

# Coordination Polymers of Lithium Based on 1,2-Bis[(2,6-diisopropyl-4-diethylmalonophenyl)imino]acenaphthene

N. L. Bazyakina<sup>a</sup>, V. G. Sokolov<sup>a,†</sup>, M. V. Moskalev<sup>a</sup>, E. V. Baranov<sup>a</sup>, and I. L. Fedushkin<sup>a, \*</sup>

<sup>a</sup> Razuvayev Institute of Organometallic Chemistry, Russian Academy of Sciences, Nizhny Novgorod, Russia

\*e-mail: igorfed@iomc.ras.ru

Received November 28, 2022; revised December 7, 2022; accepted December 7, 2022

**Abstract**—1,2-Bis[(2,6-diisopropyl-4-diethylmalonophenyl)imino]acenaphthene (Dem-Bian) with zinc chloride forms complex  $[(\text{Dem-Bian})\text{ZnCl}_2]$  (**I**). The reaction of complex **I** with *n*-BuLi proceeds with the deprotonation of the malonate fragments and gives 1D coordination polymer  $[\text{ZnCl}_2(\text{Dem-Bian})\text{Li}(\text{DME})_2]_n$  (**II**). The reaction of  $[(\text{Dem-Bian})\text{CuCl}]$  with *n*-BuLi affords 1D polymer  $[(\text{Dem-Bian})\text{Li}_2(\text{DME})_2]_n$  (**III**). Compounds **I**–**III** are characterized by elemental analysis and IR spectroscopy. Derivatives **I** and **II** are characterized by  $^1\text{H}$  NMR spectroscopy. The crystal structures of compounds **II** and **III** are determined by X-ray diffraction (XRD). Their thermal stability is studied by thermogravimetric analysis.

**Keywords:** 1,2-bis(arylimino)acenaphthene, organolithium coordination polymers, crystal structure

**DOI:** 10.1134/S1070328422600620

## INTRODUCTION

Diimine chelating ligands are presently used widely in the chemistry of transition and nontransition metals, since they make it possible to change purposefully the reactivity of the metal complexes due to the variation of substituents at the nitrogen atoms. The coordination compounds based on conformationally rigid bis(arylimino)acenaphthene (Ar-Bian) are efficient catalysts for reactions of organic synthesis [1–13], olefin polymerization [14–24], and cyclic esters [25–29]. In spite of great interest in using ligands Ar-Bian in coordination chemistry, only several examples are known for 1D and 2D coordination polymers based on bis(arylimino)acenaphthene [30–34]. It is promising to design coordination polymers including redox-active fragments because of a possibility to prepare materials capable of rearranging their properties (magnetic, spectral, electric, and others) due to changing the redox states of the ligands composing the coordination polymer. This can find use in the development of new catalysts, sorbents, and sensors, as well as methods for the separation of mixtures of liquid and gases [35–39]. It is expected that the further functionalization of Ar-Bian would provide their ability to form 2D and possibly 3D polymer frameworks owing to binding functional groups with metal atoms due to both the redox-active diimine fragment and redox-inactive functional groups and would extend the series of the presently known coordination polymers based

on Ar-Bian. The introduction of various functional groups into bis(arylimino)acenaphthene makes it possible to synthesize coordination polymers containing simultaneously metal atoms of different types, for instance, of *s* and *d* elements. It is not excluded that a similar combination would also affect specific features of coordination polymers, in particular, for their intermolecular interaction of substrates (solvents, small molecules, etc.) inside cavities according to the host–guest type due to a combination of acid-base and redox properties of the metallocenters.

We have recently synthesized Ar-Bian with the malonate substituents in *para*-positions of the phenyl rings: 1,2-bis[(2,6-diisopropyl-4-diethylmalonophenyl)imino]acenaphthene (Dem-Bian) and its copper complex  $[(\text{Dem-Bian})\text{CuCl}]$  [40]. Malonate ligands can form six-membered chelate cycles with metal cations, which is promising from the viewpoint of assembling complicated polynuclear structures and coordination polymers [41–43].

