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Synthesis and Structure of Potassium 2-(Pyridin-2-yl)-1*H*-Benzo[*d*]imidazolate and Preparation of Related Bis(diimine) Ligands

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Abstract—A potassium derivative of 2-(pyridin-2-yl)-1*H*-benzo[*d*]imidazole (BenzimidK) is synthesized and structurally characterized (CIF file CCDC no. 1478559). The complex is used for the preparation of new bis(diimine) ligands containing different diimine fragments linked by the bridging $(CH_2)_4$ group.

Keywords: potassium, benzimidazole, coordination polymers, diimine ligands

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INTRODUCTION

It is known that mononuclear complexes of copper(I), ruthenium(II), iridium(III), and europium(III) containing various derivatives of bipyridine, 1,10-phenanthroline, and benzimidazole as neutral ligands reveal efficient luminescence properties and are used as emission materials in optoelectronics and as luminescent markers in biomedical investigations [1–6]. The preparation of the luminescent binuclear iridium and rhodium complexes in which the metal atoms are linked by the bridging bis(diimine) ligand (2,2-*p*-phenylenebis(1*H*-imidazo[4,5-f][1,10]phe-nanthroline)) has recently been reported [7]. The nature of the diimine ligands exerts a substantial effect on the emission properties of the metal complexes [1–6]. Therefore, the development of new bis(diimine) ligands as a basis for the synthesis of bi- and polynuclear metal complexes with efficient luminescence properties is of great interest.

The synthesis and structure of the potassium derivative of 2-(pyridin-2-yl)-1*H*-benzo[*d*]imidazole and the preparation of related bis(diimine) ligands containing pyridinylbenzimidazole, benzimidazolylquinoline, and benzimidazolylthiazole fragments are reported in this work.

EXPERIMENTAL

All procedures with easily oxidizable and hydrolyzable substances were carried out in vacuo or in argon using the standard Schlenk technique. The solvents used were thoroughly purified and degassed. The syntheses of 2-(1*H*-benzo[*d*]imidazol-2-yl)quinoline [8] and 2-(pyridin-2-yl)-1*H*-benzo[*d*]imidazole [9] were conducted as described earlier. 4-(1*H*-Benzo[*d*]imidazol-2-yl)thiazole (Aldrich) was used as received.

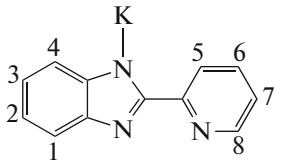
^{1}H and ^{13}C{1H} NMR spectra were recorded on a Bruker DPX-200 (^{1}H NMR: 200 MHz, ^{13}C NMR: 50 MHz) and a Bruker Avance III-400 (^{1}H NMR: 400 MHz, ^{13}C NMR: 100 MHz) spectrometers. Signal assignment was performed using 2D gradient spectroscopy: proton–proton correlation (GE-COSY) and proton–carbon correlation (GE-HSQC). Chemical shifts were indicated in ppm relative to tetramethylsilane as an internal standard.

IR spectra were recorded on an FSM 1201 FT-IR spectrometer. Samples of the compounds were prepared by pressing pellets, and the substance to KBr ratio was 1 : 200.

Melting (decomposition) points were determined in evacuated sealed capillaries (presented without correction).

Synthesis of potassium 2-(pyridin-2-yl)benzo[*d*]imidazol-1-ide (BenzimidK) (I). A mixture of 2-(pyridin-2-yl)-1*H*-benzo[*d*]imidazole (0.30 g, 1.54 mmol) and KOH (0.09 g, 1.61 mmol) was stirred in dimethylformamide (DMF) (5 mL) at room temperature. The complete dissolution of potassium hydroxide was observed in 1 h. After the solvent was removed in vacuo, the residue was recrystallized from a DMF–dimethoxyethane (DME) (2 : 1) mixture. The product was isolated as stable in air colorless crystals. The yield was 0.26 g (73%), $T_{decomp} > 250$°C.

IR (KBr), ν, cm^{-1}: 3054 m (C_{Ar}–H); 1589 m, 1565 m, 1495 s, 1450 m, 1405 vs, 1364 s, 1328 m, 1317 w, 1293 w, 1272 s, 1228 w (C_{Ar}–C_{Ar}, C_{Ar}–N, C_{Ar}–H); 1148 m (N–C); 1088 m, 798 m, 740 vs (C_{Ar}–H).



