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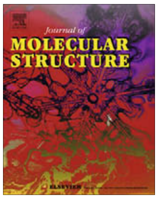

FT-IR spectroscopic investigation of some Hofmann type complexes: M(2-(1-Cyclohexenyl)ethylamine)$_2$Ni(CN)$_4$ (M = Ni, Co)

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ABSTRACT

New Hofmann type complexes in the form of M(CyHEA)$_2$Ni(CN)$_4$ (where CyHEA = 2-(1-cyclohexenyl)ethylamine; M = Ni or Co) have been prepared in powder form and their infrared spectra have been reported in the range of 4000–400 cm^{-1}. The thermal behaviour of these complexes has been investigated by differential thermal analysis (DTA) and thermo-gravimetric analysis (TGA). The results suggest that these compounds are similar in structure to Hofmann type complexes and their structures consist of polymeric layers |M–Ni(CN)$_4$|$_\infty$ with the CyHEA molecule bound to the metal atom (M).

1. Introduction

Hofmann type host structures are defined with the general formula of M(L)$_2$Ni(CN)$_4$ [1,2]. In this host structure, the L corresponds a bidentate or a pair of unidentate ligand molecules and the M corresponds a divalent transition metal. Based on this structure, metal (II) tetracyanonickelate complexes have been developed using N-donor ligands such as ammonia [3], pyridine [4], O-donor ligands such as water [5], dimethylformamide [6], dioxane [7] and S-donor ligands as dimethylthioformamide [8]. The Hofmann type host frame work is formed from infinite |M–Ni(CN)$_4$|$_\infty$ layers with four planar coordination around Ni atom. This structure provides α-type cavity similar to rectangular box for the guest molecules [9,10]. The model of the Hofmann type host structure is schematically illustrated in Fig. 1 [11,12].

In this work, we have prepared M(CyHEA)$_2$Ni(CN)$_4$ complexes (abbreviated here after as M–CyHEA–Ni), where M = Ni or Co, for the first time and spectral properties of them have been investigated in the IR region of 4000–400 cm^{-1}. We have also studied the thermal behaviour of these complexes with DTA and TGA techniques.

2. Experimental

All the chemicals used were reagent grade (Aldrich) and they were used without further purification. The complexes M–CyHEA–Ni (M = Ni and Co) were prepared as following: at first step 1 mmol of MCl$_2$ was dissolved in the distilled water, then to this solution 1 mmol of K$_2$Ni(CN)$_4$ dissolved in the distilled water was added under stirring. After a short time slightly more than 2 mmol of the liquid CyHEA were added to the mixture prepared drop wise, again under stirring. The reaction mixture was stirred for 2 days at room temperature. The obtained product was filtered and washed with water, ethanol, ether successively and dried in a desiccator which included P$_2$O$_5$.

Infrared spectra of the complexes as nujol and hexachloro-1,3-butadiene were recorded in the region of 4000–400 cm^{-1} via Perkin–Elmer FT-IR 2000 spectrometer at a resolution of 4 cm^{-1}. In the MIR region of spectrum, bands of nujol and hexachloro-1,3-butadiene were reported at 1377, 1461, 2858, 2925 cm^{-1} and 655, 793, 852, 941, 981, 1170, 1564, 1610 cm^{-1}, respectively. The compounds were analyzed for metals via a Perkin–Elmer 4300 ICP-OES and for C, H and N via a Fisons EA-1108 elemental analyser. Ni and Co metals were investigated at 231.604 and 228.616 nm, respectively. The results of elemental analysis have been as follows (found %/calculated %):

TGA and DTA curves of the complexes were recorded using a Setaram Labsys TG/DTA with ca. 6.1 mg of sample and a scanning rate of 5° min^{-1} under argon between about 0 and 220 °C temperatures.

