

## The FT-IR Spectroscopic Investigation on Cd(II) and Co(II) Transition Metals 1,5-pentanedithiol and 1,8-octanedithiol Tetracyanonickelate Complexes

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**Abstract:** FT-IR spectra of the ligands, 1,5-pentanedithiol (PDT) and 1,8-octanedithiol (ODT), with their complexes with the divalent transition metal ions Co(II) and Cd(II) are reported for the first time in the 400-4000  $\text{cm}^{-1}$  range. Furthermore the thermal behaviors of  $M(\text{PDT})\text{Ni}(\text{CN})_4$  and  $M(\text{ODT})\text{Ni}(\text{CN})_4$  ( $M = \text{Co}$  and  $\text{Cd}$ ) compounds were studied by thermo-gravimetric analysis (TGA), differential thermal analysis (DTA) and derivative thermal gravimetric analysis (DTG) in the range of (25-250)  $^{\circ}\text{C}$  and their XRD patterns and elemental analyses were presented. The spectral and thermal features suggest that the compounds are similar in structure to the Hofmann-type complexes with infinite polymeric layers formed with  $\text{Ni}(\text{CN})_4^{2-}$  ions bridged by  $\text{ML}^{+2}$  cations.

**Key words:** FT-IR, 1,5-pentanedithiol, 1,8-octanedithiol, Tetracyanonickelate, Thermal analysis

## Cd(II) ve Co(II) Geçiş Metal Yapılı 1,5-pentanedithiol ve 1,8-octanedithiol Tetrasiyanonikel Bileşiklerinin Kırmızıaltı Spektroskopisi İle İncelenmesi

**Özet:** 1,5-pentanedithiol (PDT) ve 1,8-octanedithiol (ODT) ligandlarının, iki değerlikli geçiş metal iyonları Co(II) ve Cd(II) ile oluşturdukları bileşiklerin 400-4000  $\text{cm}^{-1}$  aralığındaki FT-IR spektrumları ilk kez sunulmaktadır. Ayrıca,  $M(\text{PDT})\text{Ni}(\text{CN})_4$  ve  $M(\text{ODT})\text{Ni}(\text{CN})_4$  ( $M = \text{Co}$  ve  $\text{Cd}$ ) bileşiklerinin termo gravimetrik (TGA), diferansiyel termal (DTA), türetilmiş termal gravimetrik (DTG) analizleri (25-250)  $^{\circ}\text{C}$  aralığında incelenmiş ve XRD desenleri ile elementel analizleri verilmiştir. Spektral ve termal özellikler, bileşiklerin,  $\text{ML}^{+2}$  katyonları ile bağlanmış  $\text{Ni}(\text{CN})_4^{2-}$  iyonlarından oluşan sonsuz polimerik tabakalar ile Hofmann-tipi bileşiklere benzer yapıda olduğunu ortaya koymuştur.

**Anahtar kelimeler:** FT-IR, 1,5-pentanedithiol, 1,8-octanedithiol, Tetrasiyanonikel, Termal analiz

### 1. Introduction

Aliphatic as well as aromatic dithiols are widely used in the coordination chemistry [1, 2]. The most widely studies of aliphatic dithiols usually include their adsorptions on silver and gold [3-4].

Recently, however, 1,2-ethanedithiol (EDT) and 1,6-hexanedithiol (HDT) have been used as the ligand in the Hofmann-type structures [5-6]. On the other hand it is well-known that the infrared spectroscopy is a powerful technique to investigate the Hofmann-type host structures. The general formula for the Hofmann-type host complexes is  $\text{ML}_2\text{Ni}(\text{CN})_4$  where M is a transition metal atom having the valence of +2, L is either a bidentate or two monodentates ligand molecule [7]. The  $\text{ML}_2\text{Ni}(\text{CN})_4$

complexes form the polymeric sheets consisting of metal cyanide bridges,  $[\text{M-Ni}(\text{CN})_4]_{\infty}$ , and ligand molecules bound to the transition metals M from donor atoms ends located above or below the sheets [8]. The Hofmann-type host structures provide the  $\alpha$ -type (rectangular boxes) voids for the guest molecules [9].

The liquids, 1,5-pentanedithiol (PDT) and 1,8-octanedithiol (ODT) which contain two sulfur atoms are the derivatives of the 1,2-ethanedithiol (or EDT) compound. Recently, the adsorptions of PDT and ODT on some synthetic zeolites have been investigated by using the FT-IR spectroscopy [10]. In the present work, our purpose is to offer four new Hofmann-type host structures,  $\text{MLNi}(\text{CN})_4$  (where  $\text{M} = \text{Co}, \text{Cd}$  and  $\text{L} = \text{PDT}$  and  $\text{ODT}$ ). In this paper we report IR spectra of  $\text{M}(\text{PDT})\text{Ni}(\text{CN})_4$  ( $\text{M} = \text{Co}$  and  $\text{Cd}$ ) and  $\text{M}(\text{ODT})\text{Ni}(\text{CN})_4$  ( $\text{M} = \text{Co}$  and  $\text{Cd}$ ) tetracyanonickelate complexes for the first time. We also present elemental analysis results and X-ray diffraction patterns. Additionally, the thermal behaviors of these complexes were investigated with thermo-gravimetric analysis (TGA), differential thermal analysis (DTA) and derivative thermal gravimetric analysis (DTG).

## **2. Experimental**

### *2.1. Sample Preparation*

The 1,5-pentanedithiol (PDT) and 1,8-octanedithiol (ODT) liquids of 95% purity and potassium tetracyanonickelate (II) hydrate  $\text{K}_2[\text{Ni}(\text{CN})_4] \cdot \text{aq}$  used in this study were obtained from commercial sources (Fluka, Fluka and Aldrich, respectively) and were used without any purification. The complexes were prepared as follows: first, 1 mmol  $\text{K}_2\text{Ni}(\text{CN})_4$  was dissolved in distilled water and 1 mmol PDT (or ODT) was dropped into the mixture and stirred rapidly during 2-3 minutes. Then, 1 mmol  $\text{MCl}_2$  ( $\text{M} = \text{Co}, \text{Cd}$ ) solution in distilled water were added by dropping to this mixture and all were stirred during 3 days. The precipitates formed were filtered and washed with distilled water, ethyl alcohol and diethyl ether successively and dried at room temperature by keeping in desiccators containing silica gel [11]. The colors of the obtained complexes were brown, dark yellow, rose and fair yellow for the precipitates containing PDT and Co, PDT and Cd, ODT and Co, and ODT and Cd, respectively.

