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Potassium Carbazolyl Complexes with Coordinating Solvents: Syntheses and Crystal Structures

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Abstract—The reaction of carbazole with KOH in dimethylformamide (DMF) at 75°C for 1.5 h affords CarbK(DMF) (CarbH is carbazole) in 90% yield. The crystallization of the compound from DME, CH_3CN, and CD_3CN gives complexes $CarbK(DME)_2$, $CarbK(DMF)(CH_3CN)$, and $CarbK(DMF)(CD_3CN)$, respectively, whose structures are determined by X-ray diffraction analyses. The dissolution of $CarbK(DMF)(CH_3CN)$ in CD_3CN results in the deuterium exchange in the bound solvent to form complex $CarbK(DMF)_{0.5}(CD_2HCN)_{1.5}$, whose structure is also established by X-ray diffraction analysis.

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INTRODUCTION

Potassium carbazolyl is widely used as the starting reagent for the production of carbazole-containing polymer materials of diverse design [1, 2]. As a rule, potassium carbazolyl is obtained by the reaction of carbazole with potassium hydride in ether solvents [3] or with KOH on reflux in xylene with the continuous removal of formed water as an azeotrope [4]. These methods have substantial drawbacks associated with, in the first case, the use of potassium hydride that ignites in air and, in the second case, the necessity to conduct the synthesis at a high temperature (145°C) for a long time. Therefore, the development of more convenient methods for the synthesis of potassium carbazolyl is an urgent task.

In this work, potassium carbazolyl was found to be readily formed by the reaction of carbazole with KOH in DMF at 75°C for 1.5 h. The compound was isolated as a complex with the solvent CarbK(DMF) (**I**) (90% yield). The crystallization of the product from DME, CH_3CN, and CD_3CN affords compounds $CarbK(DME)_2$ (**II**), $CarbK(DMF)(CH_3CN)$ (**III**), $CarbK(DMF)(CD_3CN)$ (**IV**), and $CarbK(DMF)_{0.5}(CD_2HCN)_{1.5}$ (**V**), whose structures were determined by X-ray diffraction analyses.

EXPERIMENTAL

All procedures with readily 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. Carbazole (Aldrich) was used as received.

^{1}H and ^{13}C{1H} NMR spectra were recorded on Bruker DPX-200 (200 MHz for ^{1}H NMR, 50 MHz for ^{13}C NMR) and Bruker Avance III–400 (400 MHz ^{1}H NMR, 100 MHz for ^{13}C NMR) spectrometers. Chemical shifts are indicated in ppm relative to tetramethylsilane. IR spectra were recorded on an FSM 1201 FT-IR spectrometer. Samples of the compounds were prepared as suspensions in Nujol under argon. The GLC analyses of volatiles were conducted on a Tsvet 800 chromatograph (katharometer as a detector, helium as a carrier gas).

Synthesis of CarbK(DMF) (I). A solution of carbazole (2.00 g, 11.97 mmol) in DMF (15 mL) was added with stirring to a suspension of potassium hydroxide (0.87 g, 15.36 mmol) in DMF (15 mL) at ambient temperature. The reaction mixture was heated at 75°C for 1.5 h. The solution was separated from the precipitate by centrifuging, and the solvent and volatiles were evaporated in vacuo. Water (0.21 g, 96%) was found in the volatile products by GLC. The residue was washed with hexane and dried in vacuo at ambient temperature. Complex **I** was obtained in a yield of 3.00 g (90%) as a light yellow finely crystalline substance unstable in air.

^{1}H NMR (THF-d^8); δ, ppm: 7.97 d (2H, Carb, J = 7.7 Hz), 7.65 s (1H, $(CH_3)_2NC(O)\underline{H}$), 7.51 d (2H, Carb, J = 8.1 Hz), 7.17 t (2H, Carb, J = 8.1 Hz), 6.89 t (2H, Carb, J = 7.7 Hz), 2.68 s (3H, $(C\underline{H_3})_2NC(O)H$), 2.61 s (3H, $(C\underline{H_3})_2NC(O)H$.

^{13}C NMR (THF-d^8), δ, ppm: 162.67 [$(CH_3)_2N\underline{C}(O)H$], 147.99, 125.07, 124.18, 120.07, 115.79, 113.53, 35.90 [$(\underline{C}H_3)_2NC(O)H$], 30.89 [$(\underline{C}H_3)_2NC(O)H$].

