

# Polynuclear Complexes of Nickel(II) with Cyanide as Bridging Ligand

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The complexes of the types  $[\text{NiL}_2][\text{Ni}(\text{CN})_4] \cdot x\text{H}_2\text{O}$  (L = 1,2-diaminopropane (1,2-pn),  $x = 1$ ; L = 2,2'-bipyridine (bpy),  $x = 2$ ; L = *o*-phenanthroline (phen),  $x = 2$ ),  $[\text{NiL}][\text{Ni}(\text{CN})_4] \cdot x\text{H}_2\text{O}$  (L = triethylenetetramine (tta),  $x = 0$ ; L = tris(2-aminoethyl)amine (taa),  $x = 2$ ), and  $[\text{Ni}(\text{dien})(\text{H}_2\text{O})][\text{Ni}(\text{CN})_4]$  (dien = diethylenetriamine) have been prepared and studied by elemental analyses, thermal analyses, IR and electronic spectroscopy, and magnetochemical measurements. Although some of the complexes have been characterized by temperature-dependent magnetic susceptibilities in the range 94–296 K the exchange interaction was not found for  $[\text{Ni}(1,2\text{-pn})_2][\text{Ni}(\text{CN})_4] \cdot 2\text{H}_2\text{O}$ ,  $[\text{Ni}(\text{dien})(\text{H}_2\text{O})][\text{Ni}(\text{CN})_4]$ , and  $[\text{Ni}(\text{bpy})_2][\text{Ni}(\text{CN})_4] \cdot 2\text{H}_2\text{O}$ . The splitting of bands  $\nu(\text{C}\equiv\text{N})$  in infrared spectra indicates the existence of terminal and bridged cyanide groups. Polymeric structure with cyanide bridges between square-planar Ni(II) ( $S = 0$ ) and octahedral Ni(II) ( $S = 1$ ) is proposed.

The aim of our work was the preparation and physicochemical study of the polynuclear complexes of compositions  $[\text{NiL}_2][\text{Ni}(\text{CN})_4] \cdot x\text{H}_2\text{O}$  (L = 1,2-diaminopropane (1,2-pn),  $x = 1$ ; L = 2,2'-bipyridine (bpy),  $x = 2$ ; L = *o*-phenanthroline (phen),  $x = 2$ ),  $[\text{NiL}][\text{Ni}(\text{CN})_4] \cdot x\text{H}_2\text{O}$  (L = triethylenetetramine (tta),  $x = 0$ ; L = tris(2-aminoethyl)amine (taa),  $x = 2$ ), and  $[\text{Ni}(\text{dien})(\text{H}_2\text{O})][\text{Ni}(\text{CN})_4]$  (dien = diethylenetriamine). Analogous compound of the composition  $[\text{Ni}(\text{en})_2][\text{Ni}(\text{CN})_4]$  (en = ethylenediamine) is well known. The synthesis and thermal properties have been described in [1]. Černák *et al.* [2] successfully solved the crystal and molecular structure of this polymeric complex. The structure is built up of infinite  $[-\text{Ni}(\text{en})_2-\text{NC}-\text{Ni}(\text{CN})_2-\text{CN}-]_n$  chains. The *trans*-coordinated cyano groups form bridges between square-planar coordinated Ni(II) atoms and octahedral coordinated Ni(II) atoms. The structure of water solvate of the polymeric complex  $[\text{Ni}(\text{en})_2][\text{Ni}(\text{CN})_4] \cdot 2.16\text{H}_2\text{O}$  is different [3]. Chains are formed by *trans*- $\text{Ni}(\text{en})_2-\mu-(\text{NC})_2$ , *cis*- $\mu-(\text{NC})_2\text{Ni}(\text{CN})_2$ , and *cis*- $\mu-(\text{CN})_2\text{Ni}(\text{en})_2$  groups. Orendáč *et al.* [4] characterized the complex  $[\text{Ni}(\text{en})_2][\text{Ni}(\text{CN})_4]$  by measuring the temperature dependence of magnetic susceptibility in the range 50 mK–20 K and found a weak antiferromagnetic exchange interaction ( $D/k_B = (6.1 \pm 0.2)$  K,  $J/k_B = (-0.09 \pm 0.01)$  K,  $g = (2.28 \pm 0.01)$ ). Recently the compound  $[\text{Ni}(\text{tn})_2][\text{Ni}(\text{CN})_4]$  (tn = 1,3-diaminopropane) was described [5]. Feigl *et al.* [6] pre-

