

Cobalt(II) and Nickel(II) Complexes with 1-Methyl-2-Pyridin-2-yl-1H- and 1-Methyl-2-Phenyliminomethyl-1H-Benzimidazoles and the *closo*-Decaborate Anion

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Abstract—Synthesis of cobalt(II) and nickel(II) complexes with the *closo*-decaborate anion and benzimidazole derivatives ($L^1 = C_{13}N_3H_{11}$, $L^2 = C_{15}N_3H_{13}$) of the general formula $[ML_3][B_{10}H_{10}]$ ($M = Co, Ni$) is described. Complexes have been characterized by elemental analysis, IR and UV spectroscopy. The structure of a $[Ni(L^1)_3][B_{10}H_{10}] \cdot 1.797CH_3CN$ single crystal has been determined by X-ray diffraction. The imidazole and pyridine N atoms of three L^1 molecules, two of which are disordered, form the distorted octahedral environment of the Ni atom. In the crystal, the majority of complexes $[Ni(L^1)_3]^{2+}$ have the meridional configuration. The Ni–N bonds with the imidazole nitrogen atoms (2.010(4)–2.076(3) Å) are shorter than those with the pyridine atoms (2.132(4)–2.179(5) Å). This nonequivalence of the Ni–N bonds is responsible for the low magnetic susceptibility of the compound.

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The literature data on nickel(II) complexes with the boron cluster anions $[B_nH_n]^{2-}$ ($n = 10, 12$) are few in number. Structures of two aqua complexes— $[Ni(H_2O)_6][B_{12}H_{12}] \cdot 6H_2O$ and $[Ni(H_2O)_6](H_3O)_2[B_{12}H_{12}]_2 \cdot 6H_2O$ —prepared by reaction of nickel(II) carbonate or nickel(II) hydroxide with the $(H_3O)_2[B_{12}H_{12}]$ acid were determined by X-ray crystallography [1, 2]. Complexes $[NiL_3][B_nH_n]$ ($n = 10, 12$) with such ligands as benzoyl hydrazine (Bh), *meta*-nitrobenzoyl hydrazine (*m*-NBh) [3, 4], 2,2'-bipyridyle (Bipy), and 1,10-phenanthroline (Phen) [5, 6], as well as complex $[Ni(en)_3][B_{12}H_{12}]$ with ethylenediamine [7], were synthesized. These compounds were characterized by various physical and chemical methods; based on indirect analytical methods, it was assumed that nickel(II) atoms have the octahedral environment formed by three chelating ligands, and the $[B_nH_n]^{2-}$ anions are in the outer sphere of the complexes.

Among the organic ligands, 2-substituted derivatives of benzimidazole with substituents containing a multiple CN bond are of particular interest for the chemistry of complex compounds [8]. This is explained by the presence of donor nitrogen atoms of different nature in their structures, the potential ability to act as tridentate ligands, and the pharmacological properties that allow one to use complexes prepared on their basis in medicine, agriculture, and some fields

of industry. The development of the optimal conditions for the synthesis of metal complexes with benzimidazole-based organic ligands and boron cluster anions is a topical problem. Its solution allows one, on one hand, to carry out one-stage syntheses of complexes, and, on the other hand, to develop the concept of the nature of chemical bond in such compounds and of the processes of ligand replacement.

This paper describes the synthesis, structure, and physical and chemical properties of complex compounds $[ML_3][B_{10}H_{10}]$ with benzimidazole derivatives $L = C_{13}N_3H_{11}$ (L^1) or $C_{15}N_3H_{13}$ (L^2).

EXPERIMENTAL

Triethylammonium decahydro-*closo*-decaborate $(Et_3NH)_2[B_{10}H_{10}]$ was synthesized from decaborane(14) through the stage of formation of 1,6-bis(trimethylamine)decaborane as described in [9].

1-Methyl-2-(2-pyridyl)benzimidazole $C_{13}N_3H_{11}$ (L^1) was prepared according to the procedure reported in [8].