IR (ν, cm^{-1}): 3060, 3050, 3030 ν(C_{Ar}–H), 1666 ν(C=O), 1624, 1599 ν(C_{Ar}–C_{Ar}), 1327, 1291, 1235, 1141, 1102 ν(C–N), 991, 927, 874, 849, 757, 724 δ(C_{Ar}–H), 663 δ(O=C–N).

For $C_{15}H_{15}N_2OK$

anal. calcd. (%):	C, 64.51;	H, 5.41.
Found (%):	C, 64.46;	H, 5.38.

Synthesis of CarbK(DME)$_2$ (II). Compound **I** (0.48 g) was dissolved in DME (15 mL). Light yellow crystals were formed during the slow evaporation of the solvent at ambient temperature. The crystals were separated from the solution and dried in vacuo at ambient temperature. Complex **II** was obtained in a yield of 0.30 g.

^{1}H NMR (THF-d^8), δ, ppm: 7.98 d (2H, Carb, J = 7.7 Hz), 7.60 d (2H, Carb, J = 8.1 Hz), 7.18 t (2H, Carb, J = 8.1 Hz), 6.81 t (2H, Carb, J = 7.7 Hz), 3.42 s (4H, $(CH_3OC\underline{H_2}C\underline{H_2}OCH_3)$), 3.26 s (6H, $(C\underline{H_3}OCH_2CH_2OC\underline{H_3})$).

^{13}C NMR (THF-d^8), δ, ppm: 152.00, 125.87, 123.36, 120.01, 114.29, 114.11, 72.73 $(CH_3O\underline{C}H_2\underline{C}H_2OCH_3)$, 58.86 $(\underline{C}H_3OCH_2CH_2O\underline{C}H_3)$.

IR (ν, cm^{-1}): 3060, 3050, 3030 ν(C_{Ar}–H), 1628, 1602 ν(C_{Ar}–C_{Ar}), 1326, 1287, 1233, 1095 ν(C–C, DME), 1027, 991, 875, 850, 762, 726 δ(C_{Ar}–H).

For $C_{20}H_{28}NO_4K$

anal. calcd. (%):	C, 62.16;	H, 7.30.
Found (%):	C, 62.08;	H, 7.26.

Synthesis of CarbK(DMF)(CH$_3$CN) (III). Compound **I** (0.5 g) was dissolved in acetonitrile (10 mL). Light yellow crystals were formed by the slow evaporation of the solvent at ambient temperature. The crystals were separated from the solution and dried in vacuo at ambient temperature. Complex **III** was obtained in a yield of 0.3 g.

^{1}H NMR (THF-d^8), δ, ppm: 7.98 d (2H, Carb, J = 7.7 Hz), 7.69 s (1H, $(CH_3)_2NC(O)\underline{H}$), 7.50 d (2H, Carb, J = 8.1 Hz), 7.19 t (2H, Carb, J = 8.1 Hz), 6.90 t (2H, Carb, J = 7.6 Hz), 2.72 s (3H, $(C\underline{H_3})_2NC(O)H$), 2.64 s (3H, $(C\underline{H_3})_2NC(O)H$), 1.89 s (3H, $C\underline{H_3}CN$).

^{13}C NMR (THF-d^8), δ, ppm: 162.58 $[(CH_3)_2N\underline{C}(O)H]$, 147.70, 125.07, 124.31, 120.14, 116.97 $(CH_3\underline{C}N)$, 116.00, 113.36, 35.89 $[(\underline{C}H_3)_2NC(O)H]$, 30.89 $[(\underline{C}H_3)_2NC(O)H]$, 0.59 $(\underline{C}H_3CN)$.

IR (ν, cm^{-1}): 3060, 3050, 3036 ν(C_{Ar}–H), 2291, 2252 ν(C≡N), 1663 ν(C=O), 1627, 1599 ν(C_{Ar}–C_{Ar}), 1324, 1288, 1233, 1141, 1105 ν(C–N), 991, 927, 877, 844, 757, 724 δ(C_{Ar}–H), 666 δ(O=C–N).

For $C_{17}H_{18}N_3OK$

anal. calcd. (%):	C, 63.92;	H, 5.68.
Found (%):	C, 63.48;	H, 5.56.

