

# Preparation and Characterisation of the Cyano-Bridged Transition Metal Complexes Using N,N'-Diethyl Thiourea as a Ligand

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## ABSTRACT

New cyano bridged transition metal complexes,  $[\text{Cu}(\text{detu})_4\text{Ni}(\text{CN})_4] \cdot 2\text{H}_2\text{O}$  (1) and  $[\text{Zn}(\text{H}_2\text{O})(\text{detu})\text{Ni}(\text{CN})_4] \cdot 2\text{H}_2\text{O}$  (2) (detu = N, N' diethyl thiourea) have been synthesised in powder form. Their structures were illuminated by using spectroscopic, thermal and elemental analysis techniques. The nickel atom exhibits square planar geometry in these complexes by coordinating with the cyano group's nitrogen atoms. The copper atom of 1 is six coordinated with two bridging cyano groups and four detu ligands. In contrast, the zinc atom of 2 is six coordinated with four bridging cyano groups, one detu ligand and one aqua ligand. In addition, the structure of 2 is formed from polymeric layers of  $[\text{Zn}-\text{Ni}(\text{CN})_4]_\infty$  with the detu and aqua ligands bonded to the zinc atom. Thermal stabilities and decomposition products of 1 and 2 were examined in the static air atmosphere between 30 and 900 °C.

## KEYWORDS

tetracyanonickelate(II) complex, N,N'-diethyl thiourea, cyano-bridged complex, vibration spectra, thermal analysis

## 1. Introduction

Thioureas have two amino nitrogens and thiocarbonyl sulphur as potential donor atoms. They can coordinate to metal atoms using any possible donor atom but are commonly bonded to metal atoms via the sulphur atoms.<sup>1</sup> Due to the diversity of donor atoms of thioureas, they may show different binding modes to metal atoms. Numerous studies have been performed on the biological activities and metal complexes of thiourea.<sup>2,3,4</sup> Some thioureas exhibit antituberculosis, antitumor, antibacterial and anticonvulsant features as biological activity.<sup>5,6,7,8</sup> Numerous studies on spectroscopic and antibacterial properties of thiourea metal complexes have been reported.<sup>2,9</sup> A large number of structural studies of metal complexes with a thiourea ligand have been done,<sup>1,2,3,4,8,9</sup> whereas studies on the spectroscopic and crystal structures of metal complexes containing thiourea and cyano ligands are limited.<sup>10,11,12</sup>

The cyano ligand is a multifaceted ligand that can act as  $\sigma$ -donor and  $\pi$ -acceptor. Using donor atoms, the cyano anion (CN<sup>-</sup>) can either provide monodentate (C-) or bidentate (C-, N-) coordination to metal atoms and act as a bridge ligand (M-CN-M') with the participation of both donor atoms. With this feature, the cyano ligand can produce various cyano-bridged transition metal complexes. The square-planar metal complexes with the cyano bridges are generally created by transition metal ions such as nickel, palladium and platinum, which have a  $d^8$  electronic configuration.<sup>13,14</sup> Planar cyano metal anions are widely used to design these complexes.<sup>14,15,16,17</sup> Especially, square-planar tetra cyanometallate(II) ions, i.e.  $[\text{M}(\text{CN})_4]^{2-}$  (M(II) = Ni, Pd or Pt), have been widely used as building blocks of Hofmann type structures.<sup>18,19,21,22,23</sup> The vibrational spectroscopy is extensively used in the determination of the structures of Hofmann type complexes because cyano ligand gives sharp and intense  $\nu(\text{CN})$  stretching vibration between 2200 and 2100  $\text{cm}^{-1}$  in the infrared (IR) and Raman spectra.<sup>18,19,20,24</sup>

This paper reported the synthesis and characterisation of

the cyano-bridged transition metal complexes with N,N'-diethyl thiourea. Ligands with N-donor groups have been used extensively to obtain cyano bridged complexes, but cyano-bridged complexes with S-donor ligands are rare. In this study, two new cyano-bridged complexes given with molecular formula  $[\text{Cu}(\text{detu})_4\text{Ni}(\text{CN})_4] \cdot 2\text{H}_2\text{O}$  (1) and  $[\text{Zn}(\text{H}_2\text{O})(\text{detu})\text{Ni}(\text{CN})_4] \cdot 2\text{H}_2\text{O}$  (2) (detu = N,N'-diethyl thiourea) were synthesised for the first time. In order to obtain these complexes, many experiments have been done by using metals who's the first metal are copper, zinc, and cadmium. Only the complexes with copper and zinc as the first metal have been successfully synthesised. The structures of the resulting complexes were elucidated by element analysis, IR and Raman spectra, and thermal analysis.

