

Tetracyanonickelates(II) of Copper(II) with Bidentate, Tridentate, and Tetradentate *N*-Donor Ligands

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Received 19 November 2003

The following complexes, having the general formula $[\text{Cu}(\text{L})_2\text{Ni}(\text{CN})_4] \cdot x\text{H}_2\text{O}$ ($\text{L} = N$ -methylethylenediamine ($x = 0$) or 1,3-diaminopentane ($x = 2$)) and $[\text{Cu}(\text{L})\text{Ni}(\text{CN})_4] \cdot x\text{H}_2\text{O}$ ($\text{L} = 3$ -(methylamino)propylamine ($x = 0$), 3-(dimethylamino)propylamine ($x = 1$), N,N' -dibenzylethylenediamine ($x = 2$), 2,6-di(2-pyridyl)pyridine ($x = 2$), N,N' -bis(3-aminopropyl)ethylenediamine ($x = 1$), 1,3,6,10,12,15-hexaazatricyclo[13.3.1.1^{6,10}]eicosane ($x = 0$), 1,3,6,9,11,14-hexaazatricyclo[12.2.1.1^{6,9}]octadecane ($x = 0$) or 1,8-dimethyl-1,3,6,8,10,13-hexaazacyclotetradecane ($x = 0$)) have been synthesized. All the compounds have been characterized by elemental analyses, IR and UV VIS spectroscopies and magnetic measurements. The complex $[\text{Cu}(1,3\text{-diaminopentane})_2\text{Ni}(\text{CN})_4] \cdot 2\text{H}_2\text{O}$ was studied using thermal analysis (the product of the thermal decomposition of this compound is the mixture of CuO and NiO as determined by X-ray powder diffraction). The structure of the studied complexes with cyanide bridges between square-planar nickel(II) ($S = 0$) and penta- or hexacoordinated copper ($S = 1/2$) is proposed.

In general, cyano-bridged homo- and heterometallic complexes continuously keep attracting much attention in coordination chemistry, especially in the context of their interesting structures and magnetic properties [1, 2].

For instance, cyano-bridged tetracyanonickelates (II) of copper(II) are suitable model compounds for structural and magnetic studies of such systems at low temperatures, because the tetracyanonickelate anion may bridge paramagnetic ions of copper(II) partially coordinated with amine ligands and thus form binuclear [3], tetranuclear [4], octanuclear [5, 6], 1D [7–14], 2D [15, 16], and 3D [16] structures. Variety of multidimensional structures have been obtained in which $[\text{Ni}(\text{CN})_4]^{2-}$ forms a tetramonodentate bridge (by using of all the N-atoms) [13, 15] or a di(monodentate) bridge (by using of two N-atoms of *trans*- [7–10, 12, 14] or *cis*-CN groups [11, 4–6]). Recently, the T-type three-bonded coordination [16] and monodentate ligation [3, 4] of $[\text{Ni}(\text{CN})_4]^{2-}$ to copper(II) ions have also been reported.

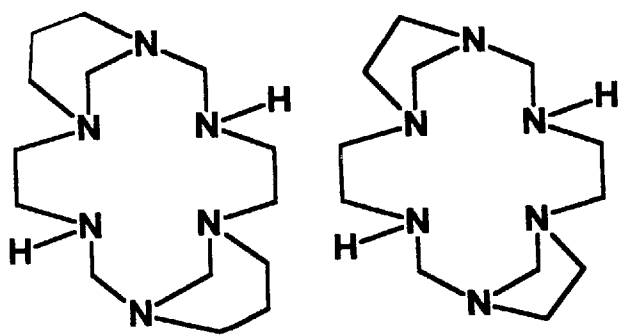
Magnetochemical study showed the presence of a very weak antiferromagnetic interaction between the copper(II) atoms through diamagnetic $[\text{Ni}(\text{CN})_4]^{2-}$ ion for the 1D compounds $[\text{Cu}(\text{en})_2\text{Ni}(\text{CN})_4]$ ($\text{en} =$ ethylenediamine, superexchange interaction parameter $J = -0.13 \text{ cm}^{-1}$) [17] and $[\text{Cu}(\text{dpt})\text{Ni}(\text{CN})_4]$ (dpt

= dipropylentriamine, $J = -0.16 \text{ cm}^{-1}$) [11].