Synthesis of CarbK(DMF)(CD$_3$CN) (IV). Compound **I** (0.14 g) was dissolved in CD_3CN (2 mL) and kept at –15°C for 12 h. Light yellow crystals that formed were separated from the solution and dried in vacuo at ambient temperature. Complex **IV** was obtained in a yield of 0.07 g.

^{1}H NMR (THF-d^8), δ, ppm: 8.02 d (2H, Carb, J = 7.7 Hz), 7.80 s (1H, $(CH_3)_2NC(O)\underline{H}$), 7.45 s (2H, Carb, J = 8.1 Hz), 7.26 t (2H, Carb, J = 8.1 Hz), 7.02 t (2H, Carb, J = 7.8 Hz), 2.77 s (3H, $(C\underline{H_3})_2NC(O)H$), 2.70 s (3H, $(C\underline{H_3})_2NC(O)H$.

^{13}C NMR (THF-d^8), δ, ppm: 162.49 $[(CH_3)_2N\underline{C}(O)H]$, 144.36, 125.19, 124.59, 120.41, 117.65, 116.93 $(CD_3\underline{C}N)$, 112.30, 35.88 $[(\underline{C}H_3)_2NC(O)H]$, 30.91 $[(\underline{C}H_3)_2NC(O)H]$, 0.17 hept. $(\underline{C}D_3CN$, J_{CD} = 20.7 Hz).

IR (ν, cm^{-1}): 3060, 3050, 3030 ν(C_{Ar}–H), 2264, 2240 ν(C≡N), 1664 ν(C=O), 1627, 1597 ν(C_{Ar}–C_{Ar}), 1326, 1291, 1233, 1139, 1106 ν(C–N), 991, 929, 876, 840, 758, 722 δ(C_{Ar}–H), 665 δ(O=C–N).

Synthesis of CarbK(DMF)$_{0.5}$(CD$_2$HCN)$_{1.5}$ (V). Compound **IV** (0.1 g) was dissolved in CD_3CN (2 mL), and the solution was kept at –15°C for 12 h. Light yellow crystals that formed were separated from the solution and dried in vacuo at ambient temperature. The yield of complex **V** was 0.04 g.

^{1}H NMR (CD_3CN), δ, ppm: 8.02 d (2H, Carb, J = 7.7 Hz), 7.87 s (0.5H, $(CH_3)_2NC(O)\underline{H}$), 7.31 d (2H, Carb, J = 8.2 Hz), 7.19 t (2H, Carb, J = 8.2 Hz), 6.90 t (2H, Carb, J = 7.8 Hz), 2.84 s (1.5H, $(C\underline{H_3})_2NC(O)H$), 2.74 s (1.5H, $(C\underline{H_3})_2NC(O)H$), 1.91 q (1.5H, $CD_2\underline{H}CN$, J_{HD} = 2.4 Hz).

^{1}H NMR (THF-d^8), δ, ppm: 8.02 d (2H, Carb, J = 7.8 Hz), 7.80 s (0.5H, $(CH_3)_2NC(O)\underline{H}$), 7.44 d (2H, Carb, J = 8.0 Hz), 7.25 t (2H, Carb, J = 8.2 Hz), 7.00 t (2H, Carb, J = 7.8 Hz), 2.79 s (1.5H, $(C\underline{H_3})_2NC(O)H$), 2.70 s (1.5H, $(C\underline{H_3})_2NC(O)H$), 1.99 q (1.5H, $CD_2\underline{H}CN$, J_{HD} = 2.5 Hz).

^{13}C NMR (THF-d^8), δ, ppm: 162.39 $[(CH_3)_2N\underline{C}(O)H]$, 144.61, 125.14, 124.68, 120.42, 117.57, 116.84 $(CD_2H\underline{C}N)$, 112.31, 35.84 $[(\underline{C}H_3)_2NC(O)H)]$, 30.90 $[(\underline{C}H_3)_2NC(O)H]$, 0.14 q $(\underline{C}D_2HCN$, J_{CD} = 20.4 Hz).

IR (ν, cm^{-1}): 3060, 3044, 3030 ν(C_{Ar}–H), 2264, 2236 ν(C≡N), 1663 ν(C=O), 1627, 1594 ν(C_{Ar}–C_{Ar}), 1324, 1288, 1233, 1138, 1105 ν(C–N), 991, 927, 874, 844, 756, 724 δ(C_{Ar}–H), 663 δ(O=C–N).