## 2. Experimental

### 2.1. Materials

Copper(II) chloride dihydrate ( $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ , 99%, Merck), zinc(II) chloride ( $\text{ZnCl}_2$ , 96%, Merck), nickel(II) chloride hexahydrate ( $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ , 97%, Merck), potassium cyanide (KCN, 96%, Sigma-Aldrich) and N,N'-diethyl thiourea ( $\text{C}_5\text{H}_{12}\text{N}_2\text{S}$ , 99%, Merck) were purchased and used.

### 2.2. Syntheses of the complexes

#### Synthesis of $\text{K}_2[\text{Ni}(\text{CN})_4] \cdot \text{H}_2\text{O}$

1 mmol of  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  (0.238 g) was dissolved in 100 ml of distilled water. 4 mmol of KCN (0.260 g) dissolved in 100 ml of distilled water was added dropwise to this solution. The prepared solution was stirred with a magnetic stirrer for 3 hours and then allowed to stand at room temperature. Within two weeks, the  $\text{K}_2[\text{Ni}(\text{CN})_4] \cdot \text{H}_2\text{O}$  complex was obtained.

#### Synthesis of $\text{M}[\text{Ni}(\text{CN})_4] \cdot \text{H}_2\text{O}$ [M = Cu(II) or Zn(II)]

1 mmol of  $\text{K}_2[\text{Ni}(\text{CN})_4] \cdot \text{H}_2\text{O}$  (0.259 g) complex was dissolved in distilled water by mixing with a magnetic stirrer for 5 minutes. The aqueous solution of 1 mmol metal chloride ( $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  = 0.170 g or  $\text{ZnCl}_2$  = 0.136 g) was added drop by drop to the

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tetracyano nickelate solution. The solutions were stirred in the magnetic stirrer at room temperature for 3 hours, and then the  $M[Ni(CN)_4] \cdot H_2O$  complex was obtained.

#### Synthesis of $[Cu(detu)_4Ni(CN)_4] \cdot 2H_2O$ and $[Zn(H_2O)(detu)(CN)_4] \cdot 2H_2O$

1 mmol 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 dissolved in 25 ml distilled water. Into this solution, 2 mmol of the ligand dissolved in a mixture of methanol (50%), ethanol (25%) and distilled water (25%) ( $detu = 0.264$  g) was added drop by drop. The solution obtained was stirred in a magnetic stirrer at 40 °C for 3 hours, and then the resulting complexes were filtered and washed with distilled water and ethanol, respectively, and dried in air. Analyses of these complexes were done for C, H and N: Anal. Found (Calcd.) (%) for  $C_{24}H_{52}N_{12}O_2S_4CuNi$  ( $M_w = 791.25$  g/mol) : C, 36.76 (36.43); H, 6.81 (6.62); N, 20.39 (21.24); for  $C_9H_{18}N_6O_3SZnNi$  ( $M_w = 414.43$  g/mol) : C, 25.56 (26.08); H, 3.16 (4.38); N, 20.02 (20.28).

### 2.3. Measurements

The complexes obtained were analysed for C, H, and N with a LECO CHN-932 analyser at the Middle East Technical University Central Laboratory in Ankara, Turkey. The infrared spectra were recorded on a Perkin Elmer 100 infrared spectrometer using KBr pellets between 4000 and 400  $cm^{-1}$  (2  $cm^{-1}$  resolution), calibrated using polystyrene and  $CO_2$  bands. Raman spectrum of the obtained complexes was recorded on a Bruker Senterra Dispersive Raman apparatus between 4000 and 250  $cm^{-1}$  using 785 nm laser excitation. Thermal analysis was carried out on Perkin Elmer Diamond TG/DTA thermal analyser instrument in a static air atmosphere with a heating rate of 10 K  $min^{-1}$  in the range of 30–900 °C.

## 3. Results and Discussion

### 3.1. Spectroscopic studies of the complexes

#### Vibrations of the *detu* ligand

The vibration spectra of the synthesised complexes are shown in Figs. 1 and 2.

