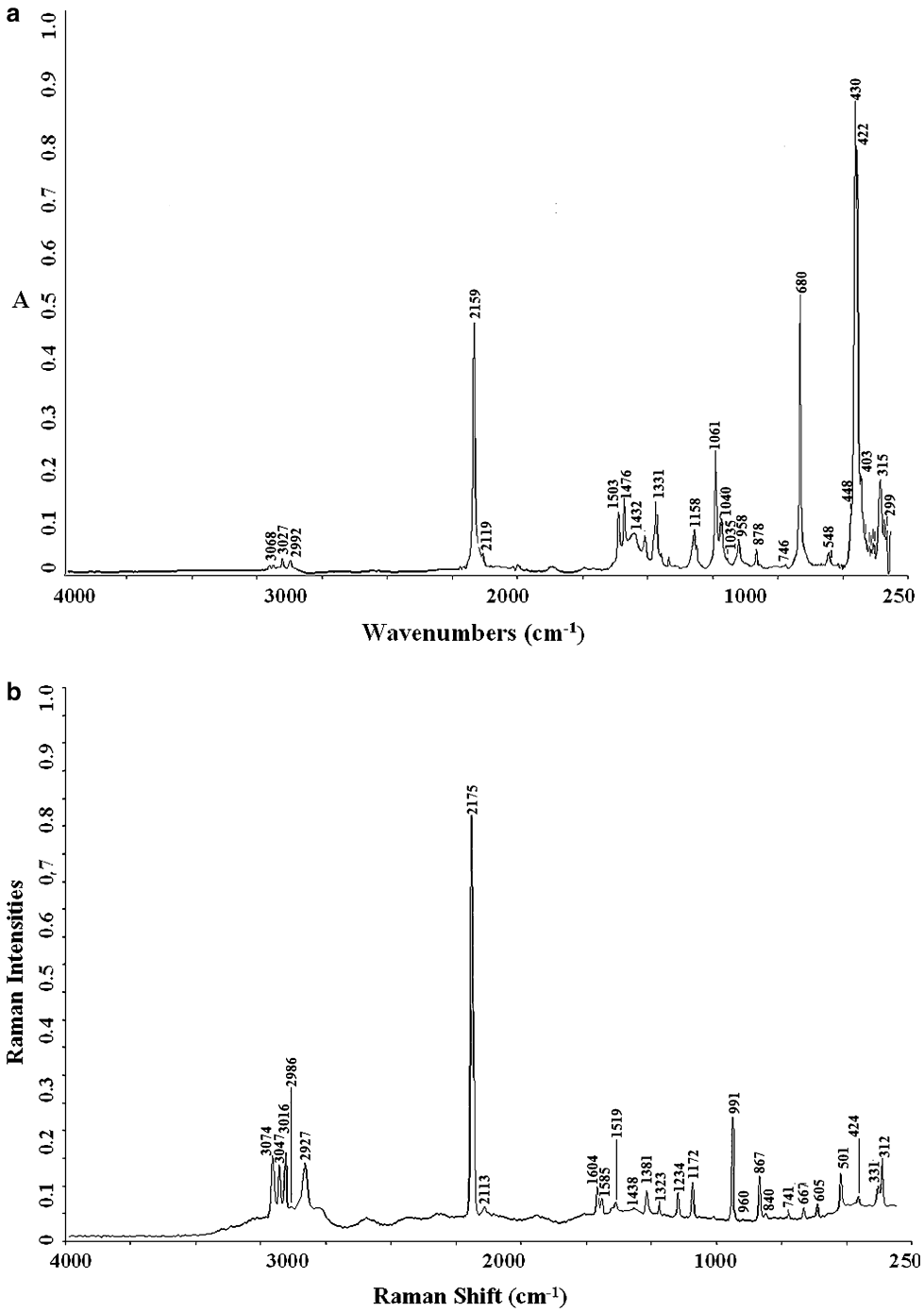


Fig. 2 FT-IR (**a**) and Raman (**b**) spectra of Cd-Ni-2,5-dmpz-Bz

coupling with M–N (ligand) bond vibrations [17, 18] and due to alterations of the ring force field [35].

Vibrations of polymeric sheet

The vibrational wavenumbers of the $Ni(CN)_4$ group vibrations of the $[Cd(C_6H_8N_2)Ni(CN)_4]\cdot C_6H_6$ ($C_6H_8N_2$ = 2,3-dmpz or 2,5-dmpz) clathrates are given in Table 2. In order to assign the bands attributable to the $Ni(CN)_4$ ion in the spectra, we refer to the work of McCullough et al. who presented vibrational data for the salt $Na_2Ni(CN)_4$ in the solid state [36]. In this salt $Ni(CN)_4$ 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 $Ni(CN)_4$ units of the complexes appear to be much higher than those for isolated $Ni(CN)_4$ ion. Such frequency shifts have been

Table 1 The vibrational wavenumbers (cm^{-1}) of ligands in Cd-Ni-L-Bz (L = 2,3-dmpz or 2,5-dmpz) clathrates