With the aim to prepare new cyano-bridged tetracyanonickelates(II) of copper(II), we have extended series of blocking amine ligands with bidentate *N*-methylethylenediamine (meen), 1,3-diaminopentane (dap), 3-(methylamino)propylamine (mapa), 3-(dimethylamino)propylamine (dmapa), and N,N' -dibenzylethylenediamine (dben), tridentate 2,6-bis(2-pyridyl)pyridine (terpy), and tetradentate N,N' -bis(3-aminopropyl)ethylenediamine (bapen), 1,3,6,10,12,15-hexaazatricyclo[13.3.1.1^{6,10}]eicosane (hatce), 1,3,6,9,11,14-hexaazatricyclo[12.2.1.1^{6,9}]octadecane (hatco), and 1,8-dimethyl-1,3,6,8,10,13-hexaazacyclotetradecane (dmehact).

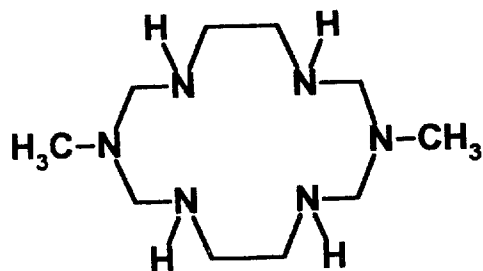
EXPERIMENTAL

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 compounds $[\text{Cu}(\text{hatce})](\text{ClO}_4)_2$, [18] $[\text{Cu}(\text{hatco})](\text{ClO}_4)_2$ [18], and $[\text{Cu}(\text{dmehact})](\text{ClO}_4)_2$ [19] were prepared using literature methods. The complexes $[\text{Cu}(\text{dap})_2](\text{ClO}_4)_2$ and $[\text{Cu}(\text{bapen})](\text{ClO}_4)_2$ were obtained by the direct reaction between $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ and dap in the mole ratio 1:2 in aqueous solution and $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ and bapen in the mole ratio 1:1



hatce

hatco



dmehact

in aqueous solution, respectively. 1,3-Diaminopentane (95 %), *N*-methylethylenediamine (95 %), *N,N'*-dibenzylethylenediamine (97 %), 2,6-di(2-pyridyl)pyridine (98 %), and *N,N'*-bis(3-aminopropyl)ethylenediamine (94 %) were products of Aldrich, 3-(methylamino)-1-propylamine (97 %), 3-(dimethylamino)-1-propylamine (98 %), and $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (pure) of Fluka and $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (anal. grade) of Lachema, Brno.

Elemental analyses of carbon, hydrogen, and nitrogen were performed on Fisons EA1108 CHN instrument.

The IR spectra were measured on a Specord M80 spectrophotometer in the range 400–4000 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 range 11 000–30 000 cm^{-1} .

Thermoanalytical study was made between room temperature and 1100°C using the Seiko TG/DTA 6200 instrument (Japan) in the air atmosphere with sample mass of 11 mg and the temperature gradient 5°C min^{-1} .

The powder X-ray diffractogram was recorded on the XRD-7 Seifert instrument.

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 $\text{Hg}[\text{Co}(\text{SCN})_4]$ was used as a calibrant. Diamagnetic corrections were made with Pascal's con-

stants for all the constituent atoms and magnetic moments were calculated using the equation $\mu_{\text{eff}}/\mu_{\text{B}} = 2.828 \text{ cm}^{-3/2} \text{ mol}^{1/2} \text{ K}^{-1/2} (\chi_{\text{m}}T)^{1/2}$.

