

# Preparation and Physical Properties of Cyanatonickel(II) Complexes with Imidazole Ligands

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Solid cyanatonickel(II) complexes of the composition  $\text{Ni}(\text{NCO})_2\text{L}_4$ , where L = imidazole, 2-methyl-, 2-ethyl-, 2-phenylimidazole, and  $\text{Ni}(\text{NCO})_2(1,2\text{-dimethylimidazole})_2 \cdot 2\text{H}_2\text{O}$  were prepared. Structural characteristics of these complexes were determined by infrared and electronic spectroscopy and magnetic moment measurements. As ascertained, the Ni(II) atom in complexes under study has a pseudooctahedral structural arrangement and the NCO groups are terminally bonded through nitrogen. The axial bonds in  $\text{Ni}(\text{NCO})_2(1,2\text{-dimethylimidazole})_2 \cdot 2\text{H}_2\text{O}$  are formed through the bidentate nitrogen atom of the cyanato groups, and molecules of water are linked through hydrogen bridges.

Recently published paper [1] described the influence of imidazole and benzimidazole ligands on structural properties of thiocyanatonickel(II) complexes. The low steric hindrance, as it followed from physicochemical studies, in  $\alpha$ -position to the donor nitrogen atom (methyl or ethyl group) of imidazole ligands does not influence lowering of the coordinated ligands number against the sterically not hindered ligands, as found with thiocyanatonickel(II) compounds with pyridine derivatives [2]. In continuation of this paper cyanatonickel(II) complexes with imidazole (iz), 2-methyl- (2-meiz), 2-ethyl- (2-etiz), 2-phenyl- (2-pheniz), and 1,2-dimethylimidazole (1,2-dimeiz) were prepared and their properties were investigated.

## EXPERIMENTAL

The nickel content in complexes was determined chelatometrically after preceding decomposition with concentrated  $\text{H}_2\text{SO}_4$  in the presence of  $\text{K}_2\text{S}_2\text{O}_8$ . Elemental analyses were carried out with a CHN analyzer (Erba).

### Complexes $\text{Ni}(\text{NCO})_2\text{L}_4$ (L = iz, 2-meiz, 2-etiz, 2-pheniz)

$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (10 mmol) dissolved in water (20  $\text{cm}^3$ ) was added to a solution of  $\text{NaNCO}$  (20 mmol) in water (20  $\text{cm}^3$ ); the respective imidazole (42 mmol) dissolved in methanol (20  $\text{cm}^3$ ) was poured into the well stirred aqueous solution. The particular complexes, formed during standing in air at room

temperature for several days, were filtered off, washed with ether and dried over KOH in a desiccator.

### Complex $\text{Ni}(\text{NCO})_2(1,2\text{-dimeiz})_2 \cdot 2\text{H}_2\text{O}$

$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (10 mmol) in water (20  $\text{cm}^3$ ) and  $\text{KNCO}$  (20 mmol) in water (20  $\text{cm}^3$ ) were mixed up and poured in the solution of 1,2-dimethylimidazole (20 mmol) in methanol (20  $\text{cm}^3$ ). The originally formed light-green suspension turned into a light-blue microcrystalline powder within some days; it was filtered off, washed with ether and dried over KOH in a desiccator.

Analytical data are listed in Table 1. All physical measurements were conducted with apparatuses and methods already reported [1].

Table 1. Elemental Analysis of Complexes  $\text{Ni}(\text{NCO})_2\text{L}_4$  and  $\text{Ni}(\text{NCO})_2\text{L}_2 \cdot 2\text{H}_2\text{O}$

$(\text{L})_x$	$M_r$	$w_i(\text{calc.})/\%$ $w_i(\text{found})/\%$			
		C	H	N	Ni
(iz) <sub>4</sub>	415.0	40.51	3.89	33.73	14.14
		39.44	4.01	33.72	13.82
(2-meiz) <sub>4</sub>	471.2	45.88	5.14	29.71	12.46
		45.08	5.14	29.71	12.35
(2-etiz) <sub>4</sub>	527.3	50.11	6.12	26.55	11.13
		49.63	6.13	26.49	11.19
(2-pheniz) <sub>4</sub>	719.5	63.44	4.48	19.45	8.16
		63.69	4.65	19.29	8.04
(1,2-dimeiz) <sub>2</sub>	371.0	38.84	5.43	22.65	15.82
		38.62	5.44	22.65	15.63

## RESULTS AND DISCUSSION

Infrared vibration bands associated with the cyanato group and skeletal Ni—N vibrations are listed in Table 2. The bands were assigned by comparing with those of free ligands [3–6] and the corresponding cyanato and thiocyanatonickel(II) complexes with each other [1].