pared the coordination compound  $[\text{Ni}(\text{bpy})_2][\text{Ni}(\text{CN})_4]$  by reaction of  $\text{Ni}(\text{CN})_2$  and bpy in ethanol. Gainsford and Curtis [7] solved the crystal and molecular structure of the complex  $[\text{Ni}(\text{hmttd})][\text{Ni}(\text{CN})_4] \cdot \text{H}_2\text{O}$  (hmttd = *N-meso*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene). The structure contains  $\text{CN}^-$  bridges between square-planar coordinated Ni(II) and octahedral coordinated Ni(II). Černák *et al.* [8] reviewed the crystallographic data of the  $[\text{Ni}(\text{CN})_4]^{2-}$  compounds. These coordination compounds have ionic, one-dimensional, a two-dimensional or a three-dimensional structure.

## EXPERIMENTAL

The starting material  $\text{K}_2[\text{Ni}(\text{CN})_4]$  was prepared by reaction between KCN and  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  in the mole ratio 4 : 1 in aqueous solution. The compound  $\text{Ni}(\text{en})_2(\text{NO}_3)_2$  was obtained by the direct reaction between  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and en in the mole ratio 1 : 2 in aqueous solution. 1,2-Diaminopropane (racemic mixture), chemically pure, tris(2-aminoethyl)amine (95 %), and triethylenetetramine (tech. 70 %) were products of Fluka and diethylenetriamine, chemically pure, of Loba Feinchemie.

Elemental analyses of carbon, hydrogen, and nitrogen were performed on Fisons EA1108 CHN instrument. Nickel was determined gravimetrically by using dimethylglyoxime.

The IR spectra were measured on Specord IR 80 spectrophotometer in the  $\bar{\nu}$  range 400–4000  $\text{cm}^{-1}$  by the nujol technique.

The electron absorption spectra (EAS) were recorded in nujol mull on the Specord M40 UV VIS spectrophotometer (Zeiss, Jena) in the  $\bar{\nu}$  range 11 000–30 000  $\text{cm}^{-1}$ .

Thermoanalytical study was recorded on the derivatograph Q-1500 (MOM, Budapest) in the air atmosphere with sample mass of 150 mg and the temperature gradient 2.5  $^{\circ}\text{C min}^{-1}$ .

The magnetic susceptibility at room temperature was measured using the Faraday method on a laboratory-designed magnetic device (Development Laboratories and Workshops, Palacký University, Olomouc). The temperature dependence of magnetic susceptibilities was measured in the 94–296 K range using the Gouy method on a magnetic balance (Newport Instruments, UK). The  $\text{Hg}[\text{Co}(\text{SCN})_4]$  was used as a calibrant. Diamagnetic corrections were made with Pascal's constants for all the constituent atoms and magnetic moments were calculated using the equation  $\mu_{\text{eff}}/\mu_{\text{B}} = 2.828 \text{ cm}^{-3/2} \text{ mol}^{1/2} \text{ K}^{-1/2} (\chi_{\text{m}} T)^{1/2}$ .

### $[\text{Ni}(1,2\text{-pn})_2][\text{Ni}(\text{CN})_4] \text{H}_2\text{O}$

A solution of  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  (0.53 g; 2.23 mmol) and 1,2-diaminopropane (0.38  $\text{cm}^3$ , 4.46 mmol) in 25  $\text{cm}^3$  of water was added to a solution of  $\text{K}_2[\text{Ni}(\text{CN})_4]$  (0.54 g; 2.24 mmol) in 25  $\text{cm}^3$  of water. The reaction mixture was concentrated by heating to 25  $\text{cm}^3$ . After cooling a solid was obtained. The pink substance was filtered off, washed with water and dried at 40  $^{\circ}\text{C}$ .

### $[\text{Ni}(\text{dien})(\text{H}_2\text{O})][\text{Ni}(\text{CN})_4]$

A solution of  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (0.65 g; 2.23 mmol) and diethylenetriamine (0.24  $\text{cm}^3$ , 2.23 mmol) in 25  $\text{cm}^3$  of water was added to a solution of  $\text{K}_2[\text{Ni}(\text{CN})_4]$  (0.54 g; 2.24 mmol) in 25  $\text{cm}^3$  of water. The pink precipitate was filtered off, washed with water and dried at 40  $^{\circ}\text{C}$ .