$[\text{Cu}(\text{meen})_2\text{Ni}(\text{CN})_4]$, $[\text{Cu}(\text{mapa})\text{Ni}(\text{CN})_4]$, and $[\text{Cu}(\text{dmapa})\text{Ni}(\text{CN})_4] \cdot \text{H}_2\text{O}$

Amine (5.4 mmol) was added to a solution of $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (1.00 g; 2.7 mmol) in 40 cm^3 of water. A small amount of solid formed was discarded. A solution of $\text{K}_2[\text{Ni}(\text{CN})_4]$ (0.65 g; 2.7 mmol) in 35 cm^3 of water was added to the reaction mixture. The microcrystalline blue solid was filtered off, washed with water and dried in desiccator over NaOH.

For meen complex *N*-methylethylenediamine (0.48 cm^3) (yield 0.4 g (40 %)), for mapa complex 3-(methylamino)-1-propylamine (0.57 cm^3) (yield 0.35 g (20 %)), and for dmapa complex 3-(dimethylamino)-1-propylamine (0.69 cm^3) (yield 0.4 g (20 %)) were used.

$[\text{Cu}(\text{dap})_2\text{Ni}(\text{CN})_4] \cdot 2\text{H}_2\text{O}$

A solution of $\text{K}_2[\text{Ni}(\text{CN})_4]$ (0.26 g; 1.1 mmol) in 25 cm^3 of water was added to a solution of $[\text{Cu}(\text{dap})_2](\text{ClO}_4)_2$ (0.50 g; 1.1 mmol) in 25 cm^3 of water. The obtained blue substance was filtered off, washed with water and dried in desiccator over NaOH. The yield was 0.7 g (80 %).

$[\text{Cu}(\text{dben})\text{Ni}(\text{CN})_4] \cdot 2\text{H}_2\text{O}$ and $[\text{Cu}(\text{terpy})\text{Ni}(\text{CN})_4] \cdot 2\text{H}_2\text{O}$

A solution of amine in 35 cm^3 of ethanol was added to a solution of Cu salt in 25 cm^3 of water. A small amount of violet solid formed was discarded. A solution of $\text{K}_2[\text{Ni}(\text{CN})_4]$ in 40 cm^3 of water was added to the reaction mixture. Immediately obtained violet solid was filtered off, washed with water and dried in air.

For dben complex *N,N'*-dibenzylethylenediamine (1.3 cm^3 ; 5.5 mmol), $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (1.00 g; 2.7 mmol), and $\text{K}_2[\text{Ni}(\text{CN})_4]$ (0.65 g; 2.7 mmol) (yield 0.4 g (30 %)), for terpy complex 2,6-di(2-pyridyl)pyridine (0.25 g, 1.1 mmol), $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (0.26 g; 1.1 mmol), and $\text{K}_2[\text{Ni}(\text{CN})_4]$ (0.26 g; 1.1 mmol) (yield 0.4 g (75 %)) were used.

$[\text{Cu}(\text{bapen})\text{Ni}(\text{CN})_4] \cdot \text{H}_2\text{O}$

A solution of $\text{K}_2[\text{Ni}(\text{CN})_4]$ (0.28 g; 1.2 mmol) in 25 cm^3 of water was added to a solution of $[\text{Cu}(\text{bapen})](\text{ClO}_4)_2$ (0.50 g; 1.1 mmol) in 25 cm^3 of water. The reaction mixture was allowed to stand overnight and then the blue-violet needle crystals were obtained. This substance was filtered off, washed with a small amount of water and dried in air. The yield was 0.3 g (60 %).