Experimentally obtained vibration frequencies of *detu* and the previously determined vibration assignments of the N,N'-dimethyl thiourea (*dmtu*) molecule are given in Table 1.<sup>25,26</sup> The vibration assignments of the *detu* ligand were not available in the literature. According to our research, the *dmtu* and *detu* have very similar spectral properties. Therefore, the *dmtu* vibration bands in the literature were used to compare with the *detu* vibration bands. In addition, the vibration assignments and wavenumbers of the ethyl group were taken from N-ethyl thiourea.<sup>27</sup>

In the IR spectrum of the *detu* ligand, characteristic vibration bands in three frequency regions are expected. These bands are  $\nu(NH)$  between 3435 and 3270  $cm^{-1}$ ,  $\nu(CN)$  at 1564  $cm^{-1}$  and  $\nu(CS)$  at 756  $cm^{-1}$ . When the *detu* ligand binds to metal atoms through sulphur atoms, significant shifts occur in the characteristic bands of the ligand. These shifts generally manifest themselves in the  $\nu(CN)$  and  $\nu(CS)$  bands.<sup>28,29</sup> Some of the  $\nu(NH)$  and  $\nu(OH)$  stretching vibration bands overlap between 3100 and 3450  $cm^{-1}$  because of the expansion of the bands. This expansion may arise from the coordination or hydrogen bonds and create spectral complexity that can not be completely unregulated. In the vibration (infrared and Raman) spectra of 1 and 2, the  $\nu(NH)$  stretching vibrations of the ligand were observed as broad bands in strong or medium density between 3100 and 3450  $cm^{-1}$ . When the *detu* ligand is attached to the metal ion via the sulphur atom, the effect of the metal on the ligand becomes more pronounced in the N-C and C=S groups of the ligand. In this case, while the  $\nu(CN)$  vibration frequencies shift upwards,

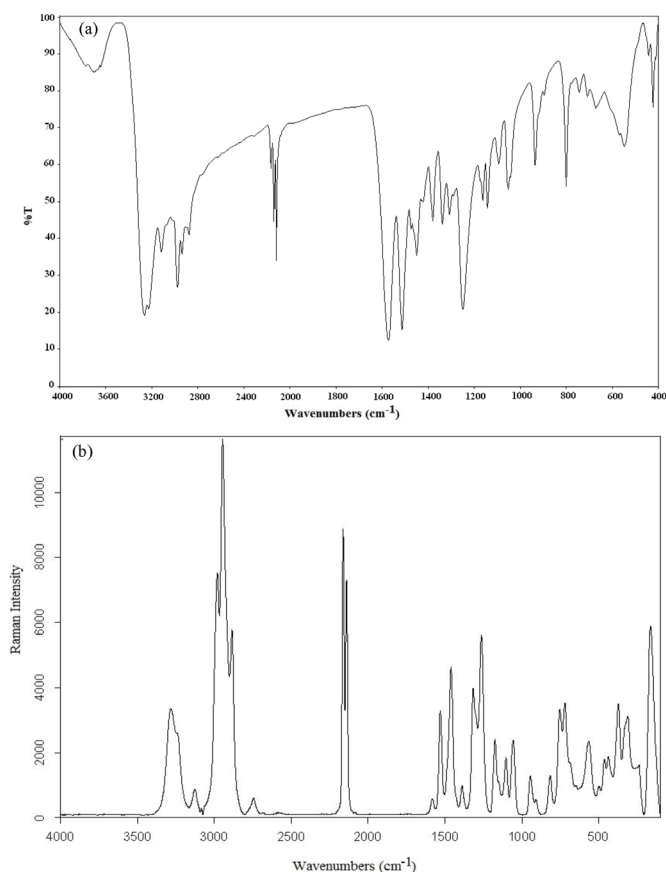


Figure 1 The IR (a) and Raman (b) spectrum of complex 1.