$[\text{Ni}(\text{tta})][\text{Ni}(\text{CN})_4]$  (starting materials  $\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  (0.82 g; 2.24 mmol), triethylenetetramine

(0.34  $\text{cm}^3$ , 2.26 mmol),  $\text{K}_2[\text{Ni}(\text{CN})_4]$  (0.54 g; 2.24 mmol)),  $[\text{Ni}(\text{taa})][\text{Ni}(\text{CN})_4] 2\text{H}_2\text{O}$  (starting materials  $\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  (0.82 g; 2.24 mmol), tris(2-aminoethyl)amine (0.33  $\text{cm}^3$ , 2.21 mmol),  $\text{K}_2[\text{Ni}(\text{CN})_4]$  (0.54 g; 2.24 mmol)),  $[\text{Ni}(\text{bpy})_2][\text{Ni}(\text{CN})_4] 2\text{H}_2\text{O}$  (starting materials  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  (0.53 g; 2.23 mmol), bpy (0.35 g; 2.24 mmol),  $\text{K}_2[\text{Ni}(\text{CN})_4]$  (0.54 g; 2.24 mmol)), and  $[\text{Ni}(\text{phen})_2][\text{Ni}(\text{CN})_4] 2\text{H}_2\text{O}$  (starting materials  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  (0.53 g; 2.23 mmol), phen  $\text{H}_2\text{O}$  (0.44 g; 2.22 mmol),  $\text{K}_2[\text{Ni}(\text{CN})_4]$  (0.53 g; 2.23 mmol)) were obtained using a reaction analogous to the preparation of  $[\text{Ni}(\text{dien})(\text{H}_2\text{O})][\text{Ni}(\text{CN})_4]$ .

The yields were 70–90 %. The pink products were insoluble in water, ethanol, methanol, chloroform, dichloromethane, acetone, dimethyl sulfoxide, and dimethylformamide.

## RESULTS AND DISCUSSION

The chemical composition of the substances prepared is given in Table 1. The data from physicochemical studies are given in Table 2 and Figs. 1–3. The new coordination compounds were prepared by precipitation from aqueous solutions  $[\text{NiL}]^{2+}$  (L = dien,

**Table 1.** The Results of Elemental Analysis

Compound $M_r$	$w_i(\text{calc.})/\%$ $w_i(\text{found})/\%$			
	C	H	N	Ni
$[\text{Ni}(1,2\text{-pn})_2][\text{Ni}(\text{CN})_4] \text{H}_2\text{O}$	31.0	5.7	28.9	30.9
387.74	31.0	6.0	28.1	30.9
$[\text{Ni}(\text{dien})(\text{H}_2\text{O})][\text{Ni}(\text{CN})_4]$	28.0	4.4	28.6	34.3
342.65	27.9	4.5	28.0	33.8
$[\text{Ni}(\text{tta})][\text{Ni}(\text{CN})_4]$	32.7	4.9	30.5	31.9
367.71	32.9	5.2	30.2	32.2
$[\text{Ni}(\text{taa})][\text{Ni}(\text{CN})_4] 2\text{H}_2\text{O}$	29.7	5.4	27.8	29.1
403.74	30.1	5.7	27.4	29.0
$[\text{Ni}(\text{bpy})_2][\text{Ni}(\text{CN})_4] 2\text{H}_2\text{O}$	50.6	3.5	19.7	20.6
569.88	51.3	3.1	20.0	20.9
$[\text{Ni}(\text{phen})_2][\text{Ni}(\text{CN})_4] 2\text{H}_2\text{O}$	54.4	3.3	18.1	19.0
617.92	53.9	3.5	17.8	18.8