The purpose of this work is to synthesize coordination polymers with Dem-Bian as the bridging organic ligand, 1,2-bis[(2,6-diisopropyl-4-diethylmalonophenyl)imino]acenaphthenezinc dichloride  $[(\text{Dem-Bian})\text{ZnCl}_2]$  (**I**), and two 1D coordination polymers of lithium containing redox-active acenaphthene-1,2-diimine fragments and redox-inactive functional malonate groups:  $[\text{ZnCl}_2(\text{Dem-Bian})\text{Li}(\text{DME})_2]_n$  (**II**) and  $[(\text{Dem-Bian})\text{Li}_2(\text{DME})_2]_n$  (**III**).

† Deceased.

## EXPERIMENTAL

Compounds **II**–**III** and  $[(\text{Dem-Bian})\text{CuCl}]$  are not resistant to air oxygen and moisture and, hence, all procedures on their synthesis, isolation, and identification were conducted in *vacuo* or under nitrogen using the Schlenk technique or a glove box (Glovebox M. Braun). The starting Dem-Bian and  $[(\text{Dem-Bian})\text{CuCl}]$  were synthesized using a known procedure [40]. Toluene, dimethoxyethane (DME), and tetrahydrofuran (THF) were dried and stored over sodium diphenylketyl. Prior to use solvents were sampled using condensation in *vacuo*. IR spectra were recorded on an FSM-1201 spectrometer (suspensions of the compounds were prepared in Nujol).  $^1\text{H}$  NMR spectra were recorded on a Bruker Advance NEO instrument (300 MHz). Deuterated benzene and deuterated THF (Aldrich) were dried over sodium diphenylketyl and placed using condensation in *vacuo* into NMR tubes containing samples of the studied compounds. Elemental analysis was carried out on a Vario EL Cube automated analyzer. Thermogravimetric analysis (TG and DTG) was conducted on a METTLER TOLEDO TGA/DSC 3+ instrument at 40–500°C in a nitrogen flow with a flow rate of 50 mL/min and a heating rate of 5 K/min. The weights of the studied samples were 16.758 and 6.950 mg for compounds **II** and **III**, respectively.

**Synthesis of 1,2-bis[(2,6-diisopropyl-4-diethylmalonophenyl)imino]acenaphthenezinc dichloride (I).** Salt  $\text{ZnCl}_2$  (0.034 g, 0.25 mmol) was added to Dem-Bian (0.2 g, 0.25 mmol) in toluene (5 mL). The mixture was heated at 100°C for 24 h. Then toluene was replaced by benzene (6 mL). The obtained yellow solution was concentrated to a volume of 2 mL and held at 10°C for 24 h. The formed yellow crystals were washed with benzene and dried in *vacuo*. The yield was 0.17 g (74%).  $T_m > 268$  (decomp.).

$^1\text{H}$  NMR (300 MHz;  $\text{C}_6\text{D}_6$ ; 300 K,  $\delta$ , ppm): 7.57 (s, 4H); 7.16 (d, 2H); 6.86–6.74 (m, 4H); 4.78 (s, 2H); 4.09–3.90 (m, 8H); 3.75 (sept, 4H); 1.43 (d, 12H); 0.93 (t, 12 H); 0.83 (d, 12 H). IR ( $\nu$ ,  $\text{cm}^{-1}$ ): 1734 s, 1661 w, 1628 m, 1598 w, 1584 m, 1421 w, 1367 m, 1338 w, 1290 m, 1262 w, 1249 w, 1220 w, 1174 m, 1148 m, 1126 w, 1094 m, 1073 w, 1030 s, 951 w, 925 w, 886 w, 864 w, 835 m, 805 w, 782 m, 676 m, 614 m, 575 w, 539 w, 511 w, 471 w.

For  $\text{C}_{50}\text{H}_{60}\text{N}_2\text{O}_8\text{Cl}_2\text{Zn}$

Anal. calcd., %	C, 63.00	H, 6.34	N, 2.94
Found, %	C, 63.10	H, 6.39	N, 2.92

**Synthesis of  $[\text{ZnCl}_2(\text{Dem-Bian})\text{Li}(\text{DME})_2]_n$  (II).** Salt  $\text{ZnCl}_2$  (0.038 g, 0.28 mmol) was added to Dem-Bian (0.2 g, 0.25 mmol) in toluene (3–4 mL). The mixture was heated at 100°C for 10 h. Unreacted  $\text{ZnCl}_2$  was separated by filtration. A solution of *n*-BuLi (23% in hexane, 0.14 g, 0.5 mmol) was added

to the resulting solution. The color of the reaction mixture changed from yellow to dark brown with the formation of a brown precipitate. Toluene was replaced by a DME–THF (1 : 1) mixture (4 mL). The obtained solution was stored at room temperature for 24 h. Dark brown crystals were decanted. The yield was 0.13 g (54%).