Assignments[a]	2,3-Dimethylpyrazine			2,5-Dimethylpyrazine			Cd-Ni-2,3 dmpz-Bz		Cd-Ni-2,5 dmpz-Bz	
	IR	Raman	Calc.[31]	IR	Raman	Calc.[31]	IR	Raman	IR	Raman
ν (CH)	3048 m	3047	3051	3081 m	3030	3031	3088 w	3088 w	3068 w	3074 m
ν (CH)	–	–	3028	3025 sh	–	3028	–	3066 w	–	3047 m
$\nu_{as}(CH_3)$	–	–	3014	3004 s	–	2989	3018w	3016 sh	3027 w	3016 m
ν (CH_3)	2993 m	2992	3013	–	2980	2989	–	3001 w	2992 w	2986 sh
ν (CH_3)	–	–	2958	2962 sh	–	2975	–	–	–	–
ν (CH_3)	2950 m	2950	2956	–	2960	2975	2954 m	2951 w	2954 m	–
$\nu_s(CH_3)$	2924 m	2920	2917	–	2921	2925	2925 m	2920 m	2924 s	2927 m
ν (CH_3)	–	–	2914	2926 s	–	2925	2910 sh	–	–	–
$\nu_{ring} + \delta$(CH)	1570 sh	1568	1572	–	1583	1584	1655 m	1577 m	–	1585 w
ν_{ring}	1538 s	1536	1552	–	1526	1539	1619 w	–	1503 m	1519 w
δ(CH) + ν_{ring}	1463 sh	1460	1461	1489 vs	–	1486	1477 m	–	1476 m	–
$\delta_{as}(CH_3)$	–	–	1454	1452 s	–	1449	–	–	–	–
$\delta_{as}(CH_3)$	1442 s	1444	1444	–	–	1441	1438 m	1438 w	–	1436 vw
$\delta_{as}(CH_3)$	1426 s	1426	1441	–	–	1441	1428 m	–	1432 m	–
$\delta_{as}(CH_3)$	–	–	1423	–	1442	1438	–	–	–	–
ν_{ring}	1401 s	1402	1395	1327 vs	–	1330	–	–	1405 s	–
$\delta_{as}(CH_3)$	1373 s	1373	1379	1380 s	–	1380	1397 s	1377 m	1397 s	1381 w
$\delta_{as}(CH_3)$	–	–	1370	–	1379	1380	1369 sh	–	1368 sh	–
δ(CH)	1267 w	1266	1263	1258 w	1304	1315	1270 w	1257 m	–	–
ν_{ring}	1167 vs	1169	1182	1166 s	–	1157	1174 s	1172 m	1171 sh	1172 m
δ_{ing}	–	–	1159	–	–	–	1145 w	–	1158 w	–
ν_{ring}	1080 w	1080	1071	1258 w	–	1250	1085 w	1080 m	1061 s	1080 vw
r(CH_3)	–	–	1061	–	–	1056	–	–	1040 w	1042 vw
r(CH_3)	1015 m	1016	1024	–	1020	1017	1013 m	–	1035 vw	–
r(CH_3) + ν_{ring}	987 s	986	977	–	1020	1017	991 m	991 m	958 w	991 s
ν_{ring}	968 s	968	971	961 m	–	965	967 m	–	–	960 w
δ_{ring}	882 m	881	871	–	–	–	885 m	871 vw	–	–
γCH	846 s	846	842	880 m	–	892	838 m	–	–	867 m
τ_{ring}	–	756	761	–	750	745	742 sh	–	746 sh	741 w
ν (CX)	539 m	540	534	–	499	486	540 w	–	550 w	–
τ_{ring}	443 s	444	460	410 s	–	417	460 sh	–	–	–
δ(CX)	424 s	425	415	–	397	400	–	–	422 s	424 w
(CC	–	281	284	–	391	381	290 m	327 m	315 m	331 w
(CC + γrg	–	246	270	–	329	320	254 m	281 m	286 m	312 m

*Abbreviations used: ν stretching, δ deformation, *w* wagging, *t* twisting, *r* rocking, *s* strong, *m* medium, *w* weak, *sh* shoulder, *v* very

observed for Hofmann-type host frameworks [4–12, 18, 32, 33] and are attributed to the mechanical coupling of the internal modes of $Ni(CN)_4$ groups are bound to a M atom in the complexes investigated. It is known that cyanide stretching modes shift to higher wavenumber in the case of the compounds that the $[Cd–Ni(CN)_4]_n$ polymeric layers, due to the mechanical coupling with M-NC modes, mostly ν(Cd-N) [32] the higher its frequency and the higher become the ν(CN) frequencies. The ν(CN) and δ(CN) vibrational wavenumbers are found to be similar to those of Hofmann-type clathrates [11], and the pyridine complexes, showing that the $[M\text{-}Ni(CN)_4]_n$ layers have been preserved. The presence of just one IR active (E_u) and two Raman active (A_{1g} and B_{1g}) CN stretching vibrations normally confirms the square planar environment around the $Ni(CN)_4$ ion [32].