**Table 2.** The Results of Physicochemical Study

Compound	$\mu_{\text{eff}}/\mu_{\text{B}}$ (T/K)	$\bar{\nu}(\nu(\text{C}\equiv\text{N}))/\text{cm}^{-1}$	
		Terminal	Bridged
$[\text{Ni}(1,2\text{-pn})_2][\text{Ni}(\text{CN})_4] \text{H}_2\text{O}$	3.11 (296.5) – 3.08 (94.4)	2128	2156
$[\text{Ni}(\text{dien})(\text{H}_2\text{O})][\text{Ni}(\text{CN})_4]$	3.10 (296.7) – 3.09 (94.4)	2128	2156
$[\text{Ni}(\text{tta})][\text{Ni}(\text{CN})_4]$	3.14 (295.1)	2124	2152
$[\text{Ni}(\text{taa})][\text{Ni}(\text{CN})_4] 2\text{H}_2\text{O}$	3.14 (295.0)	2124	2152
$[\text{Ni}(\text{bpy})_2][\text{Ni}(\text{CN})_4] 2\text{H}_2\text{O}$	3.23 (296.3) – 3.19 (94.4)	2118	2148
$[\text{Ni}(\text{phen})_2][\text{Ni}(\text{CN})_4] 2\text{H}_2\text{O}$	3.21 (298.0)	2120	2150

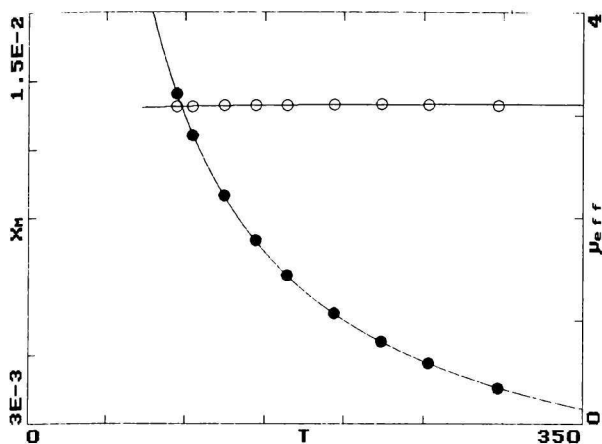


Fig. 1. Magnetic properties of  $[\text{Ni}(1,2\text{-pn})_2][\text{Ni}(\text{CN})_4] \cdot \text{H}_2\text{O}$ .  $\circ$   $\mu_{\text{eff}}/\mu_{\text{B}}$  (effective magnetic moment),  $\bullet$   $\chi_{\text{m}}/(\text{cm}^3 \text{mol}^{-1})$  (molar susceptibility corrected for diamagnetism (cgs)).

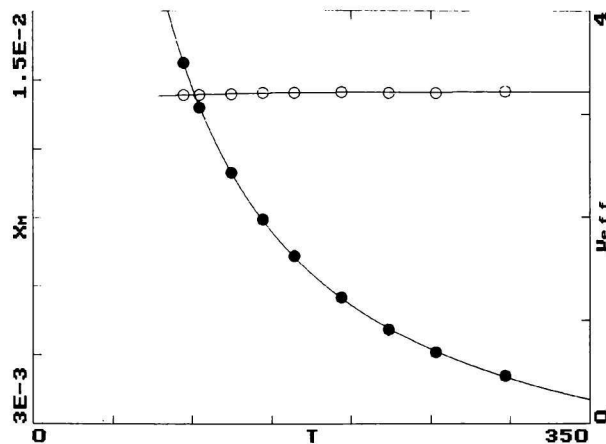


Fig. 3. Magnetic properties of  $[\text{Ni}(\text{bpy})_2][\text{Ni}(\text{CN})_4] \cdot 2\text{H}_2\text{O}$ .  $\circ$   $\mu_{\text{eff}}/\mu_{\text{B}}$  (effective magnetic moment),  $\bullet$   $\chi_{\text{m}}/(\text{cm}^3 \text{mol}^{-1})$  (molar susceptibility corrected for diamagnetism (cgs)).

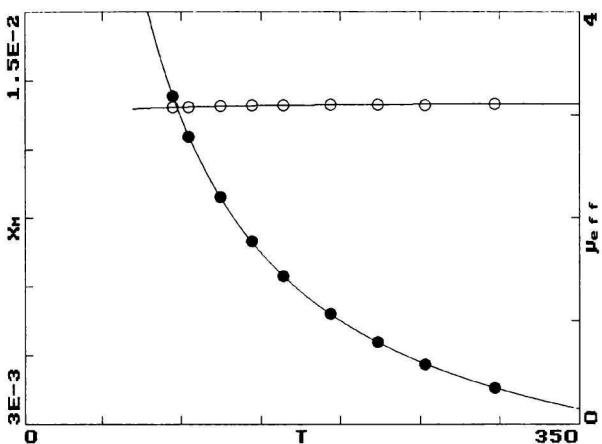


Fig. 2. Magnetic properties of  $[\text{Ni}(\text{dien})(\text{H}_2\text{O})][\text{Ni}(\text{CN})_4]$ .  $\circ$   $\mu_{\text{eff}}/\mu_{\text{B}}$  (effective magnetic moment),  $\bullet$   $\chi_{\text{m}}/(\text{cm}^3 \text{mol}^{-1})$  (molar susceptibility corrected for diamagnetism (cgs)).