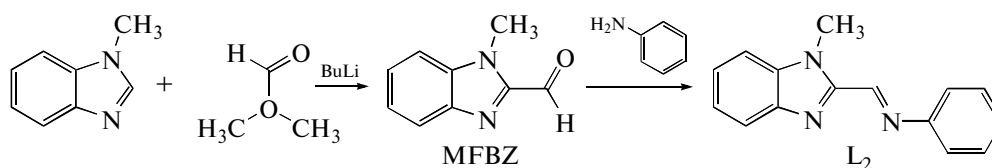
1-Methylbenzimidazo-2-yl-methylenedianiline $C_{15}N_3H_{13}$ (L^2) was synthesized through the stage of formation of 1-methyl-2-formylbenzimidazole (MFBZ) that was prepared according to the known procedure [10] (Scheme 1). The yield of MFBZ was 2.18 g (45%) from 1-methylbenzimidazole (4.00 g, 30.3 mmol) and

Table 1. Maxima of selected absorption bands in the IR spectra of the benzimidazole derivatives L and complexes $[\text{ML}_3][\text{B}_{10}\text{H}_{10}]$, ν , cm^{-1}

Compound	$\nu(\text{BH})$	$\nu(\text{C}=\text{N})$ of the imine group	$\nu(\text{C}=\text{N})$ of the benzimidazole ring	$\nu(\text{C}=\text{N})$ of the pyridine ring
$\text{L}^1 = \text{C}_{13}\text{N}_3\text{H}_{11}$	—	—	1566	1590
$[\text{Co}(\text{L}^1)_3][\text{B}_{10}\text{H}_{10}]$ (I)	2438	—	1571	1602
$[\text{Ni}(\text{L}^1)_3][\text{B}_{10}\text{H}_{10}]$ (II)	2435	—	1573	1601
$\text{L}^2 = \text{C}_{15}\text{N}_3\text{H}_{13}$	—	1630	1590	—
$[\text{Co}(\text{L}^2)_3][\text{B}_{10}\text{H}_{10}]$ (III)	2454	1604	1585	—
$[\text{Ni}(\text{L}^2)_3][\text{B}_{10}\text{H}_{10}]$ (IV)	2453	1616	1585	—

DMF (4.98 g, 68.2 mmol). MFBZ (2.18 g, 13.6 mmol) was dissolved in 15 mL of absolute EtOH, and then aniline (1.33 g, 14.3 mmol) was added. The reaction solution was stirred under dry argon atmosphere for 72 h. The precipitate was fil-

tered off, washed with water and hexane. The product was recrystallized from hot ethanol and dried under vacuum of an oil pump. Obtained: 2.72 g (85%) of 1-methyl-benzimidazo-2-yl-methylene-aniline (ligand L^2).

**Scheme 1.**

For $\text{C}_{15}\text{N}_3\text{H}_{13}$ anal. calcd. (%): C, 76.57; H, 5.57; N, 17.86.

Found L^2 (%): C, 35.13; H, 8.53; N, 13.70.

^1H NMR (DMSO- d_6 , δ , ppm): 4.12 (s, 3H, CH_3); 7.16 (m, 2H, $o\text{-C}_{\text{Ph}}\text{-H}$); 7.27–7.34 (m, 2H, $\text{C}_{\text{BZ}}\text{-H}$); 7.38 (m, 1H, $p\text{-C}_{\text{Ph}}\text{-H}$); 7.45 (m, 2H, $\text{C}_{\text{BZ}}\text{-H}$); 7.60 (m, 2H, $t\text{-C}_{\text{Ph}}\text{-H}$); 9.04 (s, 1H, $\text{N}=\text{CH}$).

^{13}C NMR (DMSO- d_6 , δ , ppm): 31.69 (CH_3); 110.67, 118.64, 120.18, 123.90, 125.01, 125.72, 129.61, 139.39, 141.77 (aromatic), 150.22 ($\text{N}=\text{CH}$), 151.89, 152.26 (aromatic).

Synthesis of $[\text{ML}_3][\text{B}_{10}\text{H}_{10}]$ ($\text{L} = \text{L}^1 = \text{C}_{13}\text{N}_3\text{H}_{11}$, $\text{M} = \text{Co}$ (**I**), Ni (**II**)); $\text{L} = \text{L}^2 = \text{C}_{15}\text{H}_{13}\text{N}_3$; $\text{M} = \text{Co}$ (**III**), Ni (**IV**)). Solid CoCl_2 or NiCl_2 (1 mmol) was added to a solution of $(\text{Et}_3\text{NH})_2[\text{B}_{10}\text{H}_{10}]$ (1 mmol) in acetonitrile (10 mL) on stirring. The reaction solution became blue or green upon the dissolution of the metal chlorides. When a solution of ligand L^1 or L^2 (3 mmol) in acetonitrile (5 mL) was added to the reaction solution, the mixture changed its color to sand or coffee, respectively. Formation of polycrystalline precipitates of sand (**I** or **II**) or coffee (**II** or **IV**) colors was observed after 2–3 h. The yield of **I–IV** was more than 80% based on boron. A single crystal of **II** · 1.797 CH_3CN suitable for X-ray crystallography was isolated directly from the reaction solution.