Vibrational bands of the guest (benzene) molecules

The assignments and the wavenumbers of the vibrational bands arising from the enclathrated benzene observed in the spectra of the compounds are given in Table 3, along

Table 2 The wavenumbers (cm^{-1}) of the $Ni(CN)_4$ vibrations of the Cd-Ni-L-Bz (L = 2,3-dmpz or 2,5- dmpz) clathrates

Assignments[a]	$Na_2Ni(CN)_4$ [35]	Cd-Ni-Pyz [18]	Cd-Ni-2,3-dmpz		Cd-Ni-2,5- dmpz	
			IR	Raman	IR	Raman
A_1g, ν(CN)	2149	(2158)vs	2149 s	2167 vs	2159 s	2175 vs
B_1g, ν(CN)	2141	(2143)vs	–	2156 s, sh	–	–
E_u, ν(CN)	2132	2133vs	2127 vw	–	–	–
	2128	–	2112 w	2106 vw	2119 vw	2113 vw
E_u, ν(NiC)	543	544w	540 w	–	549 vw	–
A_{2u}, π(NiCN)	448	–	460 w	443w	449 sh	–
E_u, δ(NiCN)	433	–	–	–	432 s	–
	421	423 vs	426 s	–	423 m	

s strong, *m* medium, *w* weak, *sh* shoulder, *br* broad, *v* very. The symbols ν, δ and π refer to valence, in-plane and out-of-plane vibrations, respectively

Table 3 The vibrational wavenumbers (cm^{-1}) of benzene in the Cd-Ni-L-Bz Clathrates (L = 2,3-dmpz or 2,5-dmpz))

Assignments[a]	Liquid Bz [36]	Cd-Cd-Pyz-bz [17]	Cd-Ni-2,3dmpz-Bz		Cd-Ni-2,5dmpz-Bz	
			IR	Raman	IR	Raman
$2\nu_8$	(3166)	(3163 m)	–	–	–	–
$\nu_8 + \nu_{19}$	3075	3088 s	3088 w	–	3087 w	–
ν_{20}, E_{1u}	3073	–	3070 vw	3071 m	3071 w	–
ν_2 A_1g	(3062)	(3062 m)	–	–	–	–
ν_{13}, B_{1u}	3048	3068 m	–	–	–	3046 m
ν_7, E_2g	(3050)	(3053sh)	–	–	–	3016 m
$\nu_5 + \nu_{17}$, E_{1u}	1955	1951 w	–	–	–	–
ν_8, E_2g	(1586)	(1586 m)	–	–	–	–
ν_{19}, E_{1u}	1479	1479 w	1478 m	1439w	1476 s	–
ν_{14}, B_{2u}	1309	–	1309 vw	1301vw	–	1323w
ν_9, E_{2g}	(1177)	(1179 m)	1175 s	1172 m	1165 w,sh	1173 m
ν_{15}, B_{2u}	1149	1147 sh	1145w	–	1158 w	–
ν_{18}, E_{1u}	1036	1035 m	1037w	1080 m	1035 w	–
ν_1, A_{1g}	(991)	(991 vs)	993w	991 s	–	–
ν_{10}, E_{1g}	(850)	(885 vw)	886w	871 vw	–	867 m
ν_{11}, A_{2u}	670	685 vs	683vs	–	680 vs	667 s
ν_6, E_{2g}	607	–	–	601 w	–	605 s