X-ray diffraction analyses were carried out on a Bruker AXS SMART APEX spectrometer for complexes **II**–**IV** and on an Oxford Xcalibur Eos spectrometer for complex **V** (graphite monochromator, MoK_α radiation, ω scan mode, λ = 0.71073 Å). Experimental sets of intensities were integrated using the SAINT [5] (**II**–**IV**) and CrysAlisPro [6] (**V**) programs. The SADABS [7] (**II**–**IV**) and SCALE3 ABSPACK [8] (**V**) programs were used for applying absorption corrections. The structures were solved by direct methods using the SHELXTL program package [9] and refined by the full-matrix least-squares method for F^2_{hkl} in the anisotropic approximation for all non-hydrogen atoms. Hydrogen atoms were placed

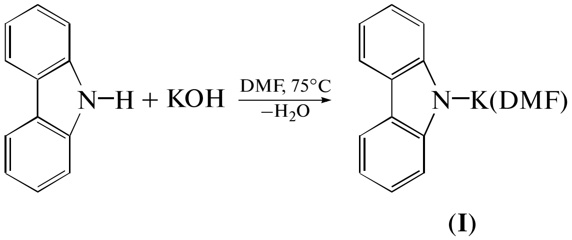
Crystallographic data and the parameters of X-ray diffraction experiments and refinement for complexes **II**–**V**

Complex	**II**	**III**	**IV**	**V**
M	771.07	319.44	322.46	306.44
T, K	100(2)	100(2)	100(2)	100(2)
Crystal system	Monoclinic	Triclinic	Triclinic	Triclinic
Space group	$P2_1/n$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a, Å	14.6915(9)	7.0989(6)	7.0608(6)	7.0521(3)
b, Å	9.4266(6)	9.4601(9)	9.4117(8)	9.3911(3)
c, Å	15.446(1)	13.149(1)	13.1070(11)	13.1055(5)
α, deg	90	70.293(1)	70.314(2)	70.242(3)
β, deg	92.740(1)	86.196(1)	86.139(2)	86.175(3)
γ, deg	90	78.899(1)	78.512(2)	78.496(3)
V, Å^3	2136.7(2)	815.8(1)	803.7(1)	800.43(5)
Z	2	2	2	2
ρ_{calcd}, g/cm^{-3}	1.198	1.300	1.333	1.271
μ_{Mo}, mm^{-1}	0.271	0.330	0.335	0.331
F(000)	824	336	336	318
Crystal size, mm	0.13 × 0.11 × 0.08	0.44 × 0.20 × 0.12	0.19 × 0.16 × 0.09	0.40 × 0.20 × 0.20
θ Range, deg	2.53–25.99	2.33–25.99	2.34–26.00	3.29–30.00
Number of collected reflections	17774	7017	6878	15639
Number of independent reflections (R_{int})	4189(0.0297)	3163(0.0201)	3100(0.0253)	4641(0.0358)
R_1/wR_2 ($I > 2\sigma(I)$)	0.0472/0.1223	0.0431/0.1128	0.0532/0.1429	0.0404/0.0855
R (for all data)	0.0607/0.1290	0.0572/0.1214	0.0774/0.1561	0.0623/0.0918
Goodness-of-fit	0.965	1.026	1.044	1.021
Residual electron density, e Å^{-3}	0.430/–0.249	0.752/–0.307	0.494/–0.602	0.423/–0.228

in the geometrically calculated positions and refined in the riding model. The H(13*A*) atoms of the DMF molecule in complexes **III**–**V** and deuterium atoms in complex **IV** were revealed from the difference Fourier electron density syntheses and refined isotropically. The DMF and CD_2HCN molecules in **V** coordinated on the K atoms are disordered over two positions with the site occupancies 0.5 (DMF) : 0.5 (CD_2HCN). The main crystallographic characteristics and X-ray diffraction parameters for compounds **II**–**V** are presented in the table. The crystallographic information for the compounds was deposited with the Cambridge Crystallographic Data Centre (nos. 927878 (**II**), 927879 (**III**), 927880 (**IV**), and 927881 (**V**); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

The complex of potassium carbazolyl with DMF (**I**) was synthesized by the reaction of carbazole with potassium hydroxide in a DMF solution



(I)

The interaction between the reactants ceases within 1.5 h at 75°C. The reaction course was monitored using GLC by the amount of formed water. Complex **I** was isolated in 90% yield as a light yellow finely crystalline substance unstable in air, well soluble in DMF, DME, and THF, and moderately soluble in acetonitrile. The compound was identified by elemental analysis and IR and NMR spectroscopy. The NMR studies showed that the methyl groups in coordinatively bound DMF were nonequivalent. The signals from protons in the ^{1}H NMR spectrum appear as two singlets with chemical shifts of 2.68 and 2.61 ppm, and the signals from the corresponding carbon atoms in the ^{13}C NMR spectrum have chemical shifts of 35.90 and 30.89 ppm.