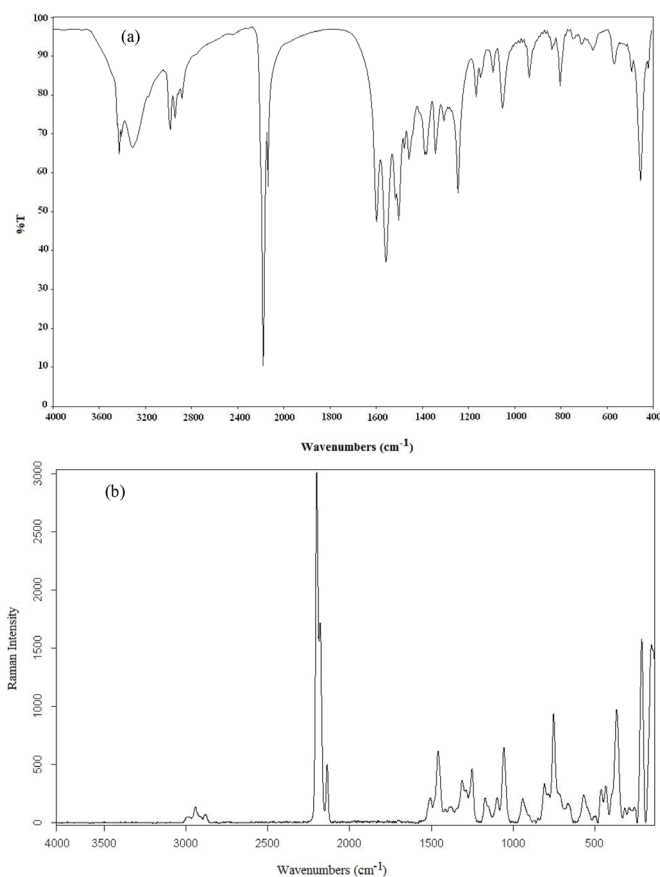


Figure 2 The IR (a) and Raman (b) spectrum of complex 2.

the  $\nu(\text{CS})$  stretching vibration frequencies are expected to shift downwards.<sup>28,29</sup> In the infrared spectrum of the detu ligand, the  $\nu(\text{CN})$  frequency was observed at 1564  $\text{cm}^{-1}$ . As expected, the  $\nu(\text{CN})$  frequency shifted to the higher frequency region as a strong and sharp band in the range of 5–30  $\text{cm}^{-1}$ . These apparent shifts in the spectra of **1** and **2** prove that the detu ligand is attached to the metal atoms through sulphur atoms. While  $\nu(\text{CS})$  stretching vibrations have appeared as a single sharp band at 756  $\text{cm}^{-1}$  in the infrared spectra of the ligand, the  $\nu(\text{CS})$  stretching vibrations in the infrared spectrum of the complexes have shifted to the high-frequency region and in the Raman spectrum to the low-frequency region.

On the contrary, in some complexes, these vibrations are strongly coupled with other modes of ligand, and therefore the  $\nu(\text{CS})$  stretching vibration frequencies shift upward. Similar observations were performed in ethyl thiourea complexes.<sup>1,30</sup> As shown in Table 1,  $\nu(\text{CH}_3)$  and  $\nu(\text{CH}_2)$  stretching vibrations in the infrared spectrum of ligand are found in the range of 3070–2840  $\text{cm}^{-1}$ . In the complexes, these stretching vibrations were identified in the range of 3070–2874  $\text{cm}^{-1}$ . It was observed that these stretching vibration frequencies shifted significantly to low or high-frequency regions according to the free ligand. In addition, the ligand includes  $\text{C}=\text{C}$  stretching vibrations between 1700 and 1200  $\text{cm}^{-1}$ ,  $\text{C}=\text{N}$  stretching vibrations between 1400 and 1300  $\text{cm}^{-1}$ , and  $\text{C}-\text{H}$  bond deformation vibrations between

1460 and 1400  $\text{cm}^{-1}$ . These vibration bands show upward or downward shifts in frequency in the complexes compared to that of the free ligand.

### Water vibrations

Water molecules have three fundamental vibrations: asymmetric and symmetric  $\nu(\text{OH})$  stretching and  $\delta(\text{HOH})$  bending. In general,  $\nu(\text{OH})$  stretching and  $\delta(\text{HOH})$  bending vibrations are found in the 3700–3200  $\text{cm}^{-1}$  region and the 1700–1600  $\text{cm}^{-1}$  region, respectively. In addition, lattice or coordinated water absorbs between 3550 and 3200  $\text{cm}^{-1}$ .<sup>31,32</sup> It was observed from the infrared spectra of the complexes that there are water molecules in the structure of the complexes, and it was determined that the water molecules in the complexes act as crystal water (uncoordinated water molecules). The  $\nu(\text{OH})$  of water molecules in the complexes were observed as broadband between 4000 and 3500  $\text{cm}^{-1}$  for uncoordinated water molecules of the complexes and at 3454  $\text{cm}^{-1}$  for coordinated water molecules of complex **2**. In the spectrum of complex **2**, stretching bands of coordinated water molecules with stretching bands of  $\text{NH}$  vibrations in the detu ligand overlap in the range of 3450–3200  $\text{cm}^{-1}$ . In addition,  $\delta(\text{OH})$  bending vibrations in the complexes overlap with other vibration bands in ligands. Elemental analysis and thermal analysis results supported the presence of water molecules in the complexes.