### *2.2. Instrumentation*

#### *a) FT-IR Spectrometer*

The FT-IR spectra of the samples were recorded in the range of  $(4000 - 400) \text{ cm}^{-1}$  at room temperature on a Perkin-Elmer spectrum One FT-IR (Fourier Transformed Infrared) Spectrometer with a resolution of  $4 \text{ cm}^{-1}$  in the transmission mode. The prepared samples were compressed into self-supporting pellet and introduced into an IR cell equipped with KBr windows.

b) *Thermal Analysis*

Thermal stability of samples was investigated using a Perkin-Elmer model thermal parametric analyzer (Beaconsfield, Beuckinghamshire, HP91QA, England) with heating at a rate of 10°C/min under pure nitrogen at a flow rate of 25ml/min.

c) *Elemental Analysis*

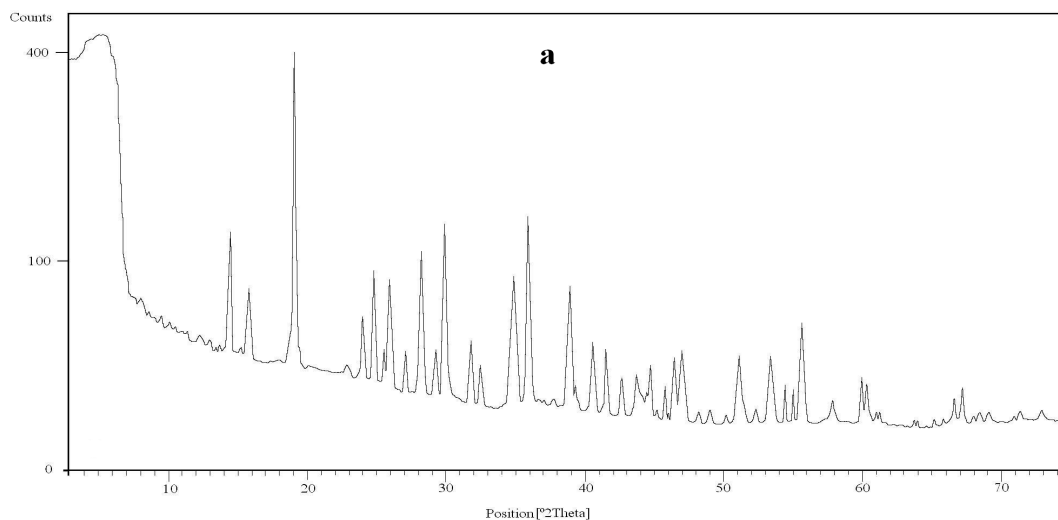
The prepared compounds were analyzed by using a LECO CHNS 932 model analyzer for C, H, N and S with the following results (found % / calculated %) which are given in Table 1. It is well-known that these analytical results are often poor for the samples available in powder form owing to partial decomposition.

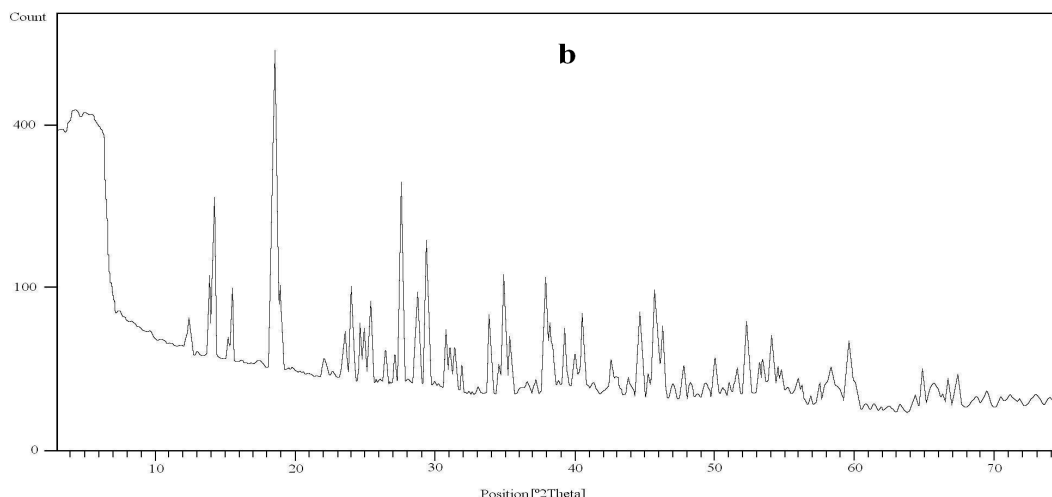
**Table 1.** Elemental analysis of MLNi(CN)<sub>4</sub> (M = Cd, Co and L = PDT and ODT) tetracyanonickelate complexes

Sample	% C	% H	% N	% S
Cd(PDT)Ni(CN) <sub>4</sub>	24.22/26.27	3.43/2.94	9.31/13.62	19.28/15.59
Co(PDT)Ni(CN) <sub>4</sub>	23.71/30.2	3.31/3.38	15.39/15.65	12.21/17.91
Cd(ODT)Ni(CN) <sub>4</sub>	25.99/31.78	3.75/4.00	9.90/12.35	11.29/14.14
Co(ODT)Ni(CN) <sub>4</sub>	23.88/36.03	3.36/4.54	16.93/14.00	5.44/16.03

d) *X-ray diffraction*

XRD patterns were recorded using a Pan analytical BV (PW 3050/60 Model) powder diffractometer with CuKα (1,54060 Å, 40 mA, 45 kV) at 0.02 steps at the rate of 0.5 per second over the range 5<2θ<75. Powder X-ray diffraction patterns of Cd(PDT)Ni(CN)<sub>4</sub> and Co(ODT)Ni(CN)<sub>4</sub> complexes which were typically chosen within the prepared samples are not efficiently distinguished from each other and are shown in Fig. 1(a) and (b), respectively.