$^1\text{H}$  NMR (300 MHz; THF- $d_8$ ; 300 K;  $\delta$ , ppm): 8.19 (d, 2H); 7.55 (t, 2H); 7.28 (s, 4H); 6.77 (d, 2H); 4.04 (q, 8H); 3.39 (sept, 4H); 1.32 (d, 12H); 1.19 (t, 12H); 0.82 (d, 12H). IR ( $\nu$ ,  $\text{cm}^{-1}$ ): 1656 s, 1598 s, 1519 s, 1426 m, 1395 m, 1341 m, 1316 s, 1288 m, 1255 m, 1225 w, 1182 m, 1084 s, 1027 m, 953 m, 944 m, 886 m, 864 s, 842 m, 820 m, 788 s, 739 m, 698 m, 603 w, 538 m, 488 m.

For  $\text{C}_{58}\text{H}_{78}\text{Cl}_2\text{Li}_2\text{N}_2\text{O}_{12}\text{Zn}$

Anal. calcd., %	C, 60.81	H, 6.86	N, 2.44
Found, %	C, 60.73	H, 6.79	N, 2.42

**Synthesis of  $[(\text{Dem-Bian})\text{Li}_2(\text{DME})_2]_n$  (III).** A solution of *n*-BuLi (23% in hexane, 0.28 g, 1.0 mmol) was added to a solution of  $[(\text{Dem-Bian})\text{CuCl}]$ , which was prepared from Dem-Bian (0.41 g, 0.5 mmol) in toluene (20 mL) and  $\text{CuCl}$  (0.05 g, 0.5 mmol). The color of the reaction mixture changed from blue to dark brown with the formation of a brown precipitate. Toluene was replaced by DME, and the precipitate was filtered off. The obtained solution was concentrated to a volume of 5 mL and stored at room temperature for 24 h. The formed dark crystals were decanted from the solution, washed with cold DME, and dried in *vacuo*. The yield was 0.2 g (39%).

IR ( $\nu$ ,  $\text{cm}^{-1}$ ): 1662 s, 1649 s, 1622 s, 1592 s, 1536 w, 1513 s, 1425 m, 1341 w, 1314 s, 1284 w, 1246 m, 1193 m, 1184 m, 1165 m, 1133 m, 1095 s, 1079 s, 1049 m, 1035 w, 1002 w, 988 w, 940 m, 922 w, 885 m, 855 s, 867 w, 853 m, 835 m, 824 m, 791 s, 782 s, 738 m, 697 w, 606 w, 574 w, 545 w, 522 m.

For  $\text{C}_{59}\text{H}_{80.50}\text{N}_2\text{O}_{12.50}\text{Li}_2$

Anal. calcd., %	C, 68.68	H, 7.86	N, 2.71
Found, %	C, 68.53	H, 7.59	N, 2.62

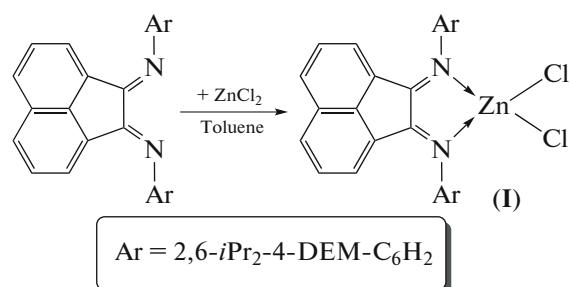
**XRD** of compounds **II** and **III** were carried out on a Bruker D8 Quest diffractometer ( $\omega$  and  $\phi$  scan modes,  $\text{MoK}_\alpha$  radiation,  $\lambda = 0.71073 \text{ \AA}$ ) at  $T = 100(2)$  K for compound **II** and on a Rigaku OD SuperNova diffractometer ( $\text{CuK}_\alpha$  radiation,  $\omega$  scan mode,  $\lambda = 1.54184 \text{ \AA}$ ) at  $T = 150(2)$  K for compound **III**. Diffraction data were collected, initial indexing of reflections was performed, and unit cell parameters were refined using the APEX3 [44] and CrysAlisPro [45] programs for compounds **II** and **III**, respectively. Experimental sets of intensities were integrated using the SAINT [46, 47] (for **II**) and CrysAlisPro [45] (for **III**) programs. The structures were solved by a direct