For $\text{C}_{39}\text{H}_{43}\text{N}_9\text{B}_{10}\text{Co}$ anal. calcd. (%): C, 58.20; H, 5.57; N, 15.66; B, 13.43; Co, 7.32.

Found for **I** (%): C, 58.15; H, 5.38; N 15.62; B, 13.40; Co, 7.24.

For $\text{C}_{39}\text{H}_{49}\text{N}_9\text{B}_{10}\text{Ni}$ anal. calcd. (%): C, 58.22; H, 5.39; N, 15.67; B, 13.44; Ni, 7.29.

Found for **II** (%): C, 58.18; H, 5.29; N 15.66; B, 13.30; Ni, 7.15.

For $\text{C}_{45}\text{H}_{49}\text{N}_9\text{B}_{10}\text{Co}$ anal. calcd. (%): C, 61.21; H, 5.59; N, 14.28; B, 12.24; Co, 6.67.

Found for **III** (%): C, 60.98; H, 5.44; N 14.19; B, 12.18; Co, 6.64.

For $\text{C}_{45}\text{H}_{49}\text{N}_9\text{B}_{10}\text{Ni}$ anal. calcd. (%): C, 61.23; H, 5.59; N, 14.28; B, 12.25; Ni, 6.65.

Found for **IV** (%): C, 60.50; H, 5.37; N 14.10; B, 12.15; Ni, 6.61.

Elemental analysis for carbon, hydrogen, and nitrogen was carried out on a Carlo Erba CHNS-3 FA 1108 automated elemental analyzer. Determination of boron and metals was performed on an iCAP 6300 Duo ICP emission spectrometer with inductively coupled plasma.

IR spectra of the initial compounds and reaction products (Table 1) were recorded on a Lumex Infracol FT-02 Fourier-transform spectrometer in the range of 4000–600 cm^{-1} at a resolution of 1 cm^{-1} . Samples were prepared as Nujol (Aldrich) mulls; NaCl pellets were used.

UV spectra of compounds suspended in glycerol were measured on an SF 103 spectrophotometer in the visible region 200–800 nm.

^1H and ^{13}C NMR spectra of a solution of L_2 in $\text{DMSO}-d_6$ were recorded on a Bruker Avance II-300 radiospectrometer at the operating frequencies of 300.3 and 96.32 MHz, respectively, with internal deuterium lock; tetramethylsilane was used as an external standard.

The static magnetic susceptibility of a polycrystalline sample of II was measured in the temperature range 300–4 K with a Quantum Design PPMS-9 AC/DC instrument.

X-ray crystallography. The set of diffraction reflections for $\text{II} \cdot 1.797\text{CH}_3\text{CN}$ was collected on a Bruker SMART APEX2 automated diffractometer at the Shared Facility Center, IGIC RAS. The data were collected and processed with the APEX2, SAINT, and SADABS programs [11]. The structure of $\text{II} \cdot 1.797\text{CH}_3\text{CN}$ was solved by the direct method using the SIR-92 program [12]. In the structure of $\text{IV} \cdot 1.797\text{CH}_3\text{CN}$, two L^1 molecules are disordered over two positions, in which the methylimidazole and pyridine fragments replace each other. The ratio of site occupancy factors is 0.953(3) : 0.047(3) for the N(1)-C(13) molecule and 0.797(4) : 0.203(4) for the N(4)-C(26) molecule. The acetonitrile molecule N(11)-C(43) is incompatible with the poorly occupied position of the N(4)-C(26) molecule; therefore, its site occupancy factor is equal to 0.797(4). The L molecules at the poorly occupied positions were refined by the least-squares procedures with restrained geometry (SAME instructions) and Ni–N bond lengths (DFIX). The thermal parameters of the minor component of the N(1)-C(13) molecule were assumed to be equal to U_{eq} of the corresponding atoms of the major component and fixed, and those of the N(4)-C(26) molecule were refined isotropically. All other non-hydrogen atoms were refined in the anisotropic approximation. Some of the hydrogen atoms were located on difference Fourier maps; the positions of the lacking hydrogen atoms were calculated. The H atoms of the methyl C(41) atom are disordered over two positions with equal occupancies (0.49(6) : 0.51(6)). Hydrogen atoms were refined by the riding model. Structure of $\text{II} \cdot 1.797\text{CH}_3\text{CN}$ was refined using the SHELXL-2013 program [13].