**Figure 1.** The powder X-ray diffraction pattern of (a) Co(PDT)Ni(CN)<sub>4</sub> and (b) Cd(ODT)Ni(CN)<sub>4</sub> compounds.

### 3. Results and discussion

#### 3.1. Infrared Studies

The results obtained from IR spectral data of M(PDT)Ni(CN)<sub>4</sub> (M = Cd, Co) and M(ODT)Ni(CN)<sub>4</sub> (M = Cd, Co) compounds can be analyzed for a) vibrating ligand molecules, b) Ni(CN)<sub>4</sub><sup>2-</sup> ion units.

##### a) Ligand Vibrations

The IR spectra of PDT (C<sub>5</sub>H<sub>12</sub>S<sub>2</sub>) and ODT (C<sub>8</sub>H<sub>18</sub>S<sub>2</sub>) liquids which are used as the bidentate ligand molecules in our work are given in Fig. 2(a) and (b), respectively. On the other hand the infrared spectra of M(PDT)Ni(CN)<sub>4</sub> (M = Cd, Co) and M(ODT)Ni(CN)<sub>4</sub> (M = Cd, Co) tetracyanonickelates are presented in Fig. 3 (a) and (b) and Fig. 4(a) and (b), respectively. Furthermore, the vibrational spectroscopic results for pure liquids and the ligand PDT and ODT molecules in our complexes are summarized in Table 2.

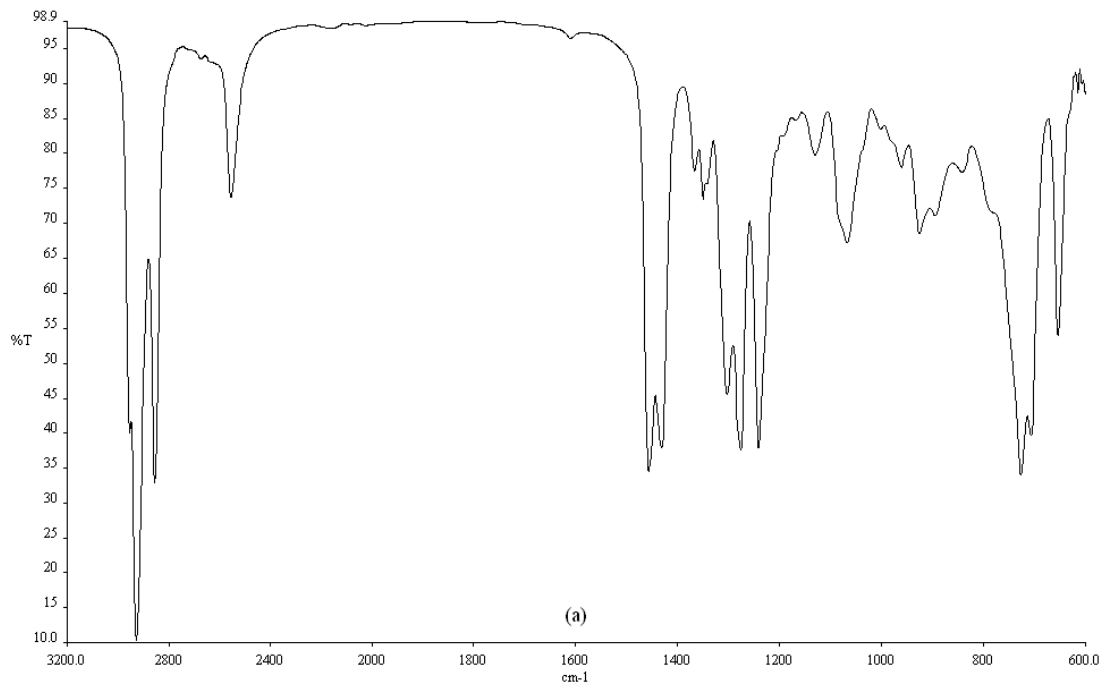
**Table 2.** The IR vibrational wavenumbers (cm<sup>-1</sup>) of the bulk PDT and ODT and ligand PDT and ODT molecules in M(PDT)Ni(CN)<sub>4</sub> (M = Co, Cd) and M(ODT)Ni(CN)<sub>4</sub> (M = Co, Cd) complexes

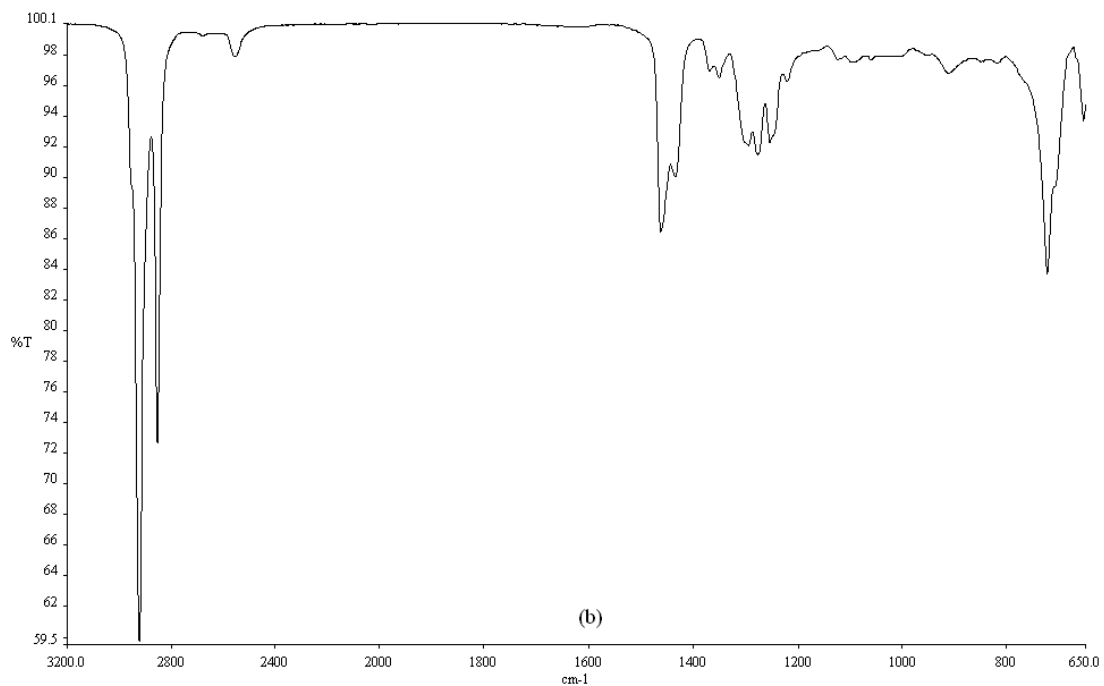
PDT	ODT	Assignments	Cd-PDT-Ni	Co-PDT-Ni	Cd-ODT-Ni	Co-ODT-Ni
2928 vs	2924 vs	$\nu_{as}(\text{CH})$	2925 s	2928 m	2925 s	2922 vs
2854 s	2852 s	$\nu_s(\text{CH})$	2851 m	2855m	2852 m	2849 s
2555 m	2556 m	SH stretch	-	-	-	-
1432s	1463 s	CH <sub>2</sub> bend	1452 m	1456 m	1460 m	1467 s
1416 m	1433 m	CH <sub>2</sub> bend	1433 w	1437 sh	1435 sh	1431 w
-	1350 w	CH <sub>2</sub> wag.	-	-	1372 w	1349 vw
1275 s	1294 m	CH <sub>2</sub> wag.	1270 m	1270 bw	1295 w	1319 m
1241 s	1253 m	CH <sub>2</sub> wag.	1231 s	1226 m	1244 m	1252 m