**Table 1** The vibrational wavenumbers of detu in complexes ( $\text{cm}^{-1}$ ).

Assignments <sup>a</sup>	dmtu <sup>a</sup> ( $\text{CHCl}_3$ ) IR	detu ( $\text{CHCl}_3$ ) IR	<b>1</b>		<b>2</b>	
			IR	Raman	IR	Raman
$\nu(\text{NH})$ free, trans	3440	3427 w	-	-	3418 w	-
$\nu(\text{NH})$ bonded, trans	3355	3270 vs	3261 vs 3224 vs	-	3300 m	-
Fermi resonance	3150	-	3114 w	-	3167 sh	-
$\nu(\text{CH}_3)^b$	2940 <sup>c</sup>	3069 m	3070 sh	-	-	-
$\nu(\text{CH}_3)^b$	2940 <sup>b</sup>	3018 w	3015 vw	-	2985 sh	2994 vw
$\nu(\text{CH}_3)^b$	-	2976 s	2975 m	2980 vw	2975 m	-
$\nu_{\text{as}}(\text{CH}_2)^c$	2927 <sup>c</sup>	2937 w	2935 w	-	2934 w	2942 w
$\nu_s(\text{CH}_2)^c$	2855 <sup>c</sup>	2876 w	2897 vw	-	2874 w	2880 vw
( $\text{NCH}_3$ )	2840	-	2874 w	2880 vw	-	-
70% $\nu_a(\text{CN})$ + 30% $\delta_a(\text{NH})$	1555	1564 vs	1569 vs	1584 w	1594 m	-
79% $\delta_s(\text{NH})$ + 10% $\nu(\text{CS})$ + 10% $\delta(\text{NCN})$	1504	1504 vs	1511 vs	1528 m	1553 m	1507 w
$\delta_a(\text{CH}_3)$	1471	1476 w	1473 vw	1468 m	1498 w	1460 m
$\delta(\text{CH}_2)^c$	1447 <sup>c</sup>	-	1448 m	-	1474 vw	-
76% $\delta_a(\text{NH})$ +24% $\nu_a(\text{CN})$ or 62% $\nu_s(\text{CN})$ +20% $\delta_s(\text{NH})$ + 18% $\nu(\text{CS})$	1420	1454 m	1419 vw	1457 m	1454 w	1415 vw
$\delta_s(\text{CH}_3)$	1354	1339 s	1378 m	1430 w	1385 m	1382 w
2x667 or $\nu(\text{CS})$ + $\delta(\text{NCS})$	1290	1284 m	1337 m	1301 s	1339 w	1312 w
$\delta(\text{NH})(47)^b$ , $\nu(\text{CN})(21)^b$ , $\delta(\text{NCN})(11)^b$	1260 <sup>b</sup>	1242 w	1247 vs	1233 w	1241 m	1252 m
$\nu(\text{NC})(58)^b$ , $\delta(\text{NH})(13)^b$	1188 <sup>b</sup>	1168 w	1161 w	1203 w	1162 w	1172 w
$\nu(\text{NC})(44)^b$ , $\tau(\text{CH}_3)(16)^b$	1148 <sup>b</sup>	1140 w	1141 w	1167 vw	1144 vw	1152 sh
( $\text{CH}_3$ ) rock or 2x $\delta(\text{NCS})$	1088	1090 m	1092 w	1103 w	1089 w	1098 w
79% $\nu_s(\text{C}'\text{N})$ +21% $\delta(\text{NCN})$	1048	1050 vs	1050 s	1028 m	1050 w	1057 m
91% $\nu_a(\text{C}'\text{N})$ +9% $\delta_a(\text{CNC}')$	882	878 w	935 s	-	933 w	942 w
83% $\nu(\text{CS})$ +10% $\nu_s(\text{CN})$ + 7% $\nu_s(\text{C}'\text{N})$	752	756 vs	799 vs	732 vs	799 m	753 s
( $\text{NH}$ ) out-of-plane bending	722	696 vw	743 w	720 m	744 vw	716 sh
53% $\delta_a(\text{CNC}')$ +35% $\delta(\text{NCS})$ + 11% $\nu_a(\text{C}'\text{N})$	650	666 vs	668 w	671 m	667 w	666 w
$\delta(\text{NCS})$	551	594 sh	602 sh	617 vw	-	569 w
33% $\delta(\text{NCN})$ +31% $\nu_s(\text{C}'\text{N})$ + 21% $\delta_s(\text{CNC}')$ +16% $\nu_s(\text{CN})$	448	-	453 sh	497 w	-	502 vw

Abbreviations used; s strong, m medium, w weak, sh shoulder, v very,  $\nu$  stretching,  $\delta$  bending and  $\tau$  rocking.