*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

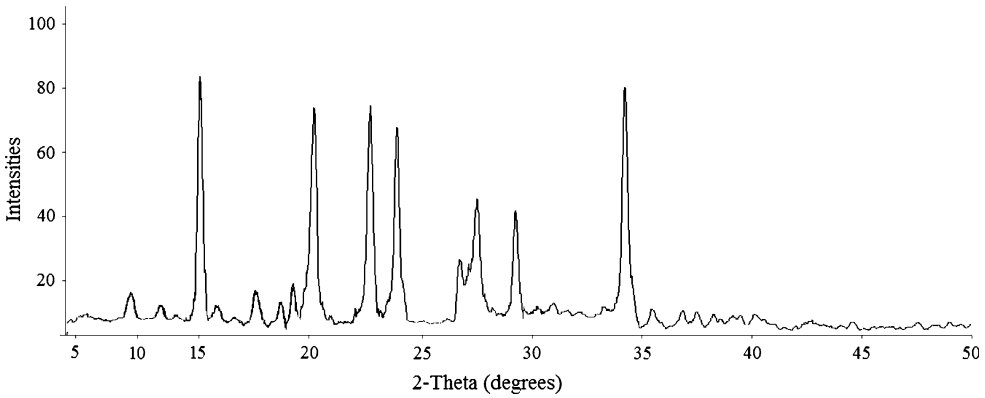


Fig. 3 X-Ray powder diffraction (XRD) pattern of Cd-Ni-2,3-dmpz-Bz

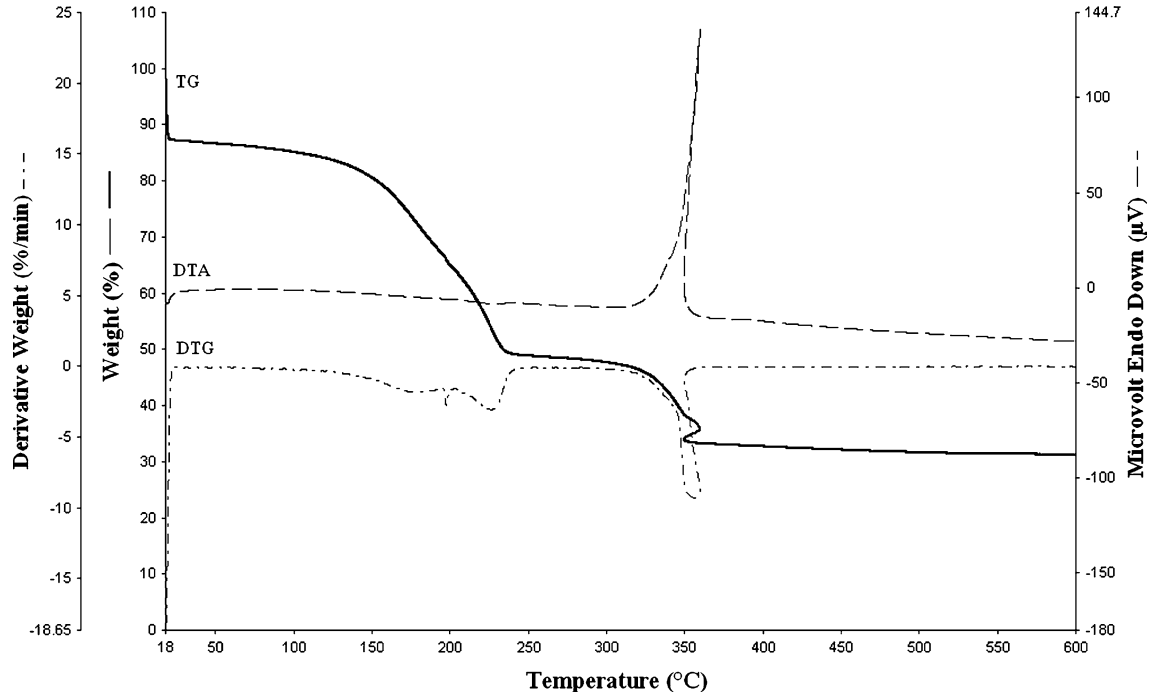


Fig. 4 The TG, DTG and DTA curves of the Cd-Ni-2,3-dmpz-Bz

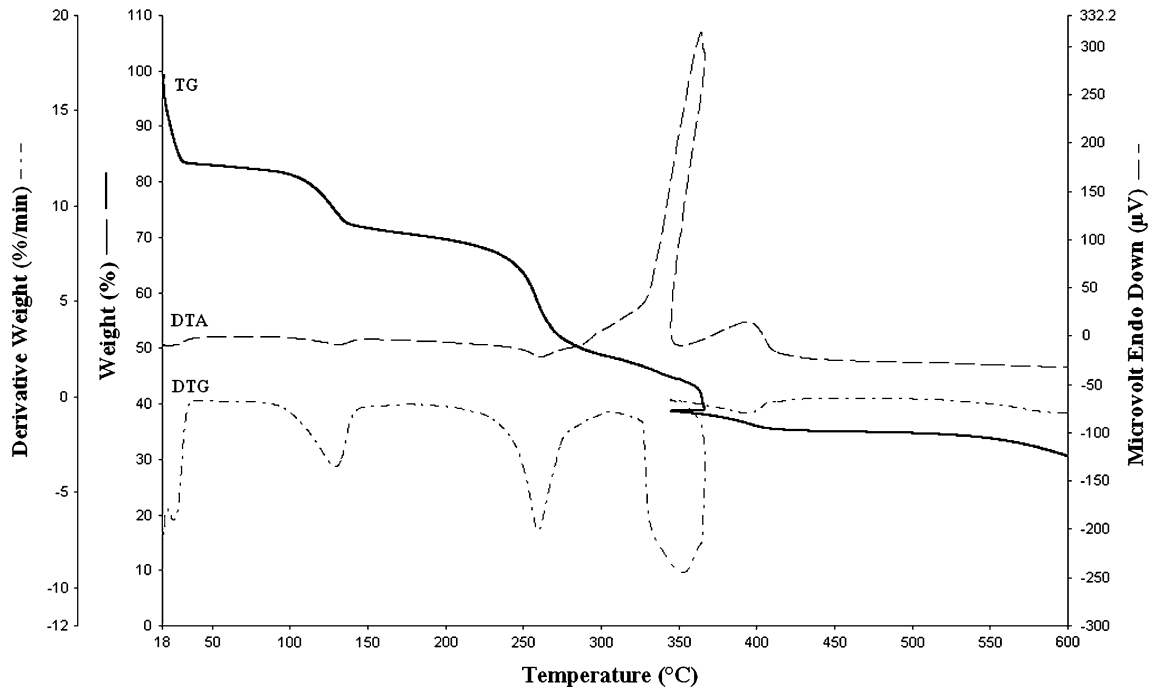


Fig. 5 The TG, DTG and DTA curves of the Cd-Ni-2,5-dmpz-Bz

with the wavenumbers of benzene in the liquid phase [37] and in the Cd-pyz-Cd-Bz [17] clathrate for comparison. The most structurally informative spectral features are the following. The CH out-of-plane mode (A_{2u}) in the spectra of the clathrates is found to be shifted to higher frequency from that of liquid benzene. Similar shifts were observed for Hofmann-type [18, 32] and Td-type clathrates [11, 13, 17] and explained by the presence of a weak hydrogen bond between the π electrons located above and below the benzene ring and the ligand molecules of the host lattices.

Table 4 Thermoanalytical data (TG, DTG, DTA) for the Cd-Ni-L-Bz (L = 2,3-dmpz or 2,5-dmpz) clathrates

Compounds	Stage	Temperature Range (°C)	DTG_{max} (°C)	Removed group	Mass loan in %		Mass loan in %		Solid decomp.product
					Calcd.	Found	Calcd.	Found	
$[Cd(2,3dmpz)Ni(CN)_4]\cdot 0{,}5C_6H_6$	1	18–24	19(+)	C_6H_6	9.24	9.82	40.47	37.55	$[Cd(2,3dmpz)Ni(CN)_4]$
	2	24–249	226(+)	$C_6H_8N_2$	25.60	24.81			$[CdNi(CN)_4]$
	3	249–364	355(-)	4(CN)	24.78	24.82			Cd + Ni
$[Cd(2.5dmpz)Ni(CN)_4]\cdot C_6H_6$	1	18–45	24(+)	C_6H_6	16.93	16.94	36.75	37.08	$[Cd(2,5dmpz)Ni(CN)_4]$
	2	45–258	131(+)	$C_6H_8N_2$	23.43	24.02			$[CdNi(CN)_4]$
	3	258–394	257(-)	4(CN)	22.69	22.29			Cd + Ni