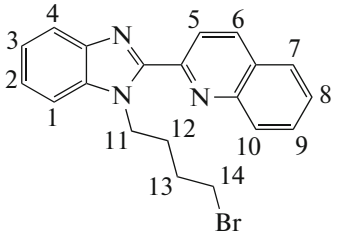
^{1}H NMR ($(CD_3)_2SO$), δ, ppm: 8.51 (d, 1H, J = 3.9 Hz, H^8), 8.30 (d, 1H, J = 7.8 Hz, H^5), 7.71 (t, 1H, J = 7.7 Hz, H^6), 7.39 (dd, 2H, J = 5.9 and 3.1 Hz, H^1 and H^4), 7.13–7.19 (m, 1H, H^7), 6.75 (dd, 2H, J = 6.0 and 3.2 Hz, H^2 and H^3). ^{13}C NMR ($(CD_3)_2SO$), δ, ppm: 159.16, 155.30, 148.59, 146.87, 135.81, 121.46, 121.26, 117.66, 116.45.

For $C_{12}H_8N_3K$

anal. calcd., %:	C, 61.80;	H, 3.43.
Found, %:	C, 61.84;	H, 3.45.

Synthesis of 2-(1-(4-bromobutyl)-1*H*-benzo[*d*]imidazol-2-yl)quinoline (L^1). A mixture of 2-(2-quinoline)benzimidazole (0.43 g, 1.76 mmoL) and KOH (0.12 g, 2.14 mmol) in dimethyl sulfoxide (DMSO) (5 mL) was stirred at room temperature for 1 h, and 1,4-dibromobutane (1.14 g, 5.28 mmol) was added. After additional stirring at room temperature for 1 h, the reaction mixture was mixed with water (25 mL). The product was extracted with chloroform (3 × 10 mL). The organic phase was washed with water and dried over $MgSO_4$. After the solvent was removed, the residue was washed with hexane and dried in vacuo at 50°C. The yield of L^1 as a viscous oily light yellow substance was 0.40 g (60%).

IR (KBr), ν, cm^{-1}: 3059 m (C_{Ar}–H); 2927 w, 2853 m (C–H); 1672 w, 1598 m, 1500 s, 1441 s, 1400 s, 1376 m, 1328 m, 1284 w, 1261 w, 1243 w (C_{Ar}–C_{Ar}, C_{Ar}–N, C_{Ar}–H); 1157 m (N–C); 837 m, 742 vs (C_{Ar}–H).



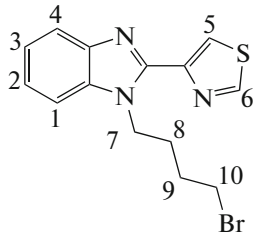
^{1}H NMR ($CDCl_3$), δ, ppm: 8.61 (d, 1H, J = 8.7 Hz, H^5), 8.27 (d, 1H, J = 8.4 Hz, H^6), 8.12 (d, 1H, J = 8.4 Hz, H^{10}), 7.92–7.72 (m, 3H, H^4, H^7, and H^9), 7.62–7.48 (m, 2H, H^1 and H^8), 7.41–7.31 (m, 2H, H^2 and H^3), 5.04 (t, 2H, J = 7.0 Hz, H^{11}), 3.45 (t, 2H, J = 6.5 Hz, H^{14}), 2.24 and 2.05 (m, 2H each, H^{12} and H^{13}). ^{13}C NMR ($CDCl_3$), δ, ppm: 150.29, 149.44, 147.26, 142.60, 136.75, 136.52, 129.82, 129.54, 127.72, 127.29, 123.79, 122.79, 121.87, 120.37, 119.02, 110.08, 44.99, 33.00, 30.11, 28.90.

For $C_{20}H_{18}N_3Br$

anal. calcd., %:	C, 63.16;	H, 4.74.
Found, %:	C, 63.20;	H, 4.79.

Synthesis of 4-(1-(4-bromobutyl)-1*H*-benzimidazol-2-yl)thiazole (L^2). A mixture of 4-(2-thiazolyl)benzimidazole (0.43 g, 2.14 mmol) and KOH (0.15 g, 2.68 mmol) in DMSO (5 mL) was stirred at room temperature for 1 h, and 1,4-dibromobutane (1.39 g, 6.43 mmol) was added. After stirring at room temperature for 1 h, the reaction mixture was mixed with water (25 mL). The product was extracted with chloroform (3 × 10 mL). The organic phase was washed with water and dried over $MgSO_4$. After the solvent was removed, the residue was washed with hexane and dried in vacuo at 50°C. The yield of L^2 as a viscous oily light yellow substance was 0.46 g (64%).