method using the “dual-space” algorithm in the SHELXT program [48] and refined by full-matrix least squares for  $F_{hkl}^2$  using the SHELXTL [49, 50] and OLEX2 [51] software in the anisotropic approximation for non-hydrogen atoms. Hydrogen atoms were placed in the geometrically calculated positions and refined isotropically by the riding model. An absorption correction was applied using the SADABS [52] (for **II**) and SCALE3 ABSPACK [53] (for **III**) programs. In the monomer of compound **III**, the DME molecule, which is coordinated via the bidentate mode on the Li(2) atom, is disordered over two positions. Uncoordinated solvate DME molecules were additionally found in the crystal of compound **III** in a ratio of 0.5 : 1 to the monomeric unit  $[(\text{Dem-Bian})\text{Li}_2(\text{DME})_2]$ . The crystallographic data and XRD experimental parameters are given in Table 1.

The structures were deposited with Cambridge Crystallographic Data Centre (CIF files CCDC nos. 2220227 (**II**) and 2220228 (**III**) and are available at [ccdc.cam.ac.uk/getstructures](http://ccdc.cam.ac.uk/getstructures)).

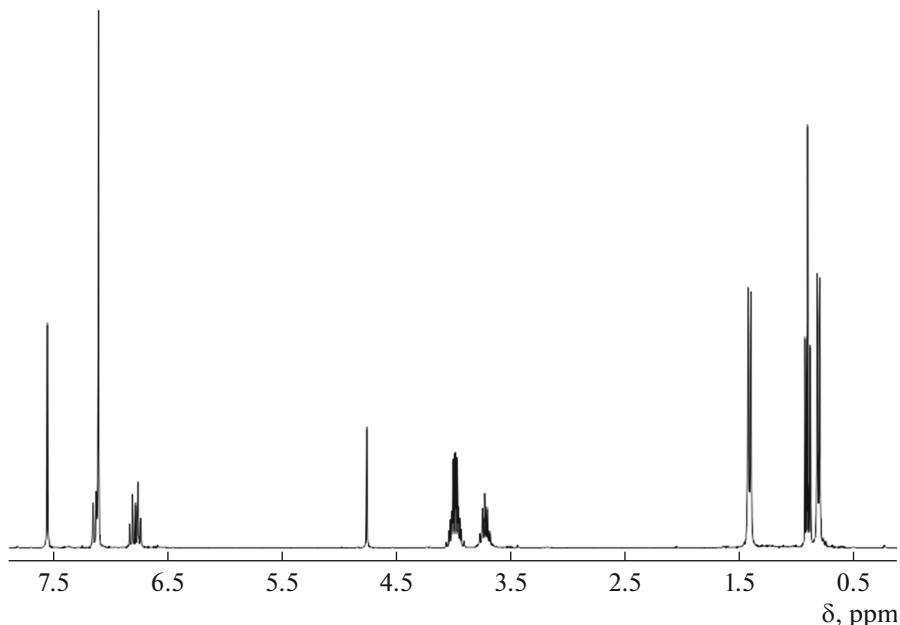
## RESULTS AND DISCUSSION

The reaction of Dem-Bian with *n*-BuLi in toluene affords a mixture of products, which were not identified. Probably, the reaction proceeds at both the malonate groups and diimine Dem-Bian fragment. The Dem-Bian adduct with zinc dichloride was synthesized to block the latter. The reaction of Dem-Bian with  $\text{ZnCl}_2$  occurs in toluene at 100°C (Scheme 1).