netic moments for complexes are typical for octahedral nickel(II) ( $\mu_{\text{eff}} = 2.7\text{--}3.4 \mu_{\text{B}}$ ) [9]. The temperature dependence of the magnetic susceptibilities of the complexes  $[\text{Ni}(1,2\text{-pn})_2][\text{Ni}(\text{CN})_4] \cdot \text{H}_2\text{O}$ ,  $[\text{Ni}(\text{dien})(\text{H}_2\text{O})][\text{Ni}(\text{CN})_4]$ , and  $[\text{Ni}(\text{bpy})_2][\text{Ni}(\text{CN})_4] \cdot 2\text{H}_2\text{O}$  leads us to conclude that the complexes are all magnetically diluted in the studied temperature range, because their magnetic moments do not significantly differ over the 94—296 K range (Fig. 1—3). The temperature dependence of the magnetic susceptibility of these complexes obeys the Curie—Weiss law, according to which the calculated values of the Weiss and Curie constants are insignificant [ $C = 1.2 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ ,  $\theta = -2.8 \text{ K}$  ( $L = 1,2\text{-pn}$ );  $C = 1.2 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ ,  $\theta = -2.1 \text{ K}$  ( $L = \text{dien}$ );  $C = 1.3 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ ,  $\theta = -2.5 \text{ K}$  ( $L = \text{bpy}$ )]; *Klička's* program was used [10]. The weak antiferromagnetic exchange interaction would be probably found at lower temperature similarly as for the complex  $[\text{Ni}(\text{en})_2][\text{Ni}(\text{CN})_4]$  [4]. The very weak spin coupling is caused by a long distance between paramagnetic Ni(II) atoms bridged by diamagnetic  $[\text{Ni}(\text{CN})_4]^{2-}$  groups.

taa or tta) or  $[\text{NiL}_2]^{2+}$  ( $L = 1,2\text{-pn}$ , bpy or phen) and  $[\text{Ni}(\text{CN})_4]^{2-}$

We propose that the prepared complexes contain square-planar coordinated Ni(II) atoms (four *C*-bonded CN groups) and octahedral coordinated Ni(II) atoms (two bidentate *N,N'* ligands (1,2-pn, bpy or phen), one tridentate *N,N',N''* ligand (dien) and molecule of water or one tetradentate *N,N',N'',N'''* ligand (taa or tta) and two *N*-bonded CN groups) with cyanide bridges as analogous complexes to  $[\text{Ni}(\text{en})_2][\text{Ni}(\text{CN})_4] \cdot x\text{H}_2\text{O}$  ( $x = 0; 2.16$ ) [2, 3].

The structure of the complex  $[\text{Ni}(\text{CN})_4]^{2-}$  is square-planar with the diamagnetic nickel(II) atom. Due to diamagnetism of  $[\text{Ni}(\text{CN})_4]^{2-}$  the paramagnetism of the prepared complexes is caused by only one atom of nickel(II). The values of effective mag-

The only one of the prepared compounds ( $[\text{Ni}(\text{tta})][\text{Ni}(\text{CN})_4] \cdot 2\text{H}_2\text{O}$ ) was studied using the thermoanalytical methods. This complex lost two molecules of crystal water from 75°C to 180°C (relative decrease of mass found (calc.)/%: 8.3 (8.9); exothermic peak in the DTA curve: 110°C) and the unsolvated complex existed in the temperature range 180—265°C. The thermal decomposition of anhydrous  $[\text{Ni}(\text{taa})][\text{Ni}(\text{CN})_4]$  began at 265°C and its decomposition was completed at 400°C. The decomposition of this complex proceeded continuously without the formation of stable intermediates. The final product of the thermal decomposition was NiO (relative decrease of mass found (calc.)/%: 64.1 (63.0); exothermic peaks in the DTA curve: 300°C and 360°C).