IR (KBr), ν, cm^{-1}: 3059 m (C_{Ar}–H); 2935 w, 2861 m (C–H); 1675 w, 1613 m, 1473 s, 1456 s, 1405 vs, 1352 m, 1334 m, 1305 s, 1284 w, 1272 w, 1248 w (C_{Ar}–C_{Ar}, C_{Ar}–N, C_{Ar}–H); 1157 m (N–C); 825 m, 743 vs (C_{Ar}–H).



^{1}H NMR ($CDCl_3$), δ, ppm: 8.93–8.78 (m, 1H, H^6), 8.36–8.31 (m, 1H, H^5), 7.83–7.78 (m, 1H, H^1), 7.46–7.42 (m, 1H, H^4), 7.33–7.29 (m, 2H, H^2 and H^3), 4.81 (t, 2H, J = 7.3 Hz, H^7), 3.39 (t, 2H, J = 6.5 Hz, H^{10}), 2.13–1.84 (m, 4H, H^8 and H^9). ^{13}C NMR ($CDCl_3$), δ, ppm: 152.89, 147.71, 146.43, 142.61, 135.59, 123.17, 122.77, 121.49, 119.68, 109.93, 44.15, 32.80, 29.80, 28.70.

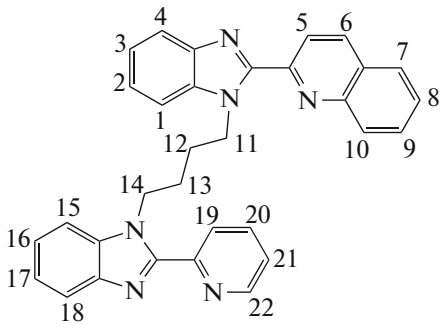
For $C_{14}H_{14}N_3SBr$

anal. calcd., %:	C, 50.06;	H, 4.20.
Found, %:	C, 50.00;	H, 4.17.

Synthesis of 2-(1-(4-(2-(pyridin-2-yl)-1*H*-benzo[*d*]imidazol-1-yl)butyl)-1*H*-benzo[*d*]imidazol-2-yl)quinoline (L^3). Complex **I** (0.29 g, 1.24 mmol) and compound L^1 (0.47 g, 1.24 mmol) in DMSO (5 mL) were stirred at 50°C for 5 h. Then the reaction mixture was cooled to room temperature and mixed with water (25 mL). The product was extracted with chloroform (3 × 10 mL). The organic phase was washed with water and dried over $MgSO_4$. After the solvent was removed,

the residue was washed with hexane and recrystallized from ethanol. The yield of L^3 as a finely crystalline colorless substance was 0.40 g (67%), mp = 235–238°C.

IR (KBr), ν, cm^{-1}: 3054 m (C_{Ar}–H); 2924 m, 2856 m (C–H); 1616 w, 1598 m, 1465 m, 1441 vs, 1400 s, 1367 m, 1331 m, 1313 w, 1275 w, 1257 w (C_{Ar}–C_{Ar}, C_{Ar}–N, C_{Ar}–H); 1154 m (N–C); 834 m, 739 vs (C_{Ar}–H).

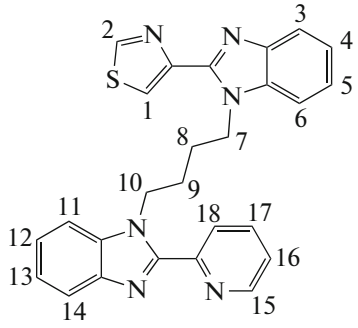


^{1}H NMR ($CDCl_3$), δ, ppm: 8.58 (d, 2H, J = 8.6 Hz, H^5 and H^{22}), 8.25 (d, 2H, J = 8.7 Hz, H^6 and H^{20}), 7.90–7.81 (m, 5H, H^7, H^9, H^{10}, H^{19}, and H^{21}), 7.53–7.51 (m, 3H, H^4, H^8, and H^{18}), 7.44–7.42 (m, 2H, H^1 and H^{15}), 7.34 (dd, 4H, J = 6.2 and 3.0 Hz, H^2, H^3, H^{16}, and H^{17}), 5.09 (br.s, 4H, H^{11} and H^{14}), 2.29 (br.s, 4H, H^{12} and H^{13}). ^{13}C NMR ($CDCl_3$), δ, ppm: 150.39, 149.52, 147.23, 142.72, 136.86, 136.49, 129.72, 129.45, 127.65, 127.21, 123.74, 122.74, 121.82, 120.43, 110.07, 45.59, 27.92.