Table 1. The Results of Elemental Analysis

Complex	$w_i(\text{found})/\% ; w_i(\text{calc.})/\%$			Colour
	C	H	N	
[Cu(meen) ₂ Ni(CN) ₄]	31.77; 32.07	5.21; 5.38	29.43; 29.92	Blue
[Cu(dap) ₂ Ni(CN) ₄] · 2H ₂ O	36.31; 36.03	7.54; 6.91	23.81; 24.01	Blue
[Cu(mapa)Ni(CN) ₄]	30.31; 30.65	3.61; 3.85	25.78; 26.72	Blue
[Cu(dmapa)Ni(CN) ₄] · H ₂ O	30.70; 31.20	4.50; 4.07	24.10; 24.25	Blue
[Cu(dben)Ni(CN) ₄] · 2H ₂ O	47.84; 47.79	4.32; 4.81	16.57; 16.72	Violet
[Cu(terpy)Ni(CN) ₄] · 2H ₂ O	45.90; 46.05	3.22; 3.05	19.95; 19.78	Blue
[Cu(bapen)Ni(CN) ₄] · H ₂ O	34.18; 34.43	6.16; 5.78	26.27; 26.77	Blue-Violet
[Cu(hatce)Ni(CN) ₄]	41.71; 42.50	5.49; 5.94	27.03; 27.53	Violet
[Cu(hatco)Ni(CN) ₄]	39.18; 39.98	6.30; 5.45	39.18; 39.98	Violet
[Cu(dmehact)Ni(CN) ₄]	36.32; 36.82	6.04; 5.74	30.15; 30.76	Violet

Table 2. Spectral and Magnetic Properties of the Complexes

Complex	UV VIS $\bar{\nu} \cdot 10^{-3}/\text{cm}^{-1}$	IR $\bar{\nu}(\text{CN})/\text{cm}^{-1}$	$\mu_{\text{eff}}/\mu_{\text{B}}$ (T/K)
[Cu(meen) ₂ Ni(CN) ₄]	17.0, 35.8	2112, 2120	1.89 (295)
[Cu(dap) ₂ Ni(CN) ₄] · 2H ₂ O	16.8	2120	1.89 (294)
[Cu(mapa)Ni(CN) ₄]	13.0, 37.2	2130, 2160	1.86 (293)
[Cu(dmapa)Ni(CN) ₄] · H ₂ O	37.4	2120, 2160, 2170	2.07 (296)
[Cu(dben)Ni(CN) ₄] · 2H ₂ O	15.4, 35.6, 37.5	2120, 2160	2.14 (293)
[Cu(terpy)Ni(CN) ₄] · 2H ₂ O	15.8	2120, 2130	1.99 (294)
[Cu(bapen)Ni(CN) ₄] · H ₂ O	17.8, 34.8	2112	1.86 (294)
[Cu(hatce)Ni(CN) ₄]	18.6	2112, 2124	1.88 (294)
[Cu(hatco)Ni(CN) ₄]	19.0	2112, 2160	1.86 (294)
[Cu(dmehact)Ni(CN) ₄]	19.2, 34.3, 36.4	2100	1.84 (295)

[Cu(hatce)Ni(CN)₄], [Cu(hatco)Ni(CN)₄], and [Cu(dmehact)Ni(CN)₄]

A solution of K₂[Ni(CN)₄] (0.23 g; 1.0 mmol) in 20 cm³ of water was added to a solution of the copper(II) complex with the macrocyclic ligand (0.50 g; 1.0 mmol) in the mixture of 100 cm³ of water and 10 cm³ of ethanol. Immediately obtained violet solid was filtered off, washed with water and dried in desiccator over NaOH.

For hatce complex [Cu(hatce)](ClO₄)₂ (yield 0.3 g (65 %)), for hatco complex [Cu(hatco)](ClO₄)₂ (yield 0.4 g (86 %)), and for dmehact complex [Cu(dmehact)](ClO₄)₂ (yield 0.1 g (20 %)) were used.

RESULTS AND DISCUSSION

The chemical composition and physicochemical data of the prepared substances are given in Table 1.

The new coordination compounds were prepared by precipitation from aqueous (or ethanolic) solutions of [Cu(L)₂]²⁺ (L = meen or dap) or [CuL]²⁺ (L = mapa, dmapa, dben, terpy, bapen, hatce, hatco or dmehact) and aqueous solution of [Ni(CN)₄]²⁻.