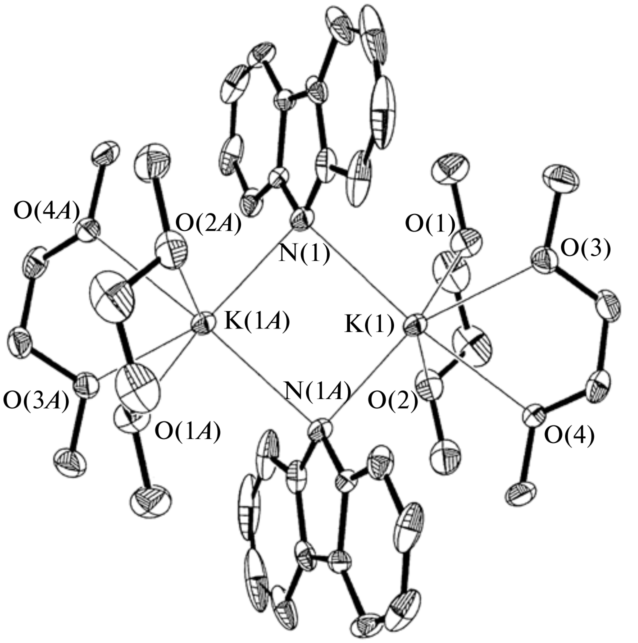


Fig. 1. Molecular structure of complex **II**. Thermal ellipsoids are given with 30% probability. Selected bond lengths: K(1)–O(1) 2.753(2), K(1)–O(2) 2.792(2), K(1)–O(3) 2.806(2), K(1)–O(4) 2.716(1), K(1)–N(1) 2.782(2), and K(1)···K(1*A*) 4.0327(9) Å and bond angles: N(1)K(1)N(1*A*) 87.96(5)°, K(1)N(1)K(1*A*) 92.04(5)°, O(1)K(1)O(3) 79.89(5)°, and O(4)K(1)O(2) 81.50(5)°.

When compound **I** is dissolved in DME, coordinatively bound DMF is replaced by two DME molecules to form complex **II**. The compound is a light yellow crystalline substance unstable in air. The data of elemental analysis and IR and NMR spectroscopy correspond to the presented formula.

The X-ray diffraction analysis of complex **II** shows that each K atom is coordinated through the bidentate mode by two terminal DME molecules and two bridging carbazole ligands (Fig. 1), due to which the coordination number of K is equal to 6.

The K(1)–O terminal bond lengths range from 2.716(1) to 2.806(2) Å. The K(1)–N(1) bridging bond is 2.782(2) Å. The K(1)N(1)K(1*A*) angle is 92.04(5)°. The molecules in the crystal structure of complex **II** are isolated.

The dissolution of complex **I** in acetonitrile or deuterated acetonitrile resulted in the incorporation of the CH_3CN or CD_3CN molecule into the coordination sphere of potassium and in the formation of derivatives **III** and **IV**. The isolated compounds are light yellow crystalline substances unstable in air. Their compositions were confirmed by elemental analysis and IR and NMR spectroscopy. As for the starting compound **I**, the NMR spectra of complexes **III** and **IV** exhibit the nonequivalence of the methyl groups of coordinatively bound DMF.

It was unexpectedly found by the NMR study of complex **III** in CD_3CN that the ^1H NMR spectrum contained no signal from coordinatively bound acetonitrile, but the signal from partially deuterated solvent CD_2HCN was observed. The ratio of integral intensities of the proton signals corresponds to the formula $\mathrm{CarbK(DMF)_{0.5}(CD_2HCN)_{1.5}}$ (**V**). The compound was isolated in the crystalline state, and its composition was confirmed by the data of NMR spectroscopy in THF-d^8. It can be assumed that the dissolution of complex **III** in CD_3CN is accompanied by the deuterium exchange in coordinatively bound acetonitrile. It should be mentioned that the examples for the deuterium exchange of solvent molecules, which are in the coordination sphere of the metal complexes, are known [10–13].