For $C_{32}H_{26}N_6$		
anal. calcd., %:	C, 77.71;	H, 5.30.
Found, %:	C, 77.80;	H, 5.29.

Synthesis of 4-(1-(4-(2-(pyridin-2-yl)-1*H*-benzo[*d*]imidazol-1-yl)butyl)-1*H*-benzo[*d*]imidazol-2-yl)thiazole (L^4). Complex **I** (0.36 g, 1.54 mmol) and compound L^2 (0.52 g, 1.54 mmol) in DMSO (5 mL) were stirred at 50°C for 5 h. Then the reaction mixture was cooled to room temperature and mixed with water (25 mL). The product was extracted with chloroform (3 × 10 mL). The organic phase was washed with water and dried over $MgSO_4$. After the solvent was removed, the residue was washed with hexane and recrystallized from ethanol. The yield of L^4 as a finely crystalline colorless substance was 0.44 g (64%), mp = 200–203°C.

IR (KBr), ν, cm^{-1}: 3078 m (C_{Ar}–H); 2924 w, 2856 m (C–H); 1613 w, 1589 m, 1456 m, 1441 s, 1405 s, 1361 m, 1328 m, 1304 w, 1261 w, 1249 w (C_{Ar}–C_{Ar}, C_{Ar}–N, C_{Ar}–H); 1154 m (N–C); 834 m, 734 vs (C_{Ar}–H).



^{1}H NMR ($CDCl_3$), δ, ppm: 8.78 (dd, 1H, J = 3.7 and 1.5 Hz, H^2), 8.56–8.54 (m, 1H, H^{15}), 8.40 (d, 1H, J = 8.0 Hz, H^{18}), 8.30 (t, 1H, J = 2.1 Hz, H^1), 7.85–7.78 (m, 3H, H^3, H^6, and H^{17}), 7.37–7.29 (m, 7H, H^4, H^5, H^{11}, H^{12}, H^{13}, H^{14}, and H^{16}), 4.85 (t, 2H, J = 6.7 Hz, H^{10}), 4.78 (m, 2H, H^7), 2.08–1.89 (m, 4H, H^8 and H^9). ^{13}C NMR ($CDCl_3$), δ, ppm: 152.73, 148.50, 147.91, 146.55, 142.85, 142.67, 136.78, 136.58, 135.71, 124.66, 123.71, 123.36, 123.06, 122.64, 121.20, 120.22, 119.77, 110.00, 109.88, 44.94, 44.55, 27.26.

For $C_{26}H_{22}N_6S$		
anal. calcd., %:	C, 69.33;	H, 4.89.
Found, %:	C, 69.40;	H, 4.96.

X-ray diffraction analysis. The crystallographic data for compound **I** were collected on a Bruker D8 QUEST automated diffractometer (MoK_α radiation, λ = 0.71073 Å). The structure was solved by a direct method and refined by full-matrix least squares on F^2 using the SHELXTL program [10]. An absorption correction was applied using the SADABS program [11]. All non-hydrogen atoms were refined in the anisotropic approximation. Hydrogen atoms were placed in the geometrically calculated positions and refined in the riding model. The crystallographic characteristics and main refinement parameters are given in Table 1.

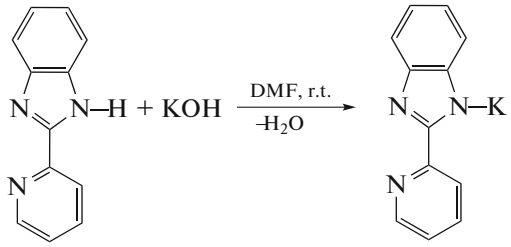
The crystallographic data for compound **I** were deposited with the Cambridge Crystallographic Data Centre (CIF file CCDC no. 1478559; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

It is known that the sodium or potassium derivatives of 2-pyridinylbenzimidazole are synthesized by the reaction of the heterocycle with NaH in DMF or with KOH in a medium of DMF or DMSO and used in further syntheses without isolation [12–14]. We attempted to obtain potassium 2-pyridinyl benzimidazolate in the individual state and to determine its physicochemical characteristics. Complex **I** was found to be formed in the reaction of 2-(pyridin-2-yl)-1*H*-benz[*d*]imidazole (BenzimidH) with potassium hydroxide in a DMF solution at room temperature.