Main crystal data, details of data collection, and characteristics of structure refinement are listed in Table 2. The crystallographic data have been deposited with the Cambridge Structural Database (CCDC no. 1044931).

RESULTS AND DISCUSSION

Compounds of the imidazole class possess physiological activity; the extent of their physiological action and its direction are determined to a considerable

Table 2. Crystallographic data, details of data collection, and characteristics of structure refinement for $\text{II} \cdot 1.797\text{CH}_3\text{CN}$

Molecular formula	$\text{C}_{42.59}\text{H}_{48.39}\text{B}_{10}\text{N}_{10.80}\text{Ni}$
FW	878.46
T , K	150(2)
Radiation, λ , Å	$\text{MoK}\alpha$, 0.71073
Space group, Z	$P\bar{1}$, 2
a , Å	10.2783(11)
b , Å	14.5696(16)
c , Å	15.7379(17)
α , deg	102.217(2)
β , deg	90.849(2)
γ , deg	107.341(2)
V , Å ³	2191.0(4)
ρ_x , g/cm ³	1.332
μ_{Mo} , mm ⁻¹	0.490
T_{min} , T_{max}	0.6317, 0.7450
$F(000)$	915
Crystal size, mm	0.24 × 0.14 × 0.06
θ range, deg	2.161–24.275
Number of reflections:	
collected	16813
unique (N) [R_{int}]	7082 [0.0461]
with $I > 2\sigma(I)$ (N_o)	4653
$R1$, $wR2$ for N_o	0.0626, 0.1468
$R1$, $wR2$ for N	0.1041, 0.1700
S	1.034
$\Delta\rho_{\text{max}}/\Delta\rho_{\text{min}}$, e/Å ³	1.097/–0.801

degree by the nature of substituents. In the present work, the benzimidazole derivatives L^1 and L^2 were used, their structures are presented in Fig. 1.

Complexes $[\text{ML}_3][\text{B}_{10}\text{H}_{10}]$ ($\text{M} = \text{Co}, \text{Ni}$; $\text{L} = \text{L}^1$ or L^2) were prepared by reaction of triethylammonium *closo*-decaborate with cobalt(II) or nickel(II) chloride and a threefold excess of benzimidazole derivatives L

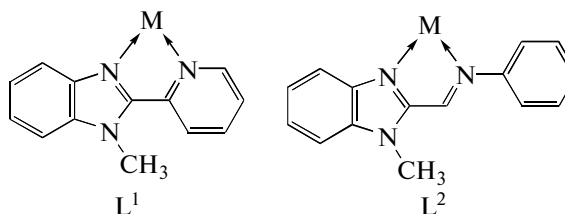


Fig. 1. Coordination of ligands L^1 and L^2 in complexes $[\text{ML}_3][\text{B}_{10}\text{H}_{10}]$.