**Table 2. (continued)**

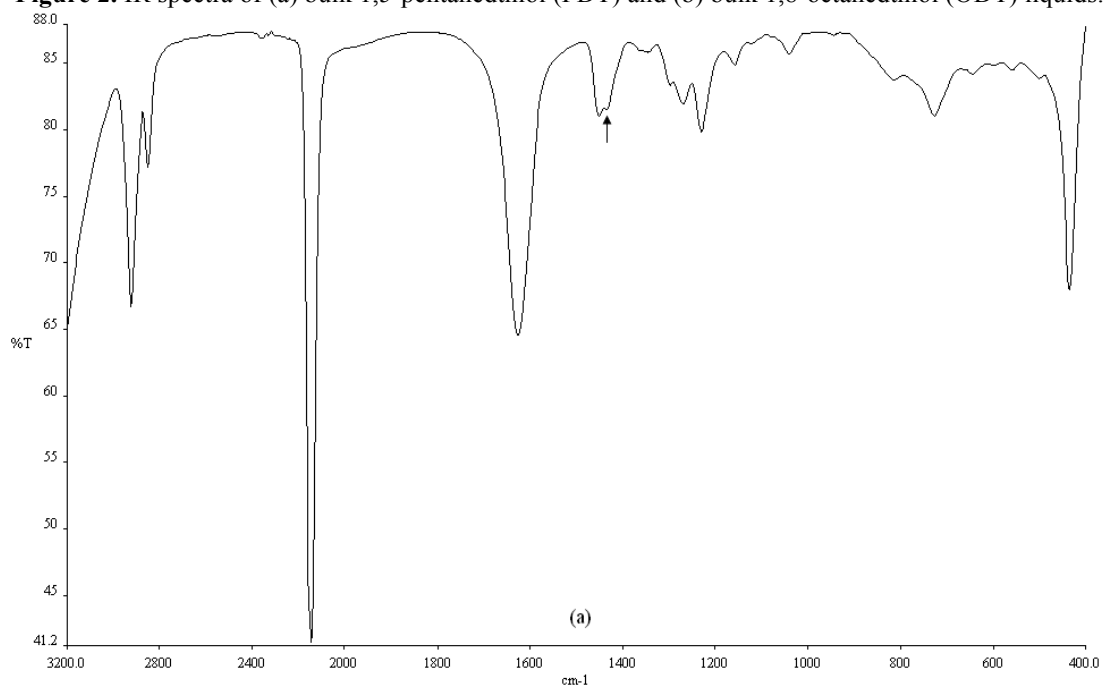
1129 m	1122 w	CH <sub>2</sub> twist	1120 m	1125 vw	1121 w	-
1067 m	1058 w	CC stretch	1041 m	1039 w	1049 m	1082 w
841 m	817 vw	CSH def.	816 w	832 bm	-	827 bm
727s	723 s	CSH def.	727 s	763 m	724 m	721 m
654 vs	-	CS stretch.	644 w	617 s	-	-