Table 1. Crystallographic data and X-ray diffraction experimental and structure refinement parameters for complex **I**

Parameter	Value
Empirical formula	$C_{24}H_{16}N_6K_2$
FW	466.63
Temperature, K	100(2)
Crystal system	Monoclinic
Space group	$P2_1/c$
a, Å	13.2678(6)
b, Å	22.1443(10)
c, Å	7.0461(3)
β, deg	91.445(1)
V, Å^3	2069.53(16)
Z	4
F(000)	960
ρ_{calcd}, g cm^{-3}	1.498
μ, mm^{-1}	0.484
Crystal size, mm	0.82 × 0.29 × 0.10
Scan range over θ, deg	1.535–28.000
Index ranges	$-17 \le h \le 17$, $-29 \le k \le 29$, $-9 \le l \le 9$
Total number of reflections	21311
Number of independent reflections (R_{int})	4988 (0.044)
GOOF (F^2)	1.024
R_1, wR_2 ($I > 2\sigma(I)$)	0.0354, 0.0919
R_1, wR_2 (all data)	0.0430, 0.0955
$\Delta\rho_{max}/\Delta\rho_{min}$, *e* Å^{-3}	0.545/–0.418



The reaction is completed within 1 h. After the solvent was removed and the product was crystallized from a DMF–DME (2 : 1) mixture, compound **I** was isolated in a yield of 73% as an air stable MF and DMSO and insoluble in THF, DME, and hexane. The data of IR and NMR spectroscopy correspond to the presented formula.

The structure of complex **I** was determined by X-ray diffraction analysis. The coordination polymer contains dimeric layers of BenzimidK molecules arranged along the crystallographic plane *a*0*c*. The structure forming elements in crystal are centrosymmetric dimeric fragments $[BenzimidK(1)]_2$ and $[BenzimidK(2)]_2$ in which the potassium atoms differ by the coordination mode of the pyridinylbenzimidazole ligands (Fig. 1, Table 2).

The pyridinylbenzimidazole ligands in dimer $[BenzimidK(1)]_2$ are symmetrically coordinated to the potassium atoms through the N(1) and N(2) atoms of the pyridine and imidazole fragments, respectively. The K(1)–N(1, 2) distances range from 2.8418(13) to 3.0473(13) Å. In dimer $[BenzimidK(2)]_2$, the organic ligand is coordinated to the K(2) atom by the N(4) and N(5) atoms, whereas the coordination to the K(2*A*) atom occurs through the N(5) and C(19, 20) atoms of the benzimidazole fragment. The K(2)–N(5) distances (2.7400(12) and 2.8650(13) Å) are somewhat shorter than similar K(1)–N(1, 2) distances in $[BenzimidK(1)]_2$. The K(2)–C(19, 20) distances are 3.1575(14) and 3.3547(15) Å, respectively. Note that the K(1)···K(1*A*) and K(2)···K(2*A*) distances