3. Results and discussion

The infrared spectra obtained for the M–CyHEA–Ni (M = Ni or Co) complexes are compatible with each other. This indicates that

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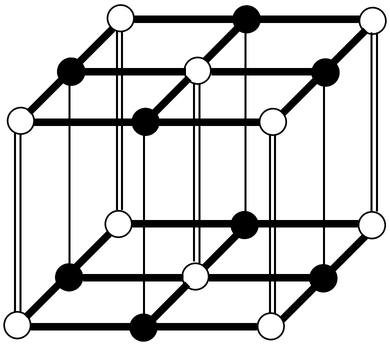

Fig. 1. The model for the Hofmann type host structure (open circle, 6-coordinate M; solid circle, square planar Ni; open column, an ambient ligand; thick line, CN bridge; thin line, edge of cavity).

the compounds have similar spectral features. The spectra of the M–CyHEA–Ni (M = Ni or Co) compounds are given in Figs. 2 and 3. The spectral analysis of each compound have been performed by taking into account the CyHEA molecule and $Ni(CN)_4$ ions individually. The spectral interpretations start with CyHEA vibrations.

3.1. 2-(1-Cyclohexenyl)ethylamine vibrations

We have studied the vibrational assignments and frequencies both experimental and theoretical study of CyHEA [13]. The calculated and experimental IR data for the CyHEA in the complexes, together with the spectral data for the CyHEA molecule are given in Table 1. The vibrational frequencies of the CyHEA molecule usually increase on the complexes compounds [13]. It is clearly observed in Table 1 that the N–H asymmetric and symmetric stretching bands which appear as a strong at 3366 and 3288 cm^{-1} attribute