where s: strong, vs: very strong, m: medium, w: weak, b: broad





**Figure 2.** IR spectra of (a) bulk 1,5-pentanedithiol (PDT) and (b) bulk 1,8-octanedithiol (ODT) liquids.



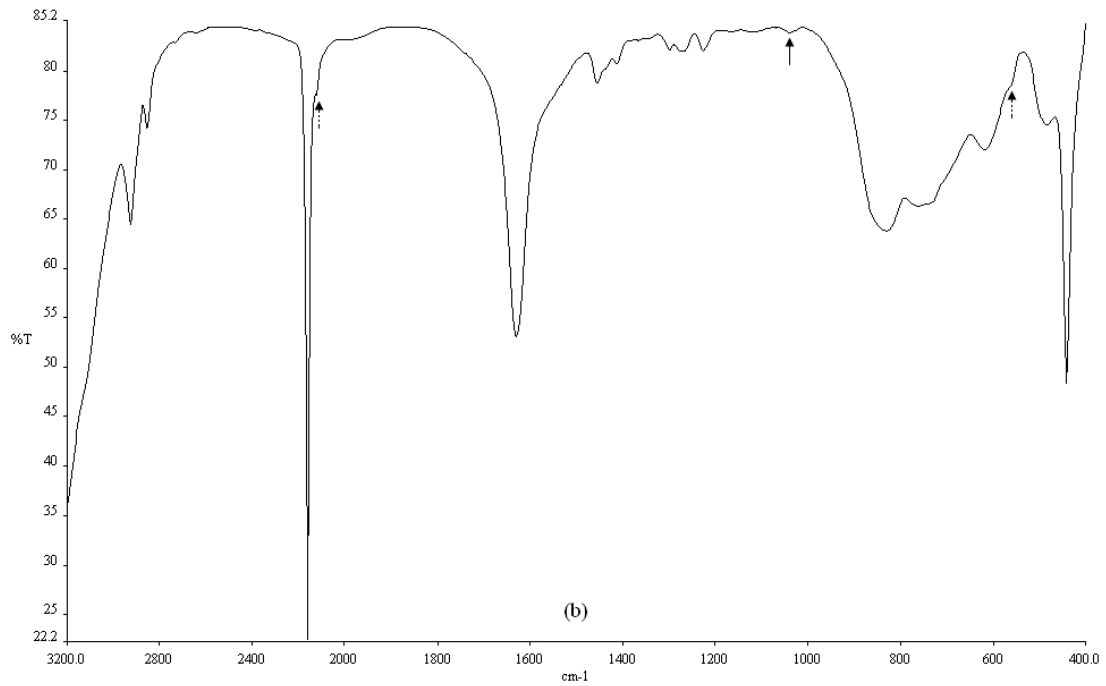
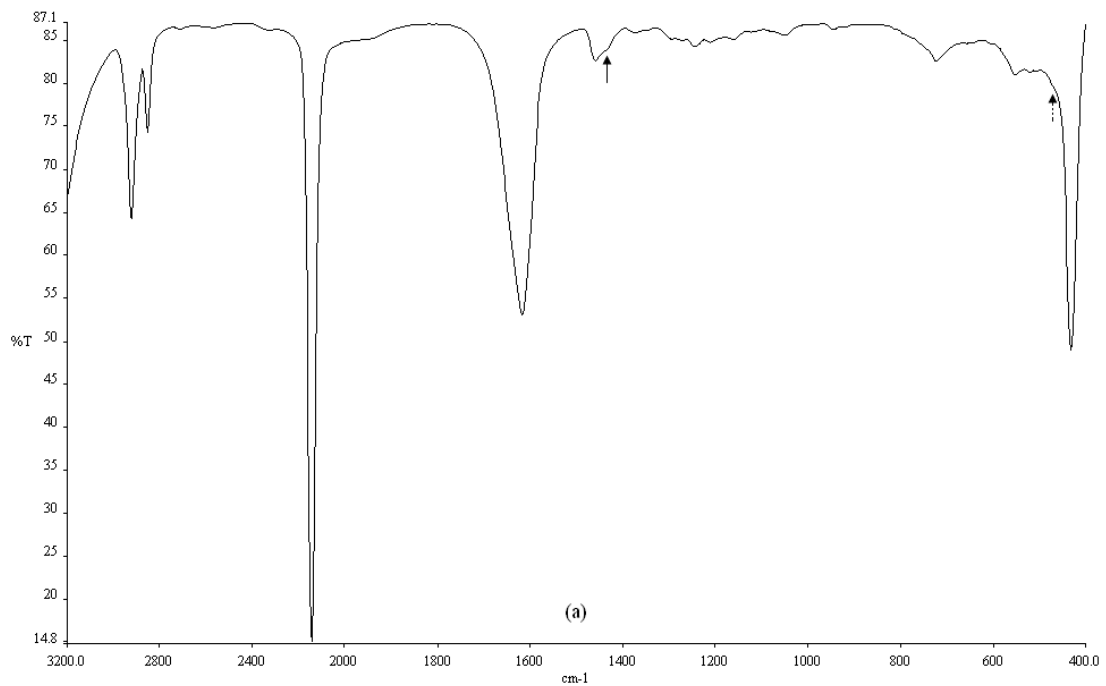
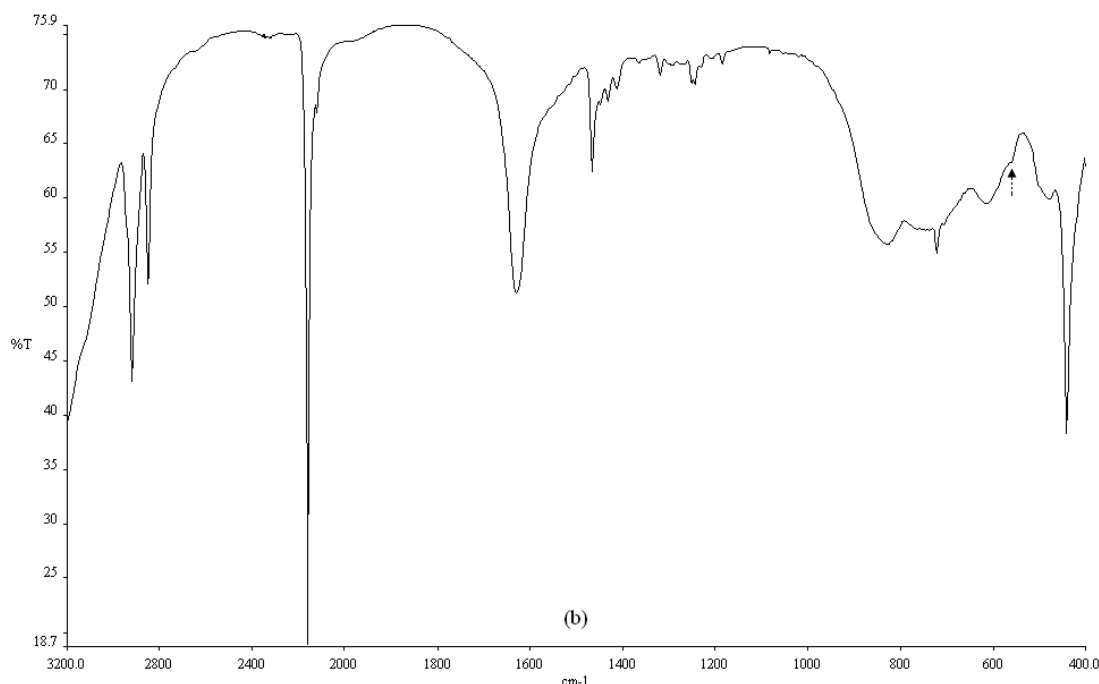


Figure 3. IR spectra of (a)  $\text{Cd(PDT)Ni(CN)}_4$  and (b)  $\text{Co(PDT)Ni(CN)}_4$  complexes.