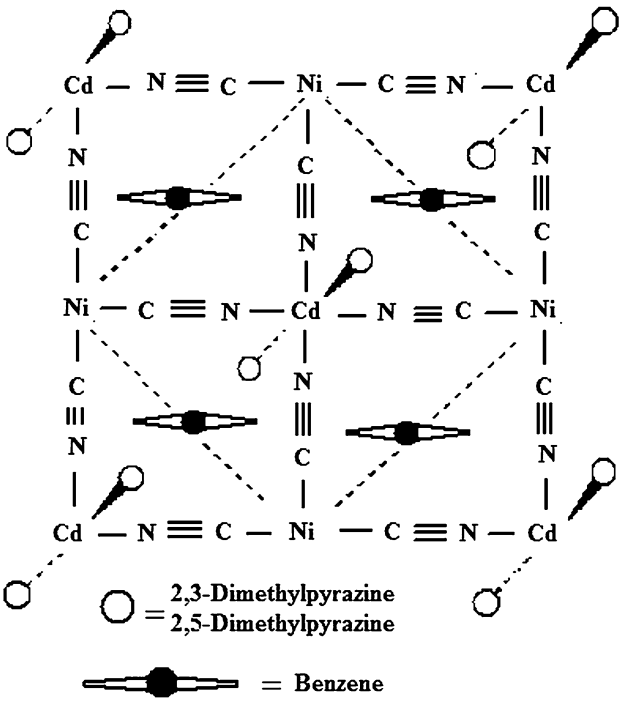
*(+): Endothermic, (−): Exothermic

Therefore, we may reasonably suggest that the frequency shifts in our compounds are due to the π electron donation from the benzene ring to the hydrogen atoms of the ligand molecules which have a more electrophilic character caused by the coordination. Based on the present spectral data it is not possible to determine the orientation of the benzene molecules in the host lattice in our compounds. As in the Hofmann-type benzene and Hofmann-Td-type benzene clathrates, the relative orientation of the H atoms of the ligand with respect to the axis of the π cloud of benzene must be the one most favorable for the hydrogen bonding [38]. The preceding discussion considered as a whole leads us the conclusion that the host lattice of these clathrates are similar to those of other Hofmann-type clathrates.

The results of the spectroscopic study show that dimethylpyrazine molecules behaves as a bidentate ligand and coordination proceeds via the nitrogen atom to the atoms of Cd(II) in the compounds. Thus, it has been established that the structure of the clathrates consists of planar polymer monolayers formed by the $Ni(CN)_4$ ions bridged by the Cd-$dmpz^{2+}$ cations. In each layer, the Ni atoms are surrounded by four carbon atoms of cyanide anions in the planar square environment. The metal atoms have six bonds each: with four nitrogen atoms of the bidentate CN^- ligands in the plane and with one donor atoms of nitrogen of the ligand molecules above and below this plane. The guest benzene molecules are enclosed in a cavity formed by the host lattice.