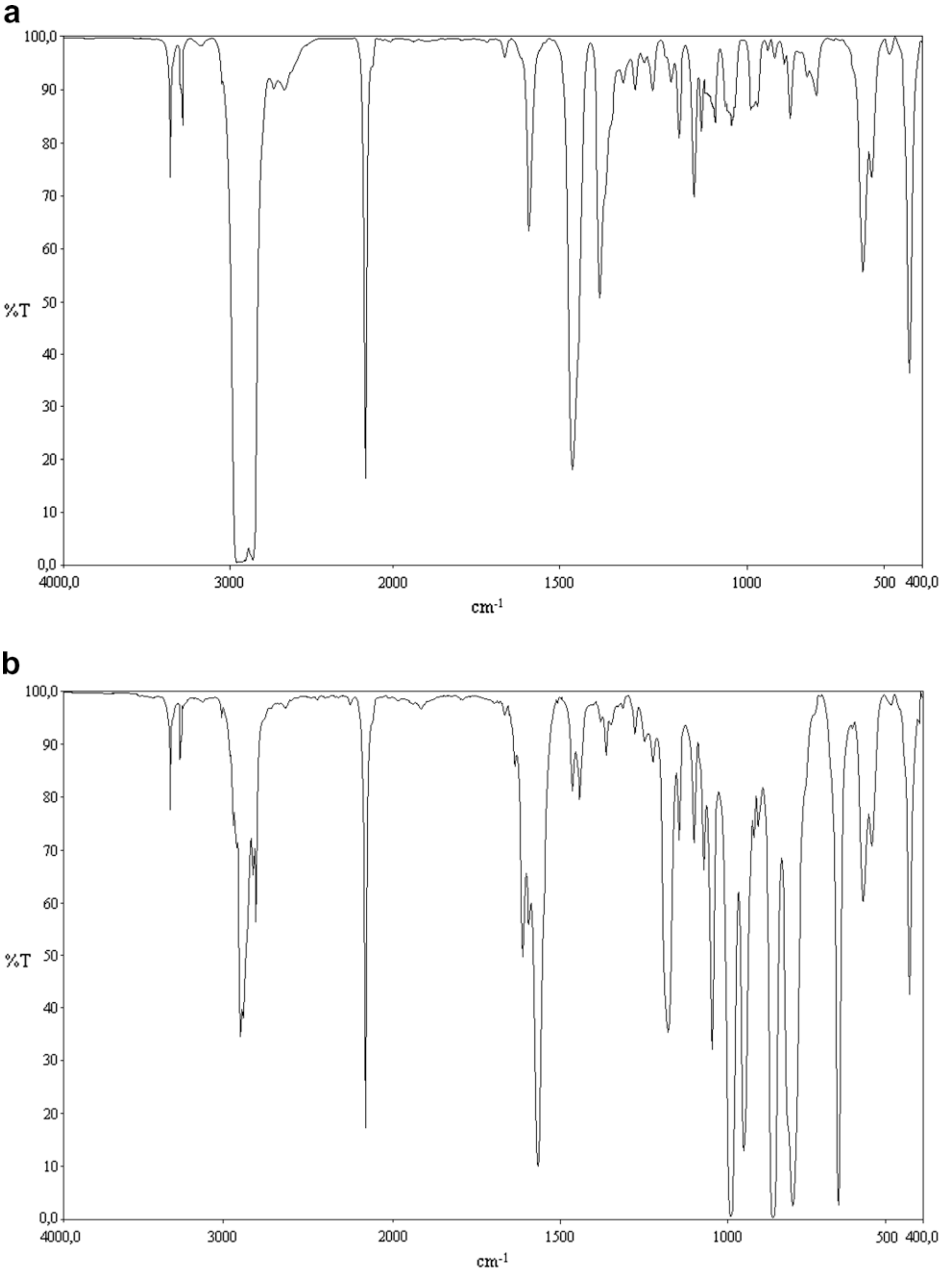

Fig. 2. Infrared spectra of Ni–CyHEA–Ni complex in nujol (a) and hexachloro-1,3-butadiene (b).