<sup>a</sup>Taken from Ref.<sup>25</sup>; <sup>b</sup>Taken from Ref.<sup>26</sup>; <sup>c</sup>Taken from Ref.<sup>27</sup>

### Vibrations of the tetracyano nickelate group

In the complexes obtained, vibration bands belonging to the tetracyano nickelate group are determined according to vibrational data of the tetracyano nickelate ion of the  $\text{Na}_2[\text{Ni}(\text{CN})_4]$  salt in the solid form.<sup>33</sup> The wavenumbers belonging to the tetracyano nickelate group in the complexes. Data for the  $\text{K}_2[\text{Ni}(\text{CN})_4] \cdot \text{H}_2\text{O}$  complex are given in Table 2. The tetracyano nickelate ion has a square planar structure. The Ni atom in this ion is located at the intersection of the diagonals. The nitrogen atoms are at the corners of the squares, and the carbon atoms are located between the nickel and nitrogen atoms. Since the tetracyano nickelate ions in the salts are not bound by  $\text{K}^+$  (or  $\text{Na}^+$ ) cations, they can be considered as isolated units in  $D_{4h}$  symmetry.<sup>34,35</sup> Therefore, when the  $\text{Ni}-\text{C}\equiv\text{N}-\text{M}$  type bridge and  $\text{Ni}-\text{C}\equiv\text{N}$  type terminal groups occur in this salt, the changes in the cyano vibration wavenumbers in this group gain importance in evaluating the structure of the complexes. In the IR spectra of **1** and **2**, the bridge-type  $\nu(\text{CN})$  stretching vibrational wavenumbers is greater than those of the terminal-type. The  $\nu(\text{CN})$  stretching vibrational wavenumbers of the terminal-type is close to that of  $\text{K}_2[\text{Ni}(\text{CN})_4] \cdot \text{H}_2\text{O}$ . From the vibration spectra of the complexes, it can be decided that the cyano groups act as a bridge or terminal ligand by examining the shifts and splitting in the frequency values of the stretching vibration bands.

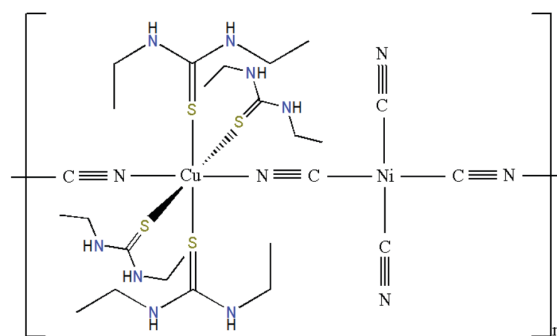
The most characteristic band in cyano complexes is the  $\nu(\text{CN})$  stretching vibration band belonging to the cyano group. This band can be easily determined in the vibration spectra of **1** and **2** since it is a sharp and strong band between 2200 and 2000  $\text{cm}^{-1}$ .<sup>31</sup> In the vibration spectra of **1** and **2**, the  $\nu(\text{CN})$  stretching vibrations have one infrared active ( $E_u$  mode) and two Raman active ( $A_{1g}$  and  $B_{1g}$  modes) modes. While the  $E_u$  symmetrical  $\nu(\text{CN})$  stretching vibration band in the infrared spectra of  $\text{K}_2[\text{Ni}(\text{CN})_4] \cdot \text{H}_2\text{O}$  is found at 2120  $\text{cm}^{-1}$ , the stretching vibrations with  $A_{1g}$  and  $B_{1g}$  symmetry resulting from Raman active  $\nu(\text{CN})$  vibration are observed at 2160  $\text{cm}^{-1}$  and 2137  $\text{cm}^{-1}$ , respectively. If there are both  $\text{Ni}-\text{C}\equiv\text{N}-\text{M}$  type bridges and  $\text{Ni}-\text{C}\equiv\text{N}$  terminal cyano groups in the structures of the cyano-bridged transition metal complexes, the  $\nu(\text{CN})$  stretching vibration band undergoes a split in the infrared spectrum.<sup>36</sup> In complex **1**, the  $\nu(\text{CN})$  stretching vibrations of the bridging cyano group are found at 2166 and 2137  $\text{cm}^{-1}$ , whereas the terminal cyano groups are observed at 2114  $\text{cm}^{-1}$  (Table 2). According to this, the  $\nu(\text{CN})$  stretching vibration frequencies in the IR spectrum of **1** are higher, around 17 and 46  $\text{cm}^{-1}$ , than those for  $\text{K}_2[\text{Ni}(\text{CN})_4] \cdot \text{H}_2\text{O}$  salt. Shifts to high frequencies are thought to occur due to mechanical coupling between the internal vibration modes of the tetracyano nickelate group and the  $\text{M}-\text{NC}$  vibrations.<sup>18,37</sup> In the IR spectrum of **2**, the  $\nu(\text{CN})$  stretching vibration frequencies are observed at 2128 and 2169  $\text{cm}^{-1}$  (Table 2). These vibration frequencies are higher, around 8 and 49  $\text{cm}^{-1}$ , than those for  $\text{K}_2[\text{Ni}(\text{CN})_4] \cdot \text{H}_2\text{O}$  salt. Therefore, all cyano groups in complex **2** act as bridged ligands. In addition,  $A_{1g}$  and  $B_{1g}$  modes resulting from Raman active  $\nu(\text{CN})$  stretching vibration have shifted to the higher frequency region in the spectrum of the complexes. There are three basic vibration bands of the cyano ligand in the IR spectrum in the range of 400–600  $\text{cm}^{-1}$ :  $\nu(\text{NiC})$ ,  $\pi(\text{NiCN})$  and  $\delta(\text{NiCN})$ . The most important of these bands is the in-plane bending vibration band  $\delta(\text{NiCN})$ . This band is found at 414  $\text{cm}^{-1}$  in the IR spectrum of  $\text{K}_2[\text{Ni}(\text{CN})_4] \cdot \text{H}_2\text{O}$  complex. In the spectrum of the complexes,  $\delta(\text{NiCN})$  is observed to shift the higher frequency region. The shift seen in this band is dependent on the metal.