Unlike complex **II**, complexes **III**–**V** are isostructural coordination polymers forming infinite chains along the *x* axis (Fig. 2).

The principal difference between complexes **III**–**V** is the composition and the number of additionally coordinated solvent molecules. Complex **III** contains DMF and CH_3CN molecules, and complex **IV** contains DMF and CD_3CN molecules. Complex **V** exhibits disordering of the DMF and CD_2HCN molecules with site occupancies of 0.5 : 0.5.

The potassium atoms in complexes **III**–**V** have the octahedral coordination and are linked to each other by three bridging ligands. The K–N distances (carbazolyl) are 2.802(1) and 2.809(1) Å in **III**, 2.779(2) and 2.808(2) Å in **IV**, and 2.7815(7) and 2.8051(8) Å in **V**, which is comparable with similar distances in complex **II** (2.782(2) Å). The K–N distances (CH_3CN, CD_3CN) in compounds **III** and **IV** lie in a noticeably narrower range of values (2.872(2)–2.887(2) Å) than the K–N distances (CD_2HCN) in **V** (2.805(1)–2.875(1) Å). The K–N distances (DMF) in **V** (2.676(2) and 2.686(2) Å) are appreciably shorter than those in **III** (2.712(1) and 2.720(1) Å) and **IV** (2.740(2) and 2.748(2) Å). A tendency of shortening the K···K (3.5495(3) Å interatomic distances is observed in a series of complexes **III**–**V** (3.5495(3) Å in **III**, 3.5304(3) Å in **IV**, and 3.5261(1) Å in **V**). Note that in dimeric complex **II** this distance (4.0327(9) Å) is much longer than in complexes **III**–**V**. The K···K distance in the polymer chains of complexes **III**–**V** is substantially longer than the doubled ionic radius for the K atom (coordination number 6, 2.76 Å) but is shorter than the doubled van der Waals radius of potassium (5.4 Å [14]). The K atoms in complexes **III**–**V** are arranged linearly, and the K(1)K(2)K(1*A*) angle is 180°. The values of K(1)N(1)K(2) angles are close to each other, being 78.47(3)° (III), 78.37(4)° (IV), and 78.27(2)° (**V**).

It should be mentioned that the structure of the nonsolvated potassium carbazolyl complex $(\mathrm{CarbK})_n$ (**VI**) [3] differs substantially from structures **III**–**V**. Unlike the linear infinite chains in complexes **III**–**V**, in complex **VI** these chains are spiral. The K···K (4.293(1) Å) and K···N (carbazolyl) (2.870(5),