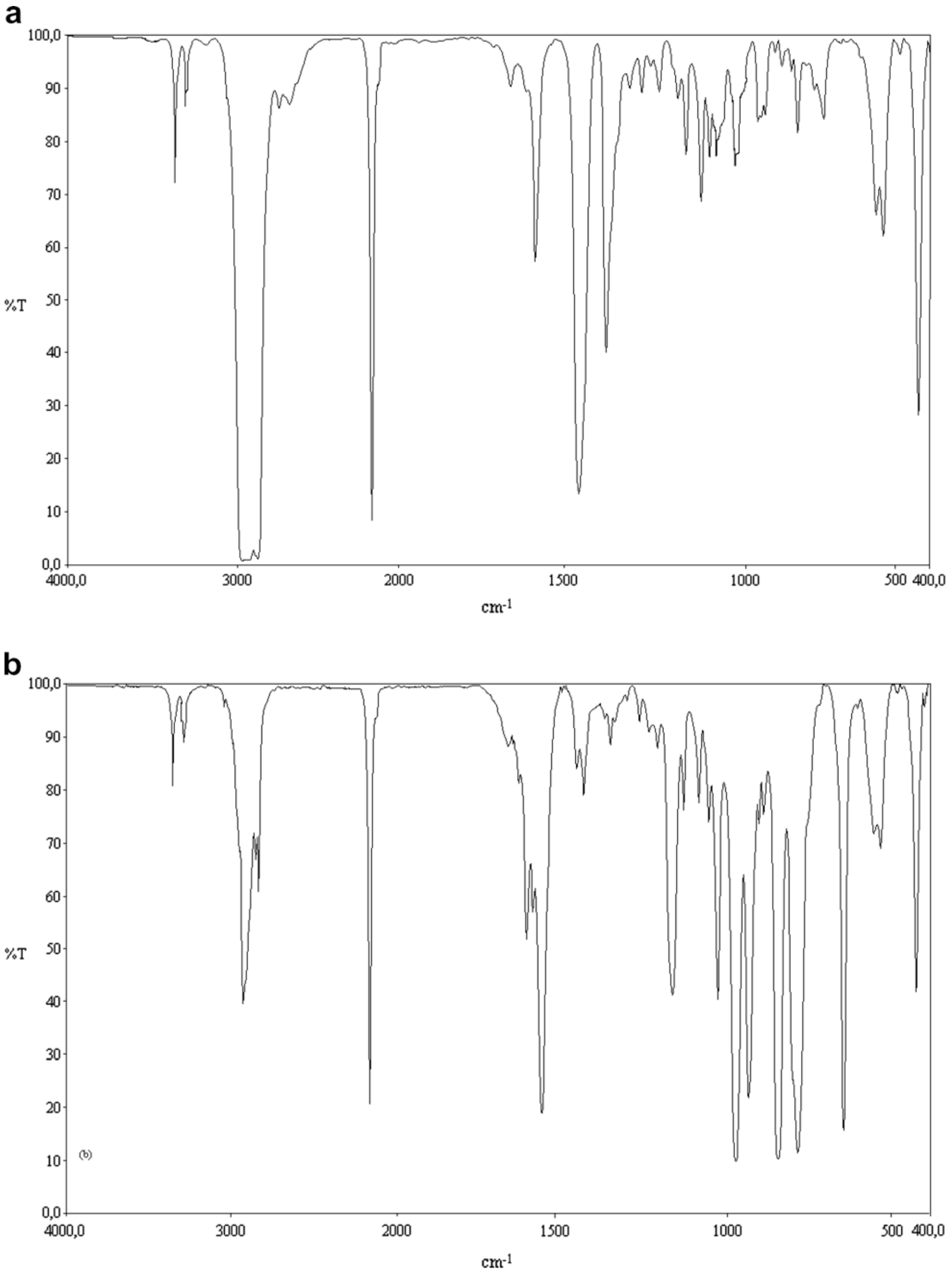

Fig. 3. Infrared spectra of Co–CyHEA–Ni complex in nujol (a) and hexachloro-1,3-butadiene (b).

to ethylamine, respectively. The strong band at 3366 $\mathrm{cm^{-1}}$ is shifted to 3354 $\mathrm{cm^{-1}}$ as a medium band. Another strong band at 3288 $\mathrm{cm^{-1}}$ shifts to 3286 $\mathrm{cm^{-1}}$ for Ni–CyHEA–Ni, and to 3287 $\mathrm{cm^{-1}}$ for the Co–CyHEA–Ni compounds. The medium brought band at 1600 $\mathrm{cm^{-1}}$ is shifted 1590 $\mathrm{cm^{-1}}$ as a medium band. Furthermore, some increase shifts are observed for the vibrational band of the CyHEA molecule in the frequency range from 448 to 857 $\mathrm{cm^{-1}}$. The downward shifts in frequencies were explained in terms of coupling of the internal vibration of the CyHEA molecule M–N vibrations. The medium ν_1 and weak ν_{23} bands at between 3000 and 3100 $\mathrm{cm^{-1}}$ result from cyclohexene while the medium C–H stretching band at 2995 $\mathrm{cm^{-1}}$ arises from ethylamine. The very strong bands attributed to ethylamine attached to cyclohexene appear at between 2830 and 2920 $\mathrm{cm^{-1}}$. Most of bands in below the 1300 $\mathrm{cm^{-1}}$ arise from cyclohexene. Similar studies [14–16] obvious that similar spectral features of coordinations are frequency shifts of ligand molecules in the complexes comparison with free ligand molecules by virtue of the ligand molecule complexed to the metal atom and also small shifts occured owing to changes in the environment.

3.2. *Ni(CN)$_4$ group vibrations*

Assignments of the bands for the $\mathrm{Ni(CN)_4}$ ion in the spectra of the present compounds have been carried out by means of vibrational data of the $\mathrm{Ni(CN)_4}^{2-}$ ion in $\mathrm{Na_2Ni(CN)_4}$ reported by McCullough et al. [17]. Since the ion is not coordinated to cations [17], it can be treated as an isolated unit. Therefore, we have used it as a reference for finding out whether coordination to the metals M is taking place. The spectral data for the $\mathrm{Ni(CN)_4}$ groups in our complexes are given in Table 2 along with McCullough et al.'s data.

The vibrational frequencies of the $\mathrm{Ni(CN)_4}$ group in the complexes appear to be much higher than those for isolated $\mathrm{Ni(CN)_4}$ ion. Such frequency shifts have been observed for other Hofmann

Table 1
The vibrational frequencies (cm^{-1}) of the CyHEA ligand molecule in the M–CyHEA–Ni (M = Ni or Co) compounds