Thermal analyses

The thermal decomposition behaviors of the clathrates were followed up to 600 °C in static air atmosphere. The thermal analysis curves of the studied compounds are similar to each other. TG, DTG and DTA curves of the clathrates are shown in Figs. 4 and 5. Thermal analysis was applied to determine the stability of the compounds and temperature ranges of liberation of ligands and included molecules [39–43]. Formation of new complexes of ethylenediamine, di and triethanolamine was also reported [39–42]. The thermal analysis results for clathrates studied are presented in Table 4. The first decomposition stage about 18–24 °C for Cd-Ni-2,3-dmpz-Bz indicates that only ½ guest benzene molecule and about 18–45 °C for Cd-Ni-2,5-dmpz-Bz indicates that only one guest benzene molecule leaves Cd-Ni-dmpz host structures. In the second decomposition stage; by heating, all of the clathrates gradually lose ligand molecules. The endothermic peaks in the temperature range of 24–249 °C for Cd-Ni-2,3-dmpz-Bz and 45–258 °C for Cd-Ni-2,5-dmpz-Bz correspond to the loss of the ligand molecules. The following stage related to exothermic removal of CN groups in the 249–364 °C (Cd-Ni-2,3-dmpz-Bz) and 258–394 °C (Cd-Ni-2,5-dmpz-Bz) temperature range. The final decomposition



Scheme 1 The model for the Hofmann-type clathrate

products, Cd + Ni, were identified by FT-IR spectroscopy. The results manifest the formation of clathrating (Scheme 1).

Conclusion

In this study, two new cadmium dimethylpyrazine (2,3-dimethylpyrazine or 2,5-dimethylpyrazine) tetracyanonickelate benzene clathrates were synthesized and investigated by vibrational (FT-IR and Raman) spectroscopy, X-ray diffraction, thermal and elemental analyses. On the basis of the spectroscopic results I propose that their structure consists of planar polymeric layers, $\{Cd–Ni(CN)_4\}_\infty$, formed from $Ni(CN)_4$ anions coordinated to the bridging 2,3- or 2,5-dimethylpyrazine molecules bound directly to the cadmium. The cadmium atoms are bound to four N atoms of the CN ions and, the Ni atoms are surrounded by four C atoms of the CN groups in a square-planar layer. The analysis of the powder X-ray spectra of the clathrates also supports the spectroscopic conclusion. However, a single crystal analysis is required to provide a certain structure.