**Figure 4.** IR spectra of (a) Cd(ODT)Ni(CN)<sub>4</sub> and (b) Co(ODT)Ni(CN)<sub>4</sub> complexes.

In the tentative assignments of IR vibrational frequencies for bulk PDT and ODT liquids we referred to some early works [5-6, 10, 12]. As seen in Table 2 and Figs. 3 and 4, the symmetric and asymmetric CH stretching vibration bands for the bulk PDT and ODT at 2854 cm<sup>-1</sup> and 2852 cm<sup>-1</sup> and 2928 cm<sup>-1</sup> and 2924 cm<sup>-1</sup>, respectively, are slightly shifted to the lower and/or higher frequency regions in tetracyanonickelates. In general, the bulk PDT and ODT vibration bands in the FT-IR spectrum correlate very well with those in the FT-IR spectrum of MLNi(CN)<sub>4</sub> complexes (where M = Co, Cd and L = PDT and ODT). However, in some frequencies of PDT and ODT a few remarkable changes occurred on bound of PDT and ODT to the transition metal atoms. Firstly, the  $\nu(\text{S-H})$  band which appears at 2555 cm<sup>-1</sup> and 2556 cm<sup>-1</sup> in the FT-IR spectrum of bulk PDT and ODT, respectively is completely missing in the FT-IR spectrum of MLNi(CN)<sub>4</sub> complexes. This indicates that the S-H bond of the PDT and ODT is broken on the bonding to the transition metal atoms (Mn, Co and Cd). This result shows that the PDT and ODT molecules bound to the transition metal atoms dissociative as a PDT<sup>-</sup> and ODT<sup>-</sup> anions. The resulting PDT<sup>-</sup> and ODT<sup>-</sup> anions were found to bind to the transition metal atom via their sulfur atoms. Assuming that the M-S-C skeleton of the PDT<sup>-</sup> and ODT<sup>-</sup> bond to metal atoms (M = Co and Cd) is nearly linear [12, 13]. However, as seen in Table 2, the shifts to the low or high frequency regions for ligand molecules in the obtained compounds are observed in many other vibrational bands. For instance, the  $\nu(\text{CS})$  stretching and the CH<sub>2</sub> torsional vibrational modes are shifted to lower frequency region at interval 2-17 cm<sup>-1</sup> and 1-4 cm<sup>-1</sup>, respectively, while the CH<sub>2</sub> wagging modes are shifted to the higher frequency region at interval 5-24 cm<sup>-1</sup>. Likewise, the CSH deformation bands 720-841 cm<sup>-1</sup> were shifted to lower or higher frequency regions for the mentioned complexes. Meanwhile the CH<sub>2</sub> wagging mode band at 1433 cm<sup>-1</sup> for Cd(PDT)Ni(CN)<sub>4</sub> and at 1337 cm<sup>-1</sup> for Cd(ODT)Ni(CN)<sub>4</sub> complexes, and the  $\nu(\text{CC})$  stretching band at 1039 cm<sup>-1</sup> for Co(PDT)Ni(CN)<sub>4</sub> compound are shown with the arrows in Fig. 3(a), Fig. 4(a) and Fig.



3(b), respectively. These shifts observed can be based on the changes of the surroundings of ligand molecules in newly formed compounds [14].

b)  $Ni(CN)_4^{-2}$  Group Vibrations

The vibrational wavenumbers of the  $Ni(CN)_4^{-2}$  anions for the mentioned complexes under study are given in Table 3. The assignments of IR vibrational modes of  $K_2Ni(CN)_4$  were based on those of the work done by McCullough and co-workers who presented vibrational data for the tetracyanonickelate group in the salt in  $Na_2Ni(CN)_4$  and Uygun *et al.* [5, 15].

**Table 3.** The IR vibrational wavenumbers ( $cm^{-1}$ ) of  $Ni(CN)_4$  groups in the  $M(PDT)Ni(CN)_4$  ( $M = Co, Cd$ ) and  $M(ODT)Ni(CN)_4$  ( $M = Co, Cd$ ) tetracyanonickelates

Assignment	$K_2Ni(CN)_4$	Cd-PDT-Ni	Co-PDT-Ni	Cd-ODT-Ni	Co-ODT-Ni
$\nu(CN)$	2121	2143 vs	2161 vs	2142 vs	2160 vs
Hot band	2085	-	2121 sh	-	2120 w
$\nu(Ni-CN)$	539	558 m w	567 sh	552 w	560 vw
$\pi(Ni-CN)$	443	499 m	484 m	471 sh	481 w
$\delta(Ni-CN)$	416	435 s	441 s	432 s	442 s

where s: strong, v: very, sh: shoulder, m: middle v: stretching,  $\pi$ : out of plane bending,  $\delta$ : in plane bending

In Fig. 3(b) the hot band at  $2121\text{ cm}^{-1}$  and the shoulder band at  $567\text{ cm}^{-1}$  are denoted with the dashed arrows. Similarly, the shoulder peak at  $471\text{ cm}^{-1}$  in Fig. 4(a) and the very weak peak at  $560\text{ cm}^{-1}$  in Fig. 4(b) are denoted with dashed arrows. As seen in Table 3 the assigned characteristic wavenumbers for  $\nu(CN)$  modes of the  $Ni(CN)_4$  anions of the complexes studied are shifted to higher region (at the interval  $21-40\text{ cm}^{-1}$ ) than that for  $K_2Ni(CN)_4$  molecule. Similar shifts to high frequency region are available for other modes of tetracyanonickelate ions. Such frequency shifts were observed for Hofmann-type host complexes [16-19]. Therefore it can be stated that the large shift in the characteristic modes of  $Ni(CN)_4$  groups can arise from the pairing between their internal vibrations and the metal-nitrogen (M-CN) bond stretching vibration.