According to the obtained spectroscopic results, while the cyano ligand acts as a terminal and bridging ligand for **1**, it only acts as a bridging ligand for **2**. In addition, the detu (for **1**) and detu and aqua (for **2**) ligands bind to metal atoms ( $\text{Cu}(\text{II})$  or  $\text{Zn}(\text{II})$ ) to form complexes. The representative illustration of the complexes is shown in Figs. 3 and 4.

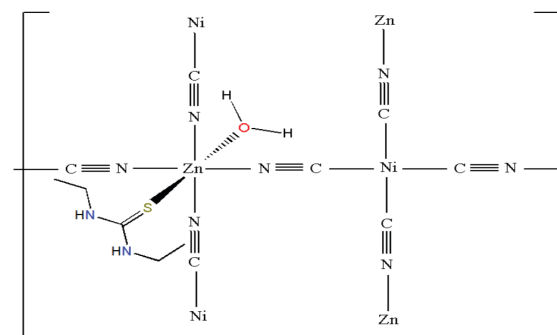
**Table 2** The vibrations wavenumbers of the  $[\text{Ni}(\text{CN})_4]^{2-}$  group in the complexes ( $\text{cm}^{-1}$ ).

Assignments <sup>33</sup>	$\text{K}_2[\text{Ni}(\text{CN})_4] \cdot \text{H}_2\text{O}$	<b>1</b>	<b>2</b>
$A_{1g} \nu(\text{CN})$	(2160) vs	(2162) vs	(2201) vs, (2180) w
$B_{1g} \nu(\text{CN})$	(2137) m	(2140) vs	(2137) m
$E_u \nu(\text{CN})$	2120 vs	2166 m, 2137 s, 2114 vs	2169 vs, 2128 m
$\nu(^{13}\text{CN})$	2084 vw	2078 vw	-
$E_u \nu(\text{NiC})$	542 w	546 vs	565 w
$A_{2u} \pi(\text{NiCN})$	443 w	444 w	489 vw
$E_u \delta(\text{NiCN})$	414 vs	423 s	451 s

Abbreviations used; s strong, m medium, w weak, v very. The symbols  $\nu$ ,  $\delta$ , and  $\pi$  refer to valence, in-plane and out-of-plane vibrations, respectively. \*Raman spectra are given in parenthesis



**Figure 3** Representation of molecular structure of complex **1** (Uncoordinated water molecules are not shown in the figure).



**Figure 4** Representation of molecular structure of complex **2** (Uncoordinated water molecules are not shown in the figure).