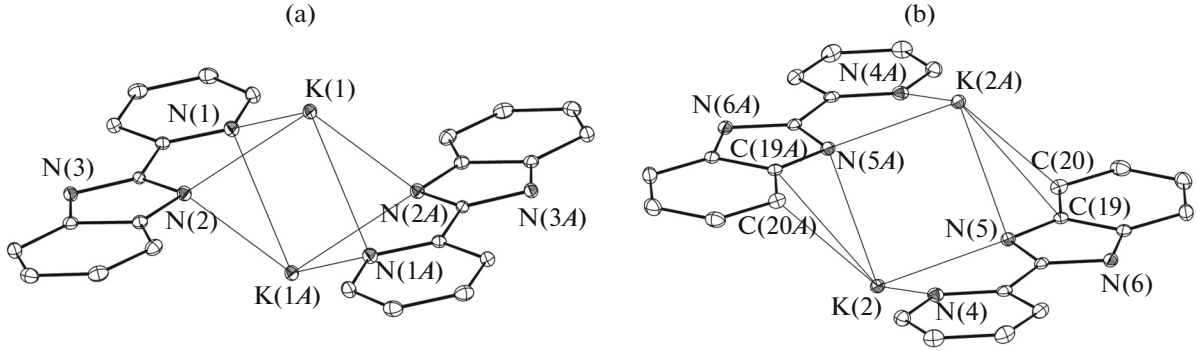


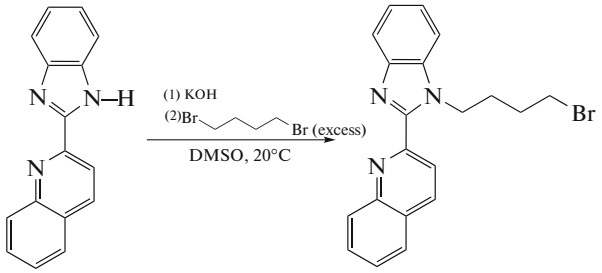
Fig. 1. Structures of the dimeric fragments (a) $[BenzimidK(1)]_2$ and (b) $[BenzimidK(2)]_2$ in crystal of complex **I**. Hydrogen atoms are omitted, and thermal ellipsoids are presented with 30% probability.

differ appreciably and are equal to 3.5233(6) and 3.9771(6) Å, respectively.

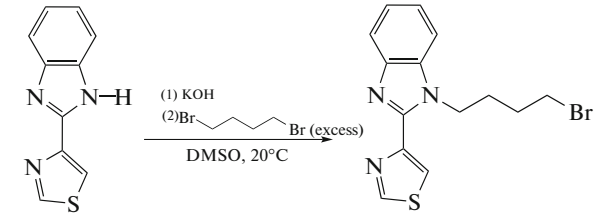
The dimeric motifs $[BenzimidK(1)]_2$ and $[BenzimidK(2)]_2$ form in crystal the corresponding one-dimensional chains A...A and B...B in which the parallel packing of the pyridinylbenzimidazole ligands takes place according to the head-to-tail type (Fig. 2).

The interplanar distance between the Benzimid ligands with the N(1–3) atoms is 3.45 Å. A similar distance between the Benzimid ligands with the N(4–6) atoms is 3.40 Å. In the chains A...A and B...B, the K(1) and K(2) atoms are additionally coordinated by the N(3) and N(6) atoms, respectively, of the adjacent dimers $[BenzimidK(2)]_2$ and $[BenzimidK(1)]_2$. The K(1)–N(3*C*) and K(2*A*)–N(6*B*) distances (2.8910(12) and 2.8641(13) Å) lie in the range of similar K–N distances in dimers $[BenzimidK(1)]_2$ and $[BenzimidK(2)]_2$ (2.7400(12)–3.0473(13) Å). An additional coordination of the pyridinylbenzimidazole ligands is observed to the potassium atoms between the A...B chains: K(1)–N(6) 2.8215(12), K(1)–C(24) 3.3866(14), and K(2*A*)–N(3*C*) 2.8648(12) Å. In the layered structure of compound **I**, the chains of dimers $[BenzimidK(1)]_2$ and $[BenzimidK(2)]_2$ alternate with each other to form a T-like packing of the Benzimid ligands between the A...B chains (Fig. 2).

Further it was found that the reaction of complex **I** with the bromobutyl-substituted derivatives of benzimidazolylquinoline (L^1) and benzimidazolylthiazole (L^2) resulted in the formation of the bis(diimine) ligands with different diimine fragments. The earlier undescribed reagents L^1 and L^2 were synthesized according to the scheme



60% (L^1)



64% (L^2)

Derivatives L^1 and L^2 are light yellow oily liquids. The compositions and structures of the products were confirmed by the data of elemental analysis and IR and NMR spectroscopy. In the ^1H NMR spectra, the characteristic signals of the protons of the methylene groups bound to the nitrogen atom appear as triplets in a range of 5.04–4.81 ppm. The signals of the protons in the $-CH_2-Br$ groups are also triplets and observed in high fields in a range of 3.45–3.39 ppm. The multiplets in a range of 2.24–1.84 ppm are assigned to the $-CH_2-CH_2-$ fragments.