3.2. Thermal Behavior

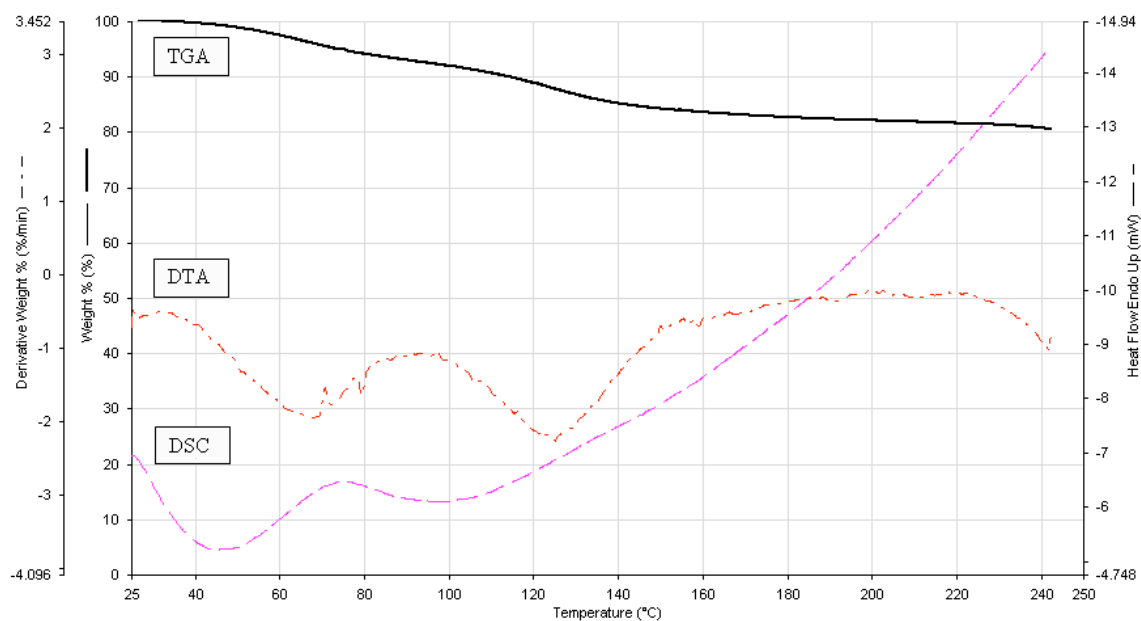
Thermal behaviors of the mentioned complexes were examined by thermo-gravimetric analysis (TGA), differential thermal analysis (DTA) and differential scanning calorimetry (DSC) techniques. The TGA, DTA and DSC curves of the  $M(PDT)Ni(CN)_4$  and  $M(ODT)Ni(CN)_4$  ( $M = Cd$  and  $Co$ ) tetracyanonickelates are given in Fig. 5(a) and (b) and in Fig. 6(a) and (b), respectively. The TGA results denote that the samples are stable at room temperature. By heating, however, all of complexes gradually lose their ligand molecules between about  $40-80\text{ }^\circ\text{C}$ . The DTA curves indicate that two endothermic transitions for  $Cd(PDT)Ni(CN)_4$ ,  $Co(PDT)Ni(CN)_4$  and  $Cd(ODT)Ni(CN)_4$

complexes and one endothermic transition for  $\text{Co}(\text{ODT})\text{Ni}(\text{CN})_4$  compound. The decomposition temperatures of  $\text{M}(\text{PDT})\text{Ni}(\text{CN})_4$  and  $\text{M}(\text{ODT})\text{Ni}(\text{CN})_4$  ( $\text{M} = \text{Cd}$  and  $\text{Co}$ ) complexes are given in Table 4.

**Table 4.** The decomposition temperatures of the  $\text{MLNi}(\text{CN})_4$  ( $\text{L} = \text{PDT}, \text{ODT}$  and  $\text{M} = \text{Co}, \text{Cd}$ ) complexes

Sample	Decomposition ( $^{\circ}\text{C}$ )	
	I	II
Cd-PDT-Ni	50	90
Co-PDT-Ni	68	125
Cd-ODT-Ni	75	130
Co-ODT-Ni	61	89

The first decomposition stage denotes the ligand molecules leave the host structure and the second stage show that the host structures decompose. Similar decomposition stages have been manifested for other Hofmann-type complexes [20-21] and clathrates [22-23].