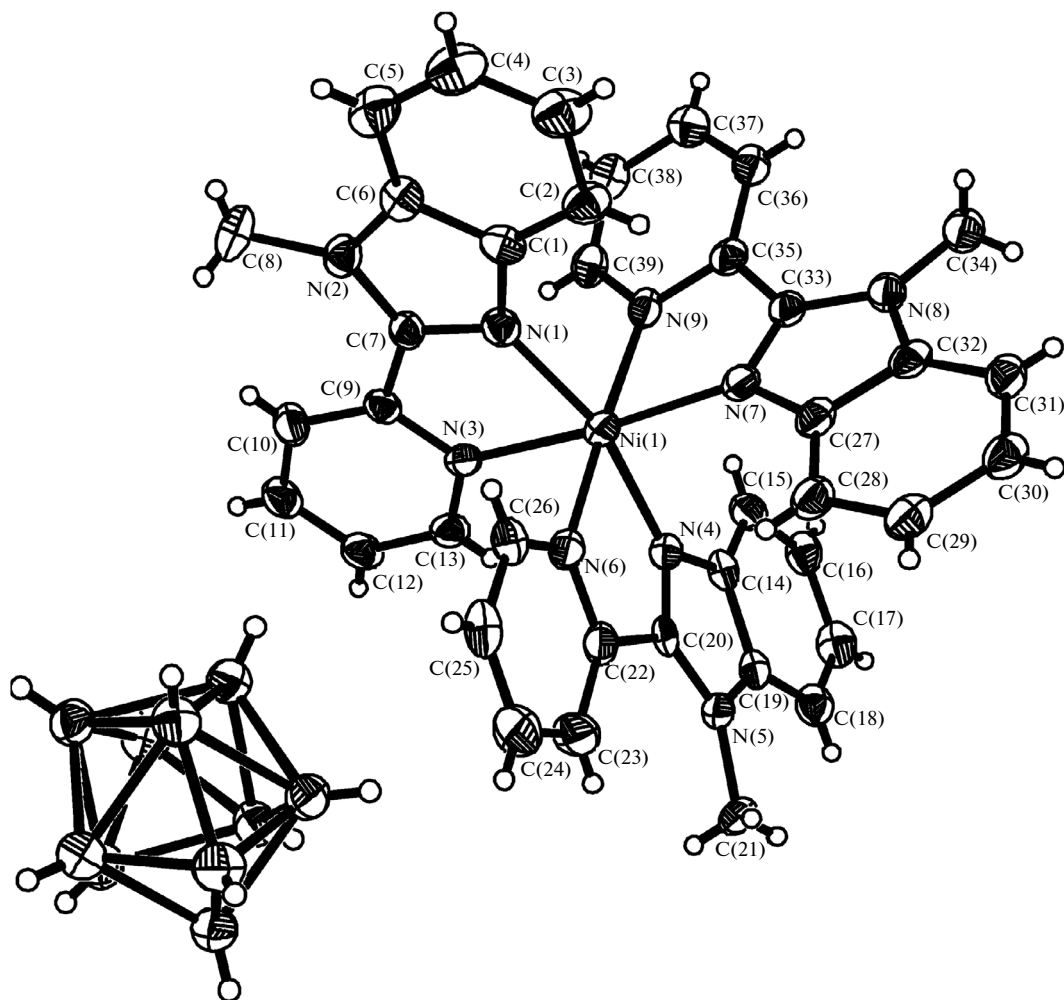
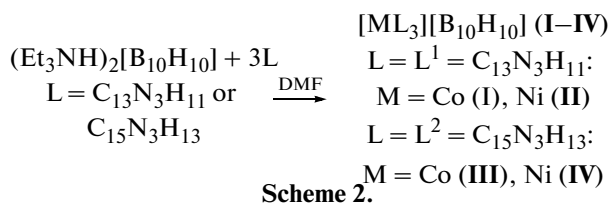


Fig. 2. Fragment of structure **II** · 1.797CH₃CN. Thermal ellipsoids are shown at the 30% probability level.

(Scheme 2). The compounds were formed selectively and in good yields.



The compositions and structures of complexes **I–IV** were determined by elemental analysis, IR, and UV spectroscopy. In the IR spectra of complexes with ligand L¹ (complexes **I** and **II**), the bands of stretching vibrations of CN bonds $\nu(\text{CN})$ of both benzimidazole and pyridine rings are located at higher frequencies as compared to the IR spectrum of the initial ligand L¹ (Table 1). This fact indicates that two nitrogen atoms of ligand L¹ participate in the coordination of the Co(II) and Ni(II) atoms, so that five-membered che-

late rings are formed. The coordination of one molecule of ligand L¹ is schematically presented in Fig. 1. The participation of the pyridine nitrogen atom in metal coordination is also confirmed by the shifts of the absorption band maxima of the pyridine ring in the range 1600–700 cm⁻¹ and the alteration of the ratio of their intensities. The high-frequency shifts of the maxima of the stretching vibrations bands of both CN bonds upon metal coordination indicate that the chelate ring is involved in the system of conjugation of the ligand.