Bis(diimine) ligands L^3 and L^4 are formed by the reactions of complex **I** with compounds L^1 and L^2, respectively, in a DMSO solution.

Table 2. Selected bond lengths (Å) and angles (deg) in complex **I**

Bond	Distance, Å	Angle	ω, deg
K(1)–N(1)	2.8418(13)	N(1)K(1)N(2)	59.23(3)
K(1)–N(2)	2.8456(12)	N(2)K(1)N(1*A*)	79.97(3)
K(1)–N(1*A*)	3.0473(13)	N(1*A*)K(1)N(2*A*)	55.04(3)
K(1)–N(2*A*)	3.0358(12)	N(2*A*)K(1)N(1)	80.22(3)
K(1)–N(3*C*)	2.8910(12)	N(1)K(1)N(1*A*)	106.60(3)
K(1)–N(6)	2.8215(12)	N(2)K(1)N(2*A*)	106.47(3)
K(1)–C(24)	3.3866(14)	N(3*C*)K(1)N(6)	89.63(4)
K(1)···K(1*A*)	3.5233(6)		
K(2*A*)–N(3*C*)	2.8648(12)	N(4)K(2)N(5)	60.40(4)
K(2)–N(4)	2.8477(12)	N(4)K(2)N(5*A*)	99.45(4)
K(2)–N(5)	2.7400(12)	N(5*A*)K(2)N(5)	89.63(4)
K(2)–N(5*A*)	2.8650(13)	K(2)N(5)K(2*A*)	90.37(4)
K(2)–N(6*E*)	2.8641(13)	N(3*C*)K(2*A*)N(6*B*)	94.57(4)
K(2)–C(19*A*)	3.1575(14)	N(3*C*)K(2*A*)N(5)	88.68(4)
K(2)–C(20*A*)	3.3547(15)	N(6*B*)K(2*A*)N(4*A*)	75.46(3)
K(2)···K(2*A*)	3.9771(6)	N(6*B*)K(2*A*)N(5*A*)	93.98(4)