We propose that the prepared compounds contain square-planar coordinated Ni(II) atoms (by four C-bonded CN groups) and penta- or hexacoordi-

nated Cu(II) atoms (by nitrogens from amines and N-bonded CN groups) with cyanide bridges as analogous by X-ray structure analysis characterized tetracyanonickelates(II) of copper(II) [3–16].

The electronic absorption spectra (Table 2) of the studied complexes result probably from superposition of spectra of [Ni(CN)₄]²⁻ and Cu(II). C-Bonded CN⁻ is a strong-field donor and the electronic spectrum of [Ni(CN)₄]²⁻ shows two weak *d*–*d* bands at 22 500 cm⁻¹ and 30 500 cm⁻¹ [20]. In the electronic absorption spectrum of Cu(II) complexes we can find a strong band corresponding to a *d*–*d* transition in the range 13 000–18 000 cm⁻¹ [21]. In the studied compounds bands in the 13 000–19 200 cm⁻¹ range may be ascribed to *d*–*d* transition of copper(II).

In the infrared spectra characteristic vibrations for $\nu(\text{C}\equiv\text{N})$ were assigned [22]. In the studied complexes $\nu(\text{C}\equiv\text{N})$ was observed in the 2100–2170 cm⁻¹ $\bar{\nu}$ range. The presence of the cyano bridge is shown by the splitting of the $\nu(\text{CN})$ stretching band. According to the literature, the formation of the cyano bridge shifts $\nu(\text{CN})$ towards higher frequencies [23]. The compounds [Cu(dap)₂Ni(CN)₄] · 2H₂O, [Cu(bapen)Ni(CN)₄] · H₂O, and [Cu(dmehact)Ni(CN)₄] exhibit in this region only one peak at 2120 cm⁻¹, 2112 cm⁻¹, and 2100 cm⁻¹, respectively. These low values usually characterize terminal bonding of

the cyano groups, but the IR spectrum of the structurally characterized 1D complex $[\text{Cu}(\text{en})_2\text{Ni}(\text{CN})_4]$ [7–10] displays only one absorption band at 2120 cm^{-1} [4, 24], too, despite the presence of bridging cyano groups in the structure.

Because of the diamagnetism of $[\text{Ni}(\text{CN})_4]^{2-}$ anion, the paramagnetism of the prepared complexes is caused by copper(II). The observed values of the magnetic moments ($1.84\text{--}2.14\ \mu_{\text{B}}$) are in accordance with the literature data for magnetically diluted compounds of copper(II) ($1.9\text{--}2.2\ \mu_{\text{B}}$) [25].

The only one of the prepared compounds ($[\text{Cu}(\text{dap})_2\text{Ni}(\text{CN})_4] \cdot 2\text{H}_2\text{O}$) was studied using the thermoanalytical methods. This complex lost one molecule of crystal water from $38\text{ }^\circ\text{C}$ to $76\text{ }^\circ\text{C}$ (relative decrease of mass found (calc.)/%: 3.1 (3.9); endothermic peak in the DTA curve: $63\text{ }^\circ\text{C}$) and complex with one molecule of water existed in the temperature range $76\text{--}157\text{ }^\circ\text{C}$. The thermal decomposition of $[\text{Cu}(\text{dap})_2\text{Ni}(\text{CN})_4] \cdot \text{H}_2\text{O}$ began at $157\text{ }^\circ\text{C}$ and its decomposition was completed at $419\text{ }^\circ\text{C}$ (exothermic peaks in the DTA curve: $178\text{ }^\circ\text{C}$, $270\text{ }^\circ\text{C}$, $352\text{ }^\circ\text{C}$, and $402\text{ }^\circ\text{C}$). The product of the thermal decomposition (observed mass loss 67 %) consists of a mixture of CuO and NiO (calculated 67 %) as was shown by its powder X-ray diffractogram.

The structure of the studied complexes with cyanide bridges between square-planar nickel(II) ($S = 0$) and penta- or hexacoordinated copper ($S = 1/2$) is proposed. Unfortunately, all our attempts to obtain the complexes in the crystalline form suitable for X-ray study failed.

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