The electronic absorption spectra of the presented complexes result probably from superposition of spectra  $[\text{Ni}(\text{CN})_4]^{2-}$  and  $\text{Ni}(\text{II})$  in the octahedral arrangement.  $\text{C}$ -Bonded  $\text{CN}^-$  is a strong field donor and the electronic spectrum of  $[\text{Ni}(\text{CN})_4]^{2-}$  shows two weak  $d-d$  bands at  $22\,500\text{ cm}^{-1}$  and  $30\,500\text{ cm}^{-1}$  [11]. In the octahedral complexes of  $\text{Ni}(\text{II})$  we can find three bands which are due to  $d-d$  transitions ( $\tilde{\nu}_1 = {}^3A_{2g}(\text{F}) \rightarrow {}^3T_{2g}(\text{F})$ ,  $\tilde{\nu}_2 = {}^3A_{2g}(\text{F}) \rightarrow {}^3T_{1g}(\text{F})$ ,  $\tilde{\nu}_3 = {}^3A_{2g}(\text{F}) \rightarrow {}^3T_{1g}(\text{P})$ ); for  $[\text{Ni}(\text{en})_3]^{2+}$   $\tilde{\nu}_1 = 11\,200\text{ cm}^{-1}$ ,  $\tilde{\nu}_2 = 18\,350\text{ cm}^{-1}$ ,  $\tilde{\nu}_3 = 29\,000\text{ cm}^{-1}$  [12]. In the present compounds bands at  $18\,000$ – $18\,500\text{ cm}^{-1}$  or band at  $29\,500\text{ cm}^{-1}$  may be ascribed as  $d-d$  transitions of octahedral  $\text{Ni}(\text{II})$  ( $\tilde{\nu}_2$  or  $\tilde{\nu}_3$ ).

In the infrared spectra characteristic vibrations for  $\nu(\text{C}\equiv\text{N})$  were assigned. In the present complexes  $\nu(\text{C}\equiv\text{N})$  was observed in the  $2118$ – $2128\text{ cm}^{-1}$  and  $2148$ – $2156\text{ cm}^{-1}$  ranges as two strong bands; the former is due to the terminal  $\text{CN}$  stretching vibration and the latter is attributable to the bridging  $\text{CN}$  stretching vibration.  $\nu(\text{CN})$  is generally shifted to a higher frequency upon bridge formation [13–17]. The infrared spectra of  $[\text{Ni}(\text{bpy})_2][\text{Ni}(\text{CN})_4] \cdot 2\text{H}_2\text{O}$  and  $[\text{Ni}(\text{phen})_2][\text{Ni}(\text{CN})_4] \cdot 2\text{H}_2\text{O}$ , respectively, contain the absorption maxima typical for coordinated  $\text{bpy}$  ( $\tilde{\nu}/\text{cm}^{-1}$ : 1596, 1444, 1152, and 416) and  $\text{phen}$  ( $\tilde{\nu}/\text{cm}^{-1}$ : 1624, 1516, 1144, 846, 724, and 644), respectively [17–19]. The band corresponding to  $\nu(\text{NH}_2)$  was found in the spectra of the complexes  $[\text{Ni}(1,2\text{-pn})_2][\text{Ni}(\text{CN})_4] \cdot \text{H}_2\text{O}$  ( $3344\text{ cm}^{-1}$ ),  $[\text{Ni}(\text{dien})(\text{H}_2\text{O})][\text{Ni}(\text{CN})_4]$  ( $3340\text{ cm}^{-1}$ ),  $[\text{Ni}(\text{tta})][\text{Ni}(\text{CN})_4]$  ( $3352\text{ cm}^{-1}$ ), and  $[\text{Ni}(\text{taa})][\text{Ni}(\text{CN})_4] \cdot 2\text{H}_2\text{O}$  ( $3330\text{ cm}^{-1}$ ) [20]. All our attempts to obtain the complexes in crystalline form suitable for X-ray study failed.

In conclusion, on the basis of physicochemical study, we propose polymeric structure of the prepared compounds with cyanide bridges and with square-planar  $\text{Ni}(\text{II})$  (chromophore  $\text{NiC}_4$ ) and octahedral  $\text{Ni}(\text{II})$  (chromophore  $\text{NiN}_6$  or  $\text{NiN}_5\text{O}$ ).

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