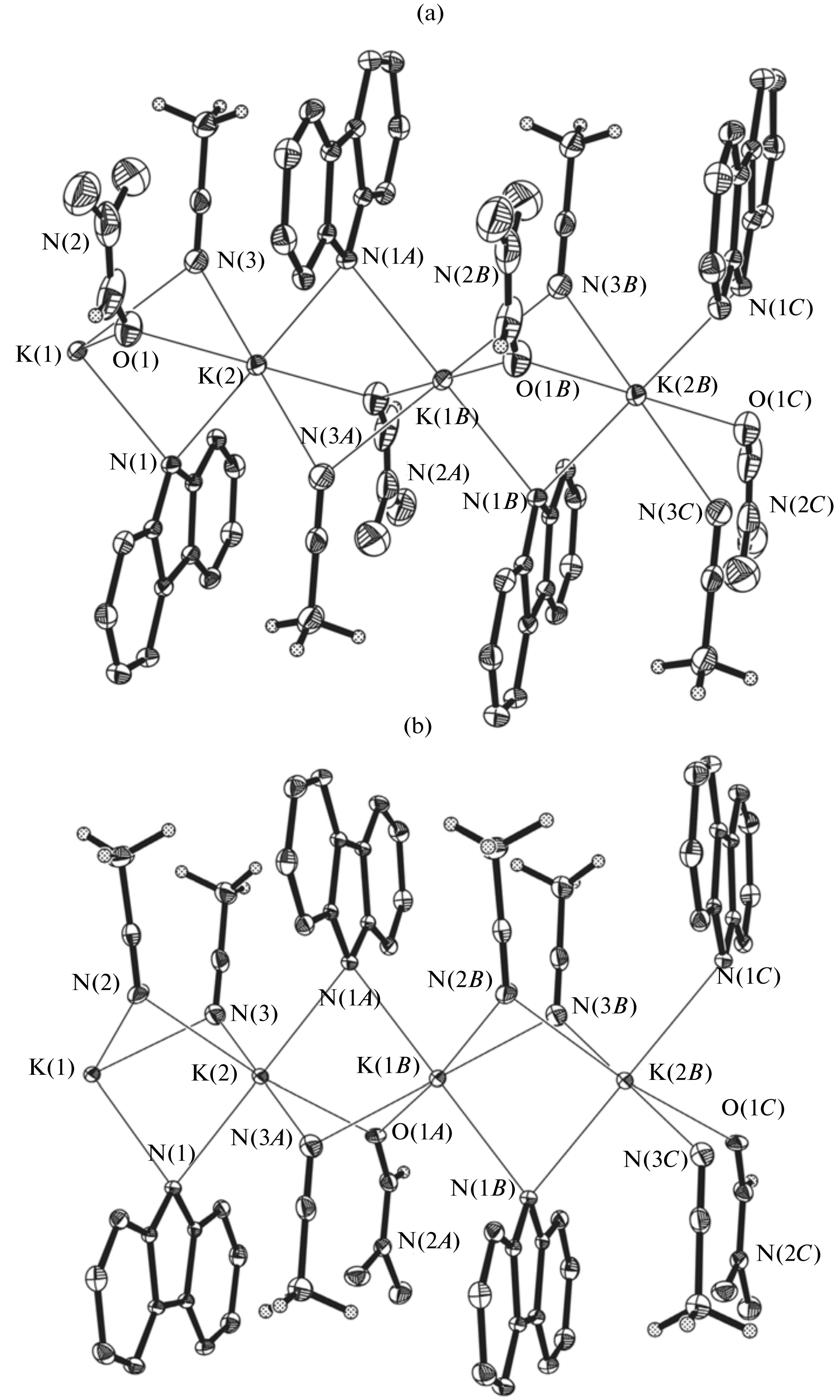


Fig. 2. Fragment of the chain of (a) $[\mathrm{CarbK(DMF)(CH_3CN)}]_n$, (b) $[\mathrm{CarbK(DMF)(CD_3CN)}]_n$, and (c) $[\mathrm{CarbK(DMF)_{0.5}(CD_2HCN)_{1.5}}]_n$ molecules along the *x* chain in crystals **III**–**V**, respectively. Thermal ellipsoids are given with 30% probability. Selected bond lengths and bond angles in **III**: K(1)–O(1) 2.720(1), K(2)–O(1) 2.712(1), K(1)–N(1) 2.802(1), K(2)–N(1) 2.809(1), K(1)–N(3) 2.887(2), K(2)–N(3) 2.887(2), and K(1)···K(2) 3.5495(3) Å and K(2)O(1)K(1) 81.60(4)°, K(1)N(3)K(2) 75.86(4)°, and K(1)N(1)K(2) 78.47(3)°; in **IV**: K(1)–O(1) 2.740(2), K(2)–O(1) 2.748(2), K(1)–N(1) 2.779(2), K(2)–N(1) 2.808(2), K(1)–N(3) 2.872(2), K(2)–N(3) 2.875(2), and K(1)···K(2) 3.5304(3) Å and K(1)O(1)K(2) 80.07(5)°, K(1)N(3)K(2) 75.81(4)°, and K(1)N(1)K(2) 78.37(4)°; in **V**: K(2)–O(1*A*) 2.676(2), K(1*B*)–O(1*A*) 2.686(2), K(1)–N(1) 2.8051(8), K(2)–N(1) 2.7815(7), K(2)–N(3) 2.874(3), K(1)–N(3) 2.8051(8), K(2)–N(4*A*) 2.8705(9), K(1*B*)–N(3*A*) 2.8745(9), and K(1)···K(2) 3.5261(1) Å and K(2)N(1)K(1) 78.27(2)°, K(2)N(4*A*)K(1) 75.73(2)°, K(2)N(3*A*)K(1) 75.51(6)°, and K(2)O(1)K(1*A*) 82.23(4)°. Symmetry procedures: (*A*) $-x, -y, -1-z$; (*B*) $-1+x, y, z$; (*C*) $-1-x, -y, -1-z$.

2.892(6) Å) distances in **VI** noticeably exceed similar distances in compounds **III**–**V**.

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