Assignment[a]	CyHEA[a] (experimental)	CyHEA[a] B3LYP (6-31G(d) (calculated)	Ni–CyHEA–Ni	Co–CyHEA–Ni
N–H a-str	3366 s	3374	3354 m	3354 m
N–H s-str	3288 s	3273	3286 m	3287 m
ν_{23}	3097 w	3080	–	–
ν_1	3043 m	3008	3043 vw	3046 vw
C–H str (CH_3)	2995 m	2993	2994 w*	2995 vw*
ν_2 + C–H str (CH_3)	2926 vs	2934	2928 vs*	2928 vs*
ν_{25} + C–H str (CH_2)	2894 vw	2901	2911 w*	2911 w*
ν_{26}	2877 vw	2899	2885 sh*	2888 sh*
ν_{27} + C–H str (CH_3)	2857 vs	2848	2855 m*	2854 m*
ν_5 + C–H str (CH_2)	2836 vs	2838	2834 vs	2834 vs
ν_6	1666 m	1662	1665 w	1665 vw
NH_2 sciss	1600 mb	1633	1590 m	1590 m
CH_2 sciss	1505 vw	1505	1505 vw	1505 vw
C–H bend (CH_3)	1473 vw	1492	1460 w*	1460 w*
ν_{28} + C–H bend (CH_3)	1448 vw	1475	–	–
ν_8	1438 s	1401	1437 m	1437 m
CH_2 wag	1384 w	1373	–	–
ν_9 + C–H bend (CH_3)	1370 vw	1363	1361 sh*	1365 sh*
ν_{10}	1344 m	1346	1343 vw	1346 vw
ν_{30}	1334 w	1329	–	–
NH_2 twist	1307 w	1313	1307 w	1307 vw
ν_{32}	1269 m	1269	1270 w	1270 w
ν_{11} + CH_2 twist	1242 w	1254	1242 vw	1242 vw
ν_{12}	1215 w	1239	1217 w	1217 vw
ν_{34}	1136 m	1133	1138 m	1138 m
(C–C,C–N) a-str	1086 w	1084	1093 m	1092 m
ν_{15}	1066 w	1068	1062 m	1061 m
ν_{35}	1049 w	1057	1038 m	1036 m
ν_{36} + CH_3 rock	1022 w	1024	–	–
ν_{16}	966 w	964	985 m	981 m
ν_{37}	919 m	953	919 vw	919 vw
ν_{17}	906 vw	942	900 vw	900 vw
ν_{38}	857 w	836	868 vw	868 vw
ν_{18} + CH_2 rock	829 m	830	819 w	820 w
ν_{19} + NH_2 wag	800 m	781	801 m	801 m
ν_{39}	720 sh	733	723 vw	723 vw
ν_{40}	647 w	671	653 vw	649 vw
ν_{20}	497 vw	499	499 vw	492 vw
ν_{41}	448 w	436	472 vw	473 vw

[a] Taken from Ref. [13]; v, very; s, strong; m, medium; w, weak; sh, shoulder; b, broad; str, stretching; bend, bending; sciss, scissoring; twist, twisting; wag, wagging; rock, rocking.

[*] In hexachloro-1,3-butadiene.

Table 2
The vibrational frequencies (cm^{-1}) of the $Ni(CN)_4$ group in the M–CyHEA–Ni (M = Ni or Co) compounds

Assignment[a]	$Na_2Ni(CN)_4$[a]	Ni–CyHEA–Ni	Co–CyHEA–Ni
$\nu_8(CN)$, E_u	2132 vs	2171 vs	2165 vs
$\nu_9(NiC)$, E_u	543 w	554 w	543 w
$\pi(NiC)$, A_{2u}	448 w	457 sh	456 sh
$\delta(NiCN)$, E_u	433 vs	441 vs	437 vs

[a] Taken from Ref. [18]; v, very; s, strong; sh, shoulder; w, weak.

type complexes [6,8,15,16,18,19] or clathrates [11,12,20,21] and are attributed to the mechanical coupling of the internal modes of $Ni(CN)_4$ with the M–NC vibrations. It follows that the N-termini of the $Ni(CN)_4$ group are bound to a M metal atom (M = Ni, Co) in the host compounds investigated.

The studies regarding the Hofmann type complexes explain that shifts arise from the mechanical coupling of the internal modes of $Ni(CN)_4$ with metal as both ends of the CN group are bounded to the transition metals [6,8,15,16,19]. According to the shifts in the present complexes can be attributed to the mechanical coupling of the internal modes of $Ni(CN)_4$ with metal.

The characteristic $\nu(CN)$ and $\delta(NiCN)$ frequencies are found to be similar to those known for the Hofmann type complexes [2,14], indicating that the $|M–Ni(CN)_4|_\infty$ layers have been preserved. If the unit cell has D_{4h} symmetry, only four fundamental vibrations are expected in the spectrum above 400 cm^{-1} [21–23].

In this work, we have discussed infrared spectroscopic properties of the prepared complexes up till now. Furthermore, in order to support the conclusions obtained in the infrared studies, we have conducted the elemental and TGA–DTA analyses of these complexes.