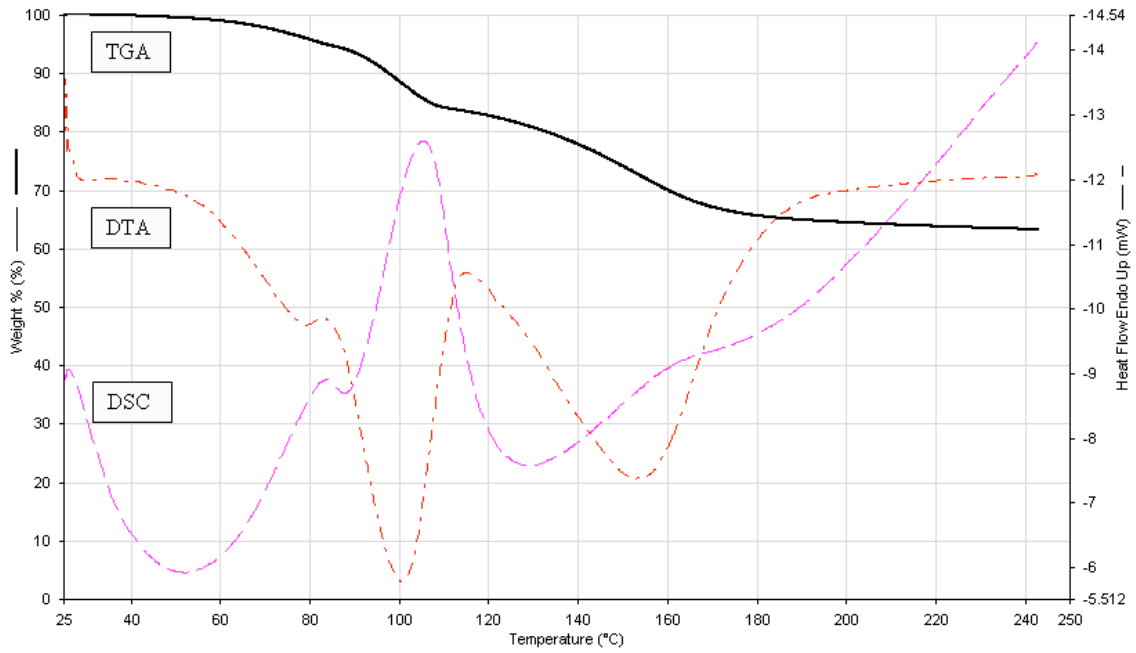
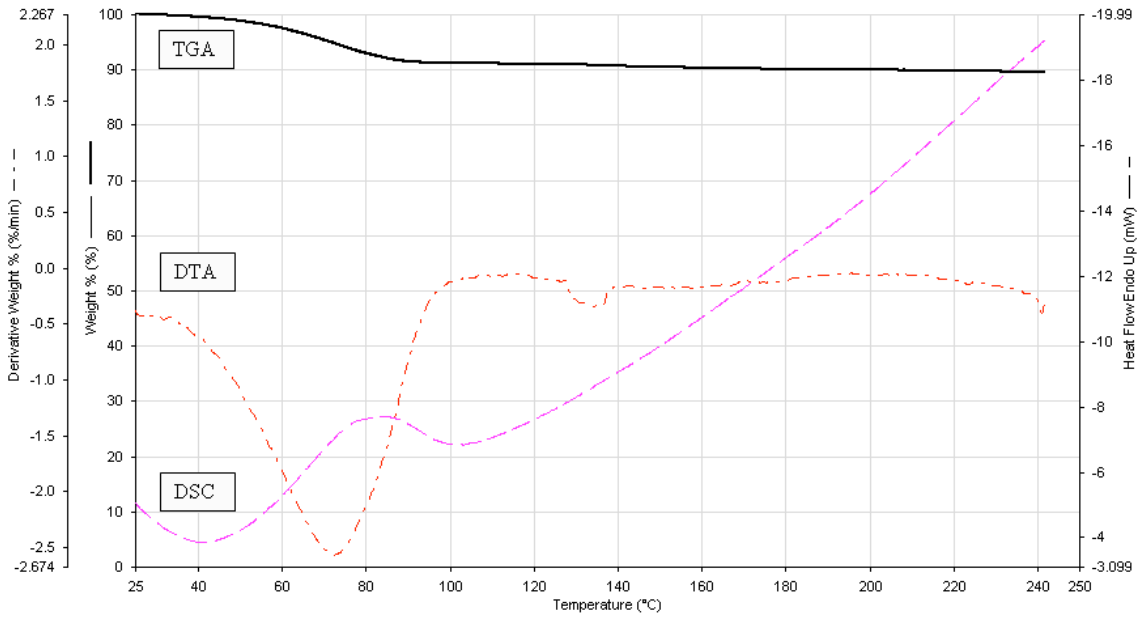
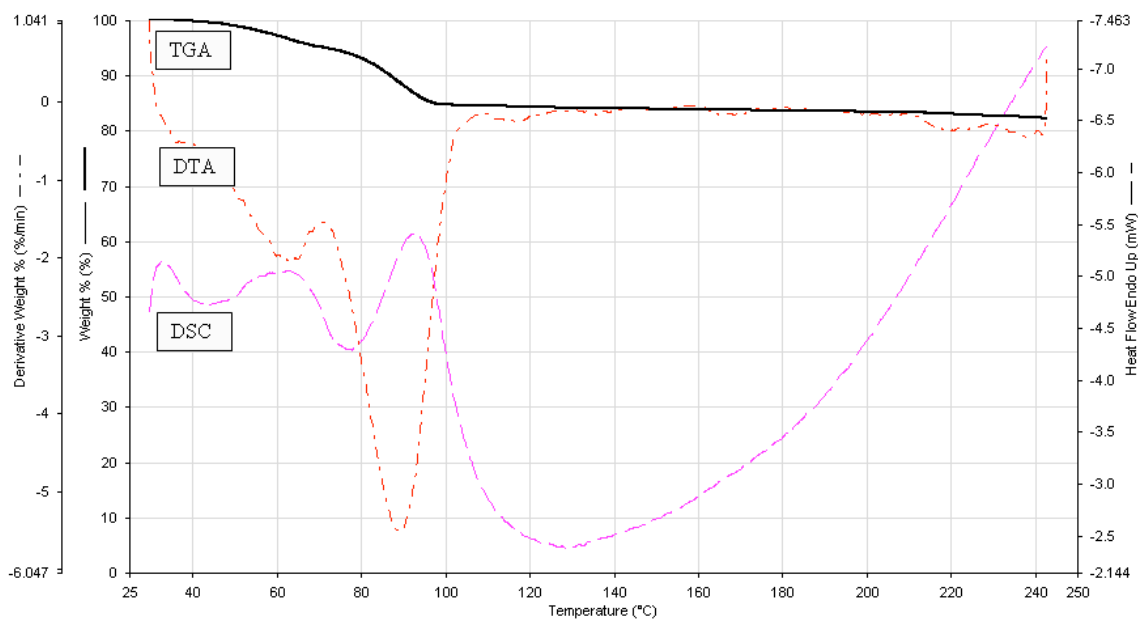


Figure 5. The TGA, DTA and DSC curves of (a) Cd-PDT-Ni and (b) Co-PDT-Ni complexes.





**Figure 6.** The TGA, DTA and DSC curves of (a) Cd-ODT-Ni and (b) Co-ODT-Ni complexes.

As a conclusion the FT-IR spectroscopic studies of four new Hofmann type complexes have shown that they have similar structures consisting of infinite two-dimensional polymeric layers formed with  $\text{Ni}(\text{CN})_4^{2-}$  ions bridged by  $[\text{M}(\text{PDT})]^{+2}$  and  $[\text{M}(\text{ODT})]^{+2}$  ( $\text{M} = \text{Cd}$  and  $\text{Co}$ ) cations. The unpaired electrons in sulfur atoms which were included in ligand PDT and ODT molecules are bonded to metal atoms and form  $-\text{M}-\text{L}-\text{M}-\text{L}-$  chains ( $\text{L} = \text{PDT}$  and  $\text{ODT}$ ). Thus the polymeric layers are held in parallel by  $-\text{M}-\text{L}-\text{M}-\text{L}-$  chains ( $\text{L} = \text{PDT}$  and  $\text{ODT}$ ). In conclusion, the compounds presented in this study,  $\text{M}(\text{PDT}$  or  $\text{ODT})\text{Ni}(\text{CN})_4$  ( $\text{M} = \text{Cd}$  and  $\text{Co}$ ), are new examples of the Hofmann-type complexes.

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