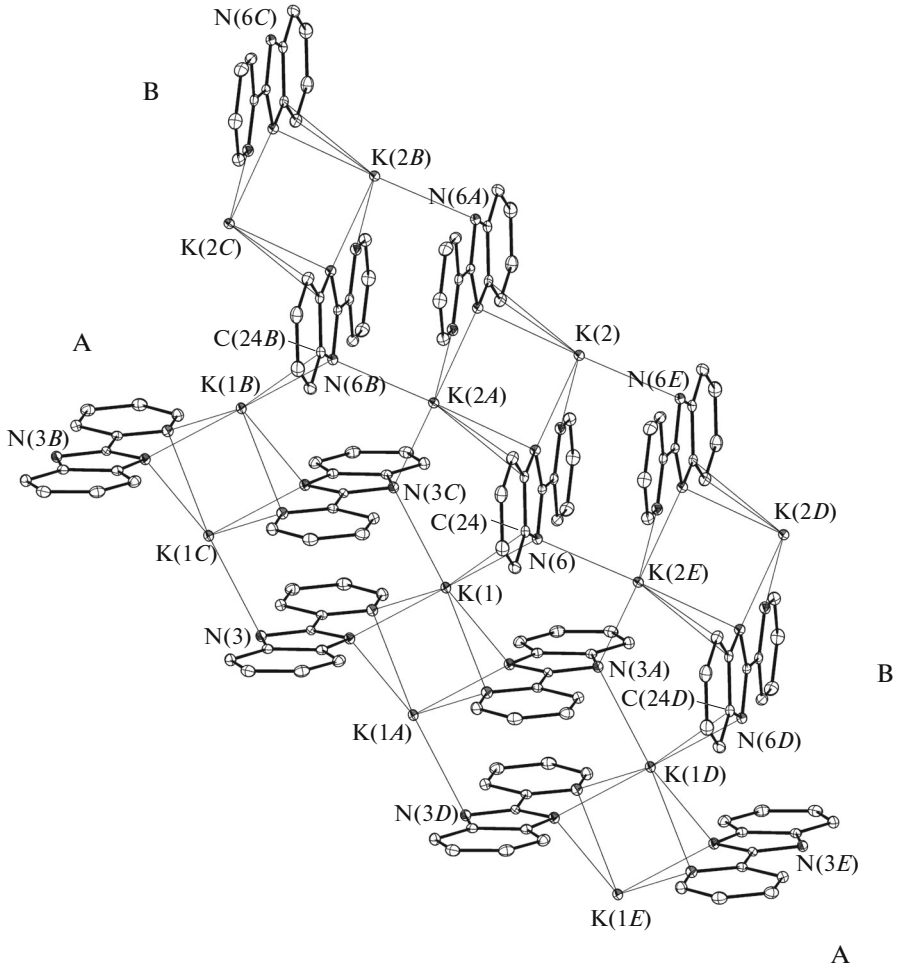
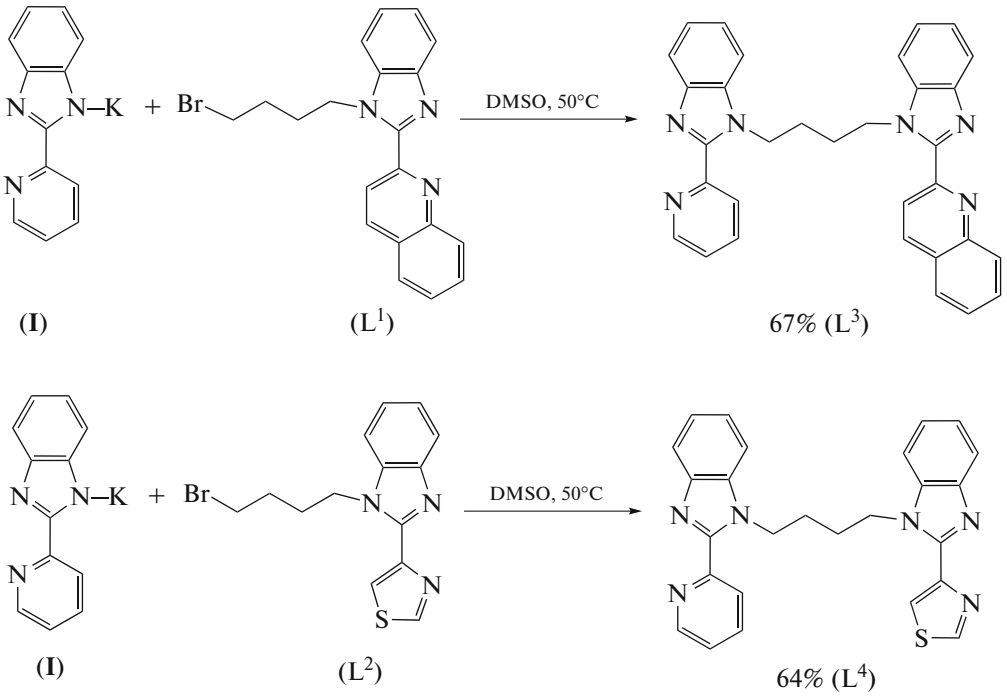


Fig. 2. Fragment of the crystal packing in complex **I**.



Compounds L^3 and L^4 are colorless finely crystalnsline substances highly soluble in DMF, DMSO, CH_2Cl_2, and $CHCl_3$, moderately soluble in THF, DME, and ethanol, and insoluble in hexane. The results of elemental analysis and IR and NMR spectroscopy confirm the compositions of products L^3 and L^4. In the ^1H NMR spectrum of ligand L^3, the signals of the protons in the $-CH_2-N$ and $-CH_2-CH_2-$ groups appear as broadened singlets with chemical shifts of 5.09 and 2.29 ppm, respectively. In the case of ligand L^4, the signals of the protons in the $-CH_2-N$ groups have the form of a triplet (4.85 ppm) and a multiplet (4.78 ppm), whereas the signals of the $-CH_2-CH_2-$ fragment are observed as a multiplet in a range of 2.08–1.89 ppm.

The binuclear copper(I) complexes possessing intense photo- and electroluminescence were synthesized from bis(diimine) ligands L^3 and L^4 in the preliminary studies. Their physicochemical and photophysical properties are currently under detail investigation.

In summary, potassium pyridinylbenzimidazolate (**I**) was synthesized and its structure was determined for the first time. New bis(diimine) ligands L^3 and L^4 containing pyridinylbenzimidazole, benzimidazolylquinoline, and benzimidazolylthiazole fragments were synthesized on the basis of complex **I**. Compounds L^3 and L^4 can be used as bridging ligands for the synthesis of various bi- and polynuclear complexes of transition and non-transition metals.

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