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References

1. Thalladi, V.R., Gehrke, A., Boese, R.: C–H group acidity and the nature of C–H···N interactions: crystal structural analysis of pyrazine and methyl substituted pyrazines. New J. Chem. **24**, 463–470 (2000)
2. Arenas, F., Lopez-Navarrete, J.T., Marcos, J.I., Otero, J.C.: Vibrational spectrum and internal rotation in 2,3-dimethylpyrazine. J. Mol. Struct. **192**, 107–115 (1989)
3. Arenas, F., Lopez-Navarrete, J.T., Marcos, J.I., Otero, J.C.: Vibrational spectrum and internal rotation in 2,5-dimethylpyrazine. J. Mol. Struct. **162**, 263–272 (1987)
4. Kürkçüoğlu, G.S., Yesilel, O.Z., Kavlak, İ., Büyükgüngör, O.: Syntheses, spectral and thermal analyses of heteronuclear aqua (2-methylpyrazine)metal(II) complexes with tetracyanonickelate ion and crystal structure of $[Cd(H_2O)(2mpz)Ni(\mu–CN_4)]_n$ complex. Struct. Chem. **19**, 879–888 (2008)
5. Kantarcı, Z., Bayrak, C.: Infrared spectroscopic and gravimetric studies on the dicyclopentylaminemetal(II) tetracyanonickellate(II) host-aromatic guest systems. J. Incl. Phenom. **45**, 59–67 (2003)
6. Kantarcı, Z., Gümüş, Z., Özışık, H.: Vibrational spectroscopic studies on the dicycloheptylaminecobalt(II) tetracyanonickellate(II) host-aromatic guest systems. J. Incl. Phenom. **53**, 219–229 (2005)
7. Mathey, Y., Mazieres, C.: Les phases cyanures de nickel(II) hydratés. Can. J. Chem. **52**, 3637–3644 (1974)
8. Kantarcı, Z., Bülbül, M.: Infrared spectroscopic and gravimetric studies on the dicyclohexylaminemetal(II) tetracyanonickellate(II) host-aromatic guest systems. J. Incl. Phenom. **40**, 105–116 (2001)
9. Akyüz, S., Dempster, A.B., Morehouse, R.L.: Host–guest interactions and stability of Hofmann-type benzene and aniline clathrates studied by i.r. spectroscopy. Spectrochim. Acta **30A**, 1989–2004 (1974)
10. Bayarı, S., Kantarcı, Z., Akyüz, S.: An infrared spectroscopic study on Hofmann-type complexes of dimethyl sulfoxide. J. Mol. Struct. **351**, 19–24 (1995)
11. Kasap, E., Kantarcı, Z.: Vibrational spectroscopic studies on the en-Td-type benzene clathrates: M(ethylenediamine)M′(CN)4·$2C_6H_6$ (M = Mn or Cd, M′ = Cd or Hg). J. Incl. Phenom. **23**, 1–9 (1995)
12. Bayarı, S., Bayrak, C., Kantarcı, Z.: Vibrational spectroscopic studies on the Td-type adeninemetal(II)tetracyanometallate(II) benzene clathrates: M(ad)(2)M'$(CN)_4$·C_6H_6 (M = Mn or Cd, M′ = Cd or Hg). J. Incl. Phenom. **38**, 23–35 (2000)
13. Bayarı, S., Kantarcı, Z., Akyüz, S.: An infrared and Raman spectroscopic study of Td-type 4,4′-bipyridylcadmium(II) tetracyanometallate (II) benzene (1/2) clathrates: $Cd(C_{10}H_8N_2)Cd(CN)_4$·$2C_6H_6$ and $Cd(C_{10}H_8N_2)Hg(CN)_4$·$2C_6H_6$. J. Incl. Phenom. **17**, 291–302 (1994)
14. Kürkçüoğlu, G.S., Hökelek, T., Yeşilel, O.Z.: Synthesis, IR spectrum, thermal property and crystal structure of cyano-bridged heteronuclear polymeric complex, $[Cd(teta)Ni(\mu\text{-}CN)_2(CN)_2]$·$2H_2O$. Struct. Chem. **19**, 493–499 (2008)
15. Kürkçüoğlu, G.S., Yesilel, O.Z., Kavlak, İ., Büyükgüngör, O.: Synthesis, IR spectrum, thermal analysis and crystal structure of cyano-bridged heteronuclear polymeric complex: $[Zn(teta)Ni(\mu\text{-}CN)_2(CN)_2]_n$. Zeitsc. für anorg. und allg. Chem. **635**, 175–178 (2009)
16. Kantarcı, Z., Davarcıoğlu, B., Bayrak, C.: An infrared spectroscopic study of pyrazine-and 4,4′-bipyridyl-Td-type clathrates: Mn(pyrazine)$M(CN)_4$ benzene (M = Cd or Hg) and Mn(4,4′-bipyridyl)$M(CN)_4$.benzene (M = Zn, Cd or Hg). J. Incl. Phenom. **39**, 115–121 (2001)
17. Ekici, N., Kantarcı, Z., Akyüz, S.: An infrared and Raman spectroscopic study of pyrazinecadmium (II) tetracyanometalate (II) Benzene (1/1) clathrates: $Cd(C_4H_4N_2)Cd(CN)_4$·C_6H_6 and $Cd(C_4H_4N_2)Hg(CN)_4$·C_6H_6. J. Incl. Phenom. **10**, 9–18 (1991)
18. Akyüz, T., Akyüz, S., Davies, J.E.D.: Vibrational spectroscopic studies of three dimensional host lattices formed by pyrazine bridges between tetracyanonickelate layers. J. Incl. Phenom. **9**, 349–354 (1990)
19. Iwamoto, T.: Chapter 2. In: Atwood, J.L., Davies, J.E.D., MacNicol, D.D. (eds.) Inclusion compounds, vol. 1, p. 29. Academic Press, London (1984)
20. Hagan, M.: Clathrate inclusion compounds, p. 5. Reinhold Publishing Corporation, Chapman & Hall, New York (1962)
21. Yuge, H., Iwamoto, T.: Crystal structures of *catena*-[diligatocadmium(II) tetra-μ-cyanocadmate(II)] host clathrates: diamminecadmium(II) tetracyanocadmate(II)-benzene(1/2), diamminecadmium(II) tetracyanocadmate(II)-aniline(1/2), ethylenediaminecadmium(II) tetracyanocadmate(II)-aniline(1/2), and a novel type bis(aniline)cadmium(II) tetracyanocadmate(II)-aniline(2/1). J. Incl. Phenom. **14**, 217–235 (1992)
22. Kuroda, R.: A new type clathrate compound: the crystal structure of $Cd(NH_3)_2Hg(CN)_4$·$2C_6H_6$. Inorg. Nucl. Chem. Lett. **9**, 13–18 (1973)
23. Yuge, H., Iwamoto, T.: Dıfferent coordınatıon behavıor of 1,2-diaminoethane (en) and tetracyanonickelate(II) upon accommodatıon of polar guest molecules in their metal-complex hosts-crystal-structures of $[M(en)_2Ni(CN)_4]$·$2phNH_2$ (M = Ni, Cu, Zn or Cd) and $[(Cd(en))_2(en)(Ni(CN)_4)_2]$.4phOH. J. Chem. Soc. Dalton Trans. 1237–1242 (1994)
24. Nishikiori, S., Iwamoto, T.: Crystal structures of ethylenediaminecadmium(II) tetracyanocadmate(II)-benzene(1/2) and ethylenediaminecadmium(II) tetracyanocadmate(II). J. Incl. Phenom. **3**, 283–295 (1985)