In the IR spectra of complexes **III** and **IV** with ligand L², the bands of stretching vibrations of C=N bonds of the imine group and of CN bonds of the benzimidazole group are observed; the maxima of both bands are shifted to the lower frequencies as compared to their position in the IR spectrum of the noncoordinated ligand L² (Table 1). These changes in the IR spectra testify to the bidentate coordination of the

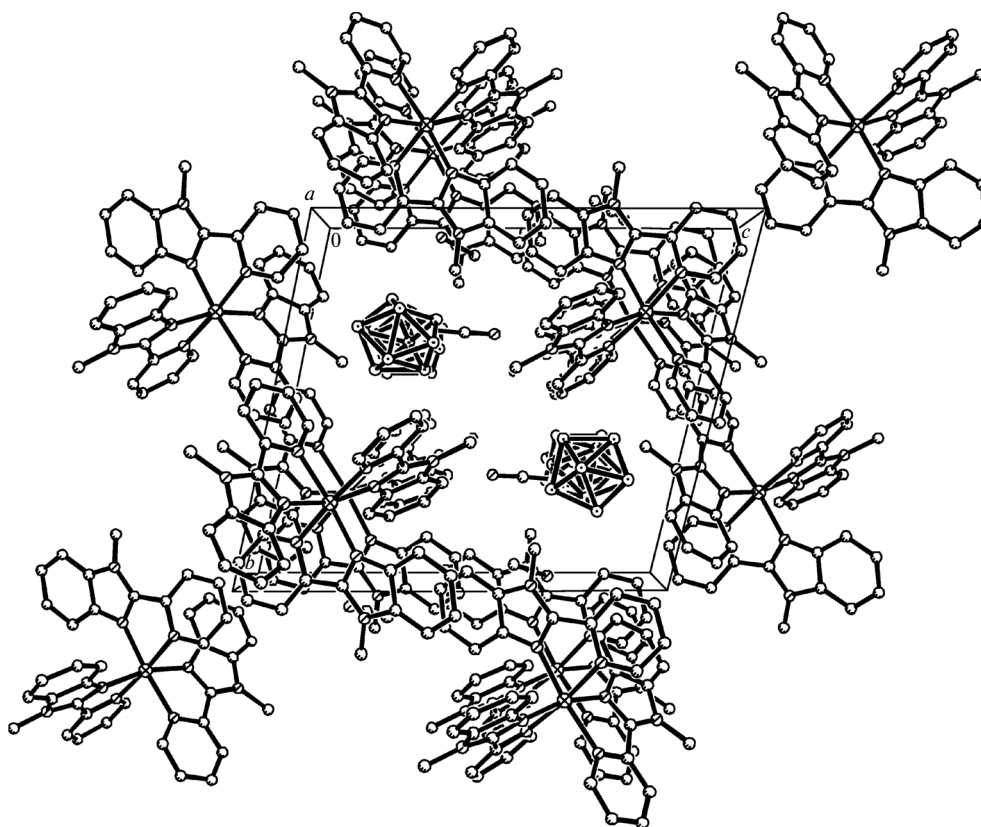


Fig. 3. Projection of structure $\text{II} \cdot 1.797\text{CH}_3\text{CN}$ along the a axis. The H atoms are omitted.

benzimidazole derivative L^2 through two nitrogen atoms with the formation of five-membered metallocycles.

In the region of stretching vibrations of BH bonds of the IR spectra of **I–IV** (Table 1), there is an intense $\nu(\text{BH})$ band with the maximum near 2450 cm^{-1} . The absence of bands in the range $2400\text{--}2000\text{ cm}^{-1}$ typical of $\nu(\text{BH})_{\text{MHB}}$ stretching vibrations of coordinated *closo*-decaborate anion indicates that the $[\text{B}_{10}\text{H}_{10}]^{2-}$ anion is located in the outer sphere.

According to the data of the UV spectra, the energy of the intramolecular charge transfer in ligand L^1 in complexes **I** and **II** (330 and 335 nm, respectively) is lower than in the noncoordinated ligand (305 nm). A similar decrease in the energy with respect to that in the noncoordinated ligand L^2 (340 nm) is found for complexes with L^2 (~370 nm for both **III** and **IV**).

According to the elemental analysis, the metal-to-ligand ratio in complexes **I–IV** is 3 : 1. This allows us to conclude that the coordination number of Co and Ni is six due to the metal coordination by three bidentate ligands L.