All complexes revealed very strong, mainly split bands at  $\tilde{\nu} = 2140\text{--}2248\text{ cm}^{-1}$  corresponding to  $\nu_{\text{as}}$  vibration of the NCO group. Splitting of  $\nu_{\text{as}}$  bands indicates lowering of symmetry for the complexes studied [7]. This effect can be caused by a rising influence of the steric hindrance due to the presence of a substituent in C-2 position on the imidazole ring. Splitting of the  $\nu_{\text{as}}$  band can also be due to the crystal structure.

The  $\nu_s$  vibration appears mainly as a medium intense band at  $\tilde{\nu} = 1330\text{--}1377\text{ cm}^{-1}$ , the bending vibration of the cyanato group occurs as medium bands at  $\tilde{\nu} = 602\text{--}653\text{ cm}^{-1}$ . These values indicate a terminal binding of NCO groups through the nitrogen atom [8]. The  $\text{Ni}(\text{NCO})_2(1,2\text{-dimeiz})_2 \cdot 2\text{H}_2\text{O}$  complex showed  $\delta(\text{NCO})$  splitting within  $46\text{ cm}^{-1}$ , this being in favour of a bridging function of the NCO group with a bidentate nitrogen atom [8, 9].

Broad and rather complex bands of  $\nu(\text{OH})$  stretching vibrations of  $\text{Ni}(\text{NCO})_2(1,2\text{-dimeiz})_2 \cdot 2\text{H}_2\text{O}$  concentrated at approximately  $\tilde{\nu} = 3400\text{ cm}^{-1}$  are characteristic of water molecules bonded by hydrogen bridges [10]. The medium band at  $\tilde{\nu} = 653\text{ cm}^{-1}$  might be ascribed to the wagging vibration of water [11], but we would prefer the first alternative, *i.e.* the bridging function of the NCO group. It seems probable that water is not co-ordinated in this complex, because no additional band corresponding to Ni—OH<sub>2</sub> stretching vibration of coordinated water was found in the  $400\text{ cm}^{-1}$  wavenumber region in comparison with analogous thiocyanatonickel(II) complex [1].

The stretching vibrations of Ni—NCO and Ni—N(organic ligand) appeared at  $\tilde{\nu} = 200\text{--}400\text{ cm}^{-1}$ . The  $\nu(\text{Ni—NCO})$  stretching vibration occurred as a strong band at  $\tilde{\nu} = 280\text{--}295\text{ cm}^{-1}$ , the  $\nu(\text{Ni—N(L)})$  stretching vibration as a strong band at  $\tilde{\nu} = 242\text{--}260\text{ cm}^{-1}$  [12]. Complex  $\text{Ni}(\text{NCO})_2(\text{iz})_4$  reveals only one strong and broad band in this region at  $\tilde{\nu} = 261\text{ cm}^{-1}$ , embodying probably both stretching vibrations. Bands around  $\tilde{\nu} = 220\text{ cm}^{-1}$ , observed in the spectra of complexes  $\text{Ni}(\text{NCO})_2(\text{iz})_4$  and  $\text{Ni}(\text{NCO})_2(2\text{-etiz})_4$  are most probably associated with the bending  $\delta(\text{Ni—N—C})$  vibration [13].

Imidazole and its derivatives coordinate to Ni(II) atom by the tertiary nitrogen atom, as evidenced by the X-ray analysis of  $\text{Ni}(\text{NCS})_2(\text{iz})_4$  [14]. The pyrrole nitrogen atom participates probably in hydrogen bonds through its acid hydrogen in the crystal structure of compounds.

Electronic spectra of these cyanatonickel(II) complexes in solid state exhibit one simple and two split bands in the region under examination. Splitting of two energetically poorer bands is evidently taking place provided there is symmetry  $D_{4h}$ , although a spin-forbidden transition to  $^1E_g(^1D)$  level can occur. Wavenumbers  $\tilde{\nu}_1$  and  $\tilde{\nu}_2$  of bands could be, respecting these facts [15, 16], ascribed to the transitions  $^3B_{1g} \rightarrow ^3E_g^a$  and  $^3B_{1g} \rightarrow ^3B_{2g}$  or  $^3B_{1g} \rightarrow ^3A_{2g}$  and  $^3B_{1g} \rightarrow ^3E_g^b$ . Transitions  $^3B_{1g} \rightarrow ^3E_g^c$  and  $^3B_{1g} \rightarrow ^3A_{2g}$  are obviously incorporated in the band of  $\tilde{\nu}_3$ , which is already overlapped by the charge-transfer band.