We have calculated the percentage amount of C, H, N, Ni and M in our complexes with the help of molecular weight of those compounds. The calculated values have been compared with the experimental data and the results have been given in Table 3. According to these results, the calculated values are in compliance with the experimental findings.

3.3. Thermal behaviour

The TGA and DTA curves of the compounds are given in Fig. 4. 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 40 and 140 °C. DTA curves show two endothermic transitions for present compounds. The first decomposition stage about 90 °C indicates that the CyHEA ligand molecule leaves host structure. The second decomposition stage about 150 °C is decomposition of cyanide to yield the respective metals. The decomposition temperatures of

Table 3
Elemental analysis and colours of the M–CyHEA–Ni (M = Ni or Co) compounds

Empirical formula of sample (formula weight)	Colour	Elemental analysis, found/calculated (%)			
		C	H	N	Ni
Ni($C_8H_{15}N$)$_2$Ni(CN)$_4$ (471,87,944)	Violet	50.94 (50.91)	6.32 (6.40)	17.55 (17.80)	24.50 (24.87)
Co($C_8H_{15}N$)$_2$Ni(CN)$_4$ (472,11,924)	Pink	48.94 (50.87)	5.95 (6.40)	16.85 (17.80)	12.24 (12.43)

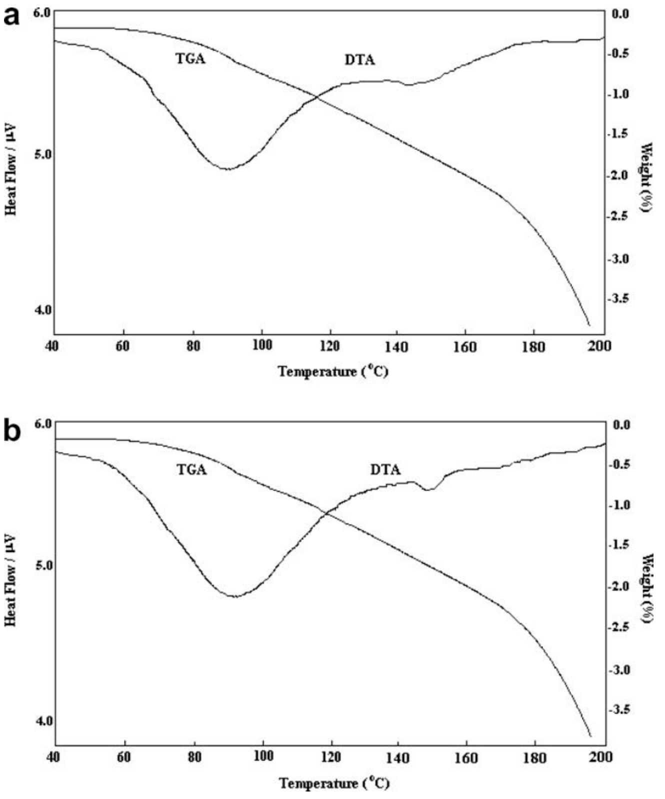

Fig. 4. TGA and DTA curves of the Ni–CyHEA–Ni (a) and Co–CyHEA–Ni (b) complexes.

Table 4
The decomposition temperatures (°C) of M–CyHEA–Ni (M = Ni or Co) compounds

Sample	Decomposition	
	First	Second
Ni($C_8H_{15}N$)$_2$Ni(CN)$_4$	93.21	153.82
Co($C_8H_{15}N$)$_2$Ni(CN)$_4$	92.81	151.32

M–CyHEA–Ni (M = Ni, Co) complexes are given in Table 4. Such decomposition stages have been observed for other Hofmann type complexes [24] and clathrates [25].

As a result, the similarities of the spectral features found for the present compounds with the Hofmann type complexes let us conclude that the compounds presented in this study are further examples of Hofmann type complexes.

4. Conclusion

The IR spectroscopic study of two new complexes has shown that they have similar structures consisting of infinite two-dimensional polymeric layers formed with Ni(CN)$_4$ ions bridged by M(CyHEA)$_2$ (M = Ni and Co) cations and CyHEA molecules in compounds have been coordinated in the chair form as a unidentate ligand coordinating only through the NH nitrogen. In conclusion, the compounds presented in this study are further examples of the Hofmann type complexes.

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