According to the X-ray diffraction data, crystals of **II** · $1.797\text{CH}_3\text{CN}$ are built of complex cations $[\text{Ni}(\text{C}_{13}\text{N}_3\text{H}_{11})_3]^{2+}$, the $[\text{B}_{10}\text{H}_{10}]^{2-}$ anions, and solvate acetonitrile molecules (Fig. 2). Three imidazole and

three pyridine nitrogen atoms form a distorted octahedral environment around the Ni atom. The $[\text{Ni}(\text{L}^1)_3]^{2+}$ complexes, in which disordered L^1 molecules occupy the main positions, have the meridional configuration. In these complexes, the Ni–N bonds with the imidazole nitrogen atoms (2.010(4)–2.076(3) Å) are shorter than those with the pyridine nitrogen atoms (2.132(4)–2.179(5) Å). Molecules $\text{C}_{13}\text{N}_3\text{H}_{11}$ are flattened. Torsion angles N(1)C(7)C(9)N(3), N(4)C(20)C(22)N(6), and N(7)C(33)C(35)N(9) characterizing the relative rotation of the imidazole and pyridine rings are -4.9° , -12.7° , and -18.1° , respectively. The complex with the minor component of the N(4)–C(26) molecule and the main component of the N(1)–C(13) molecule has the facial configuration. The other combinations of molecules correspond to the meridional isomer. Note that, in the Cambridge Structural Database there is only one compound containing complex cation $[\text{M}(\text{L}^1)_3]^{2+}$ with the same ligand, namely, $[\text{Fe}(\text{C}_{13}\text{N}_3\text{H}_{11})_3](\text{F}_3\text{CSO}_3)_2 \cdot 0.5\text{H}_2\text{O}$ [14]. Complex $[\text{Fe}(\text{C}_{13}\text{N}_3\text{H}_{11})_3]^{2+}$ has the meridional configuration. The Fe–N bond lengths with the imidazole and pyridine nitrogen atoms (1.942–2.038 and 1.991–2.047 Å, respectively) differ to a smaller extent than the Ni–N bond lengths in **II** · $1.797\text{CH}_3\text{CN}$.

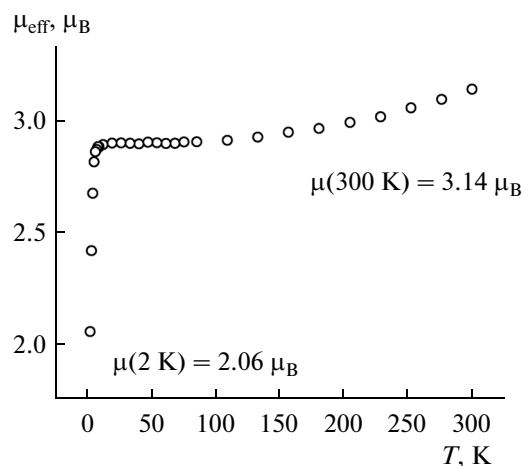


Fig. 4. Temperature dependence of the magnetic susceptibility of complex **II** · 1.797CH₃CN.

In crystal **II** · 1.797CH₃CN, [Ni(L¹)₃]²⁺ complex cations are packed into wavy layers parallel to the *ac* plane (Fig. 3). Channels extended along the *a* axis, in which B₁₀H₁₀²⁻ anions and acetonitrile molecules are located, are formed between neighboring layers. The shortest contacts between ten independent H atoms of the borohydride anion and H atoms of ligand L¹ or acetonitrile fall in the range of 2.28–2.56 Å. The splitting of absorption bands usually observed in the IR spectra of compounds with specific B–H···H–N interactions is not found in the IR spectrum of **II** · 1.797CH₃CN.

The values of the magnetic moment for octahedral nickel(II) complexes vary in the range of 3.0–3.4 μ_B. Figure 4 shows the plot of the magnetic moment of compound **II** versus temperature. The magnetic moment of complex **II** equal to 3.14 μ_B corresponds to a distorted octahedral environment because of the nonequivalence of the Ni–N bonds in the complex.

Thus, we have developed the method to synthesize cobalt(II) and nickel(II) complexes with 1-methyl-2-pyridin-2-yl-1*H*- and 1-methyl-2-phenyliminomethyl-1*H*-benzimidazoles and the *closo*-decaborate anion [ML₃][B₁₀H₁₀] (M = Co, Ni; L = C₁₃N₃H₁₁ or C₁₅N₃H₁₃). The complexes were isolated selectively in a good yield and characterized by elemental analysis, IR, and UV spectroscopy. The structure of complex

[Ni(C₁₃N₃H₁₁)₃][B₁₀H₁₀] · 1.797CH₃CN was determined by X-ray crystallography. The distorted octahedral environment formed by the imidazole and pyridine nitrogen atoms of three ligand molecules is responsible for the low magnetic moment of the complex. The complexes are promising for application in various fields of science and technology owing to the combination of properties of the metals, benzimidazoles, and boron clusters composing them.

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