25. Kasap, E., Kantarcı, Z.: Vibrational spectroscopic studies on the Hofmann-Td-type clathrates: $M(NH_3)_2M'(CN)_4{\cdot}2C_6H_6$ (M = Mn or Cd and M′ = Cd or Hg). J. Incl. Phenom. **20**, 33–41 (1995)
26. Hendra, P.J., Powel, D.P.: The infrared spectra and structures of metal complexes of 1,4-dioxan, 1,4-dithian, 1,4-thioxan, piperazine, and 1,4-dimethylpiperazine. J. Chem. Soc. 5105–5112 (1960)
27. Kantarcı, Z., Sertbakan, T.R., Kasap, E.: Infrared spectroscopic study of T_d-type piperazinemetal(II) tetracyanometallate(II) benzene(1/1) clathrates: $Cd(C_4H_{10}N_2)Cd(CN)_4{\cdot}C_6H_6$ and $Cd(C_4H_{10}N_2)Hg(CN)_4{\cdot}1{,}25C_6H_6$. Spectr. Lett. **38**, 583–594 (2005)
28. Aygün, M., Utlu, G., Gökçe, A.G., Akyüz, S., Özbey, S.: The two-dimensional coordination polymer poly[bis(3-methylpyridine)cadmium(II)]-tetra-μ-cyano-nickel(II)]. Acta Crystallog. **C60**, 117–118 (2004)
29. Cernak, J., Paharova, J., Skorsepa, J., Massa, W.: Tetracyanometallates with complex dien cations: $[Ni(dien)_2][Ni(CN)_4]{\cdot}2H_2O$ and $[Ni(dien)_2][Pd(CN)_4]$. A. Anorg. Allg. Chem. **628**, 344–348 (2002)
30. Andreeva, L., Minceva-Sukarova, B.: Vibrational spectra of partially debenzenated analogues in some en-T_d type clathrates. J. Mol. Struct. **408–409**, 431–434 (1997)
31. Arenas, J.F., Centeno, S.P., Lopez-Tocon, J.T., Otero, J.C.: Scaled quantum mechanical force field of dimethylpyrazines: vibrational assignments. J. Mol. Struct. **744–747**, 289–293 (2005)
32. Arenas, J.F., Marcos, J.I., Otero, J.C.: Vibratıonal-spectrum and internal-rotation in 2,5-dimethylpyrazine. J. Phys. Chem. **162**, 263–272 (1987)
33. Sungur, A., Akyüz, S., Davies, J.E.D.: Vibrational spectroscopic studies of 4,4′-bipyridyl metal(II) tetracyanonickelate complexes and their clathrates. J. Incl. Phenom. **5**, 491–497 (1987)
34. Akyüz, S., Dempster, A.B., Morehouse, R.L., Susuki, S.: An infrared and Raman spectroscopic study of some metal pyridine tetracyanonickelate complexes. J. Mol. Struct. **17**, 105–125 (1973)
35. Suzuki, S., Orville-Thomas, W.J.: Molecular force field of pyridine and its application to pyridine–metal complexes. J. Mol. Struct. **37**, 321–327 (1977)
36. McCullough, R.L., Jones, L.H., Crosby, G.A.: An analysis of the vibrational spectrum of the tetracyanonickelate (II) ion in crystal lattice. Spectrochim. Acta **16**, 929–944 (1960)
37. Painter, P.C., Koening, J.L.: A normal vibrational analysis of benzene. Spectrochim. Acta **33A**, 103–110 (1977)
38. Ruiz, E., Novoa, J.J., Alvarez, S.: Ab initio study of the intermolecular interactions in the Hofmann clathrates. J. Phys. Chem. **99**, 2296–2306 (1995)
39. Cernak, J., Chomic, J., Potacnak, I.: Thermal and some other properties of the complexes crystallizing from the system Ni(II)-en-$[Ni(CN)_4]^{2-}$-H_2O. J. Thermal. Anal. **35**, 2265–2277 (1989)
40. Cernak, J., Potacnak, I., Chomic, J.: Preparation and thermal properties of the complexes crystallizing from the system Zn(II)-en-$[Ni(CN)_4]^{2-}{\cdot}H_2O$. J. Thermal. Anal. **39**, 849–862 (1993)
41. Cernak, J., Skorsepa, J., Chomic, J., Potacnak, I., Hoppan, J.: Preparation and some properties of tetracyano complexes $M(en)M'(CN)_4$ (M = Cd(II), Mn(II); M′ = Ni(II), Cd(II)). J. Therm. Anal. **41**, 91–98 (1994)
42. Bubanec, J., Sopkova, A.: About the thermal decomposition of tetracyanocomplexes. J. Thermal. Anal. **50**, 831–841 (1997)
43. Yılmaz, V.T., Karadağ, A.: Thermal decomposition of Hofmann-type complexes of di- and triethanolamine. Thermochim. Acta **348**, 121–127 (2000)