In the electronic spectrum of  $\text{Ni}(\text{NCO})_2(2\text{-pheniz})_4$  also the band due to the electron transition of highest energy in the tetragonal symmetry contains probably two components (presence of a shoulder at  $\tilde{\nu} = 23\,100\text{ cm}^{-1}$ ). This splitting can indicate lowering of the ligand field symmetry brought about by the presence of a bulky C<sub>6</sub>H<sub>5</sub> group in  $\alpha$ -position to the donor nitrogen atom; this fact is probably also backed by the twist of imidazole and benzene rings. It is, moreover, possible that one component

Table 2. Infrared ( $\tilde{\nu}/\text{cm}^{-1}$ ) and Electronic Spectral Data and Magnetic Moments at 293 K

(L) <sub>x</sub>	$\nu_{\text{as}}(\text{NCO})$	$\nu_s(\text{NCO})$	$\delta(\text{NCO})$	$\nu(\text{Ni—NCO})$	$\nu(\text{Ni—N(L)})$	$\tilde{\nu}_3 \cdot 10^{-3}$ cm <sup>-1</sup>	$\tilde{\nu}_2 \cdot 10^{-3}$ cm <sup>-1</sup>	$\tilde{\nu}_1 \cdot 10^{-3}$ cm <sup>-1</sup>	$\mu_{\text{eff}}/\mu_B$
(iz) <sub>4</sub>	2205 vs 2192 vs	1330 m	640 m	261 s, br		27.7	17.3 13.3	10.7 7.2	2.98
(2-meiz) <sub>4</sub>	2233 vs 2221 vs	1377 m	602 m	280 s	242 s	26.7	16.4 13.4 sh	10.0 8.3 sh	3.02
(2-etiz) <sub>4</sub>	2248 vs 2140 vs	1337 m	627 m 620 m	284 s	249 vs 246 vs	26.3	16.0 13.4 sh	8.7 7.1 sh	3.35
(2-pheniz) <sub>4</sub>	2237 vs 2180 sh	a	630 m	295 vs	260 s	25.2 23.1 sh	14.5 12.9 sh	8.4 7.0	3.18
(1,2-dimeiz) <sub>2</sub>	2230 vs	1347 m	653 m 607 m	295 vs	250 s	26.0	15.6 13.8 sh	10.1 8.7	3.28

a) Overlapped by the ligand band.

of this band belongs to the triplet — singlet transition to  $^1T_{2g}(D)$  level in the tetragonal symmetry [17, 18].

All complexes studied showed magnetic moment values at room temperature (Table 2) in the 2.98—3.35  $\mu_B$  range; they are in accordance with those given for magnetically diluted octahedral complexes of Ni(II) [19].

The temperature dependence of magnetic susceptibility of the complex  $Ni(NCO)_2(1,2\text{-dimeiz})_2 \cdot 2H_2O$  obeys the Curie—Weiss law according to which the calculated values of Weiss  $\theta$  and Curie  $C$  constants were insignificant ( $-4.16$  K and  $1.2203 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ , respectively). Magnetic moment of this compound is virtually temperature independent. Obviously, no interaction between Ni(II) ions takes place through mediation of nitrogen bridge atoms from cyanato groups down to boiling temperature of liquid nitrogen.

## CONCLUSION

The Ni(II) atom of all the above-mentioned complexes is supposed to be in a tetragonal bipyramidal environment on the basis of indirect physical measurements. Donor atoms are the nitrogens both of cyanato groups and imidazole ligands. The cyanato group in compound  $Ni(NCO)_2(1,2\text{-dimeiz})_2 \cdot 2H_2O$  behaves as a bridge by the bidentate nitrogen atom, and molecules of water are bound by hydrogen atoms in the crystal structure. The proposed view on the structure of this compound could be made more accurate by X-ray structural analysis of a monocrystal. Unfortunately no suitable crystals were prepared. Steric hindrance in  $\alpha$ -position in respect of the donor nitrogen atom does not come into effect in the stoichiometry and consequently, in the steric

arrangement of these complexes. The probably lower aromaticity of imidazole and thereby longer bonds than with pyridine caused the substituent in  $\alpha$ -position to be more remote and as a result, it cannot manifest a sufficient steric effect.

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