### 3.2. Thermal study

Thermal decomposition curves of **1** and **2** are obtained in a static air atmosphere between 30 and 900 °C. Thermal curves of **1** and **2** are given in Figs. 5 and 6. When these curves are examined, the thermal decomposition of **1** and **2** takes place in two stages, and these decomposition curves support the unit formulas of **1** and **2**. Thermal decomposition curves of **1** and **2** are similar and stable up to 97 °C. In the first step, the detu and water molecules were endothermically separated from the structure of the complexes in the temperature range of 97–359 °C (Found (Calcd.) (%) = 68.76 (71.39) for **1** and 97–417 °C (Found (Calcd.) (%) = 41.24 (44.43) for **2**). In the second step, the cyano groups were between 359 and 752 °C for **1** [Found (Calcd.) (%) = 11.67 (13.15)] and between 417 and 682 °C for **2** [Found (Calcd.) (%) = 23.12 (25.11)] exothermically released from the structures of the complexes. In the complexes, the DTA curve of detu, cyano and water molecules followed a complex process, with maximum peaks at 300, 322, 372 and 514 °C for **1**, and 261, 346, 426, 565 and 592 °C for **2**. The peaks observed



in 372 and 514 °C for **1** and 426, 565 and 592 °C for **2** belong to cyano ligands. Finally, metal oxides (CuO, ZnO and NiO) were found as final products [Found (Calcd.) (%) = 19.57 (19.49) for **1** and 35.64 (37.66) for **2**]. Similar decomposition products have been observed in previously made cyano complexes.<sup>32, 38</sup>

#### 4. Conclusions

We have reported the spectroscopic and thermal analysis of two new cyano-bridged complexes as  $[\text{Cu}(\text{detu})_4\text{Ni}(\text{CN})_4] \cdot 2\text{H}_2\text{O}$  (**1**) and  $[\text{Zn}(\text{H}_2\text{O})(\text{detu})\text{Ni}(\text{CN})_4] \cdot 2\text{H}_2\text{O}$  (**2**) (detu = N, N' diethyl thiourea). According to the spectroscopic analysis of these complexes, the environment of the nickel atom in the complexes is showed square planar geometry by binding four cyano ligands to the nickel atoms, while the environment of the copper and zinc atoms in the complexes is showed octahedral geometry. The environment of the copper atom in complex **1** is surrounded by two cyano and four detu ligands and forms the one-dimensional structure of the complex. The environment of the zinc atom in complex **2** is surrounded by four cyano ligands, one aqua ligand and one detu ligand in an octahedral geometry, and the cyano ligands are bonded between the zinc and nickel atoms to form  $[\text{Zn}-\text{Ni}(\text{CN})_4]_\infty$  polymeric layers. The detu and aqua ligands are bound from above and below to the zinc atoms in these layers. In these two complexes, the detu ligand acted only as a monodentate ligand by binding to metal atoms (Cu(II) or Zn(II)) from the S atom. The structures of the resulting complexes were also supported using thermal and elemental analysis techniques.

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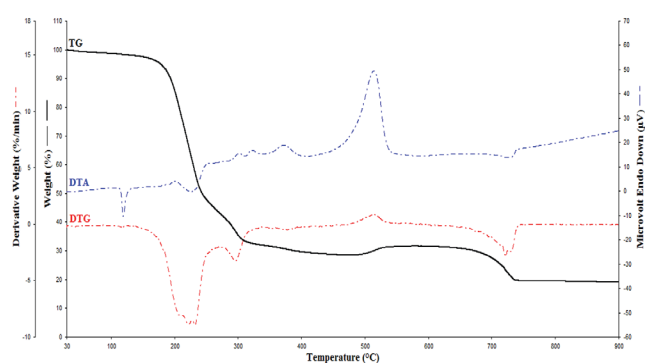


Figure 5 The TG, DTG and DTA curves of **1**.

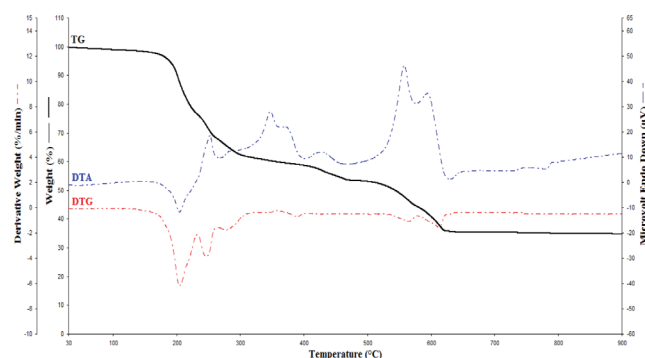


Figure 6 The TG, DTG and DTA curves of **2**.

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