**Scheme 1.**

The reaction product, compound  $[(\text{Dem-Bian})\text{ZnCl}_2]$  (**I**), was isolated as yellow crystals from a concentrated benzene solution upon its storage at 10°C for 24 h. Compound **I** was characterized by NMR and IR spectroscopy. The IR spectrum exhibits an intense absorption band at 1734  $\text{cm}^{-1}$  characteristic of stretching vibrations of the C=O bond in the diethyl malonate substituent. The corresponding band in the spectrum of free diimine is observed at 1742  $\text{cm}^{-1}$ . In the <sup>1</sup>H NMR spectrum of compound **I** (Fig. 1), the protons of the isopropyl groups appear as doublets at 0.83 ppm (12H) and 1.43 ppm (12H) and a septet at 3.75 ppm (4H). The signals of the protons of the diethyl malonate substituents are observed as a triplet at 0.93 ppm (12H), a multiplet at 4.09–3.90 ppm (8H), and a singlet at 4.78 ppm (2H). The protons of the naphthalene moiety give a doublet at 7.16 ppm (2H) and a multiplet at 6.86–6.74 ppm (4H). The singlet at 7.57 ppm (4H) is assigned to the aromatic protons of the 2,6-*i*-Pr<sub>2</sub>-4-Dem-C<sub>6</sub>H<sub>2</sub> substituents. The signals in the <sup>1</sup>H NMR spectrum of compound **I** are somewhat shifted compared to those of free Dem-



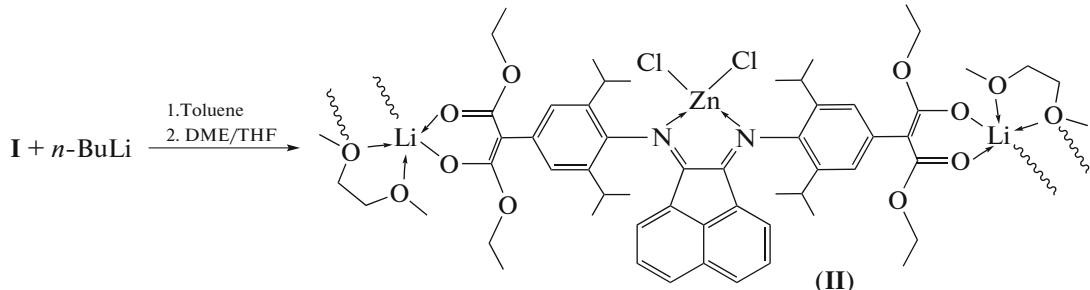
**Fig. 1.** <sup>1</sup>H NMR spectrum of compound **I** (300 MHz, C<sub>6</sub>D<sub>6</sub>, 300 K).

**Table 1.** Crystallographic data and experimental and structure refinement parameters for compounds **II** and **III**

Parameter	Value	
	<b>II</b>	<b>III</b>
Empirical formula	C <sub>58</sub> H <sub>78</sub> N <sub>2</sub> O <sub>12</sub> Cl <sub>2</sub> Li <sub>2</sub> Zn	C <sub>59</sub> H <sub>80.50</sub> N <sub>2</sub> O <sub>12.50</sub> Li <sub>2</sub>
<i>FW</i>	1145.37	1031.63
Crystal system	Orthorhombic	Monoclinic
Space group	<i>Pbcn</i>	<i>P2<sub>1</sub>/c</i>
<i>a</i> , Å	21.0450(12)	12.5793(12)
<i>b</i> , Å	15.1104(9)	16.5259(14)
<i>c</i> , Å	18.9466(12)	27.553(3)
α, deg	90	90
β, deg	90	91.745(10)
γ, deg	90	90
<i>V</i> , Å <sup>3</sup>	6025.0(6)	5725.2(10)
<i>Z</i>	4	4
ρ <sub>calc</sub> , g/cm <sup>3</sup>	1.263	1.197
μ, mm <sup>-1</sup>	0.555	0.665
<i>F</i> (000)	2424	2218
Crystal size, mm	0.71 × 0.46 × 0.39	0.14 × 0.12 × 0.08
Measurement range over θ, deg	2.59–27.55	3.12–66.00
Indices of ranges	–27 ≤ <i>h</i> ≤ 27, –19 ≤ <i>k</i> ≤ 19, –24 ≤ <i>l</i> ≤ 24	–14 ≤ <i>h</i> ≤ 12, –19 ≤ <i>k</i> ≤ 19, –32 ≤ <i>l</i> ≤ 32
Number of measured reflections	69342	22329
Number of independent reflections ( <i>R</i> <sub>int</sub> )	6928 (0.0383)	9979 (0.1350)
Number of reflections with <i>I</i> > 2σ( <i>I</i> )	5660	3085
Absorption correction (max/min)	0.8017/0.6463	1.00000/0.71111
Data/restraints/parameters	6928/0/357	9979/220/809
GOOF	1.081	0.873
<i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> ( <i>I</i> > 2σ( <i>I</i> ))	0.0465, 0.1182	0.0829, 0.1746
<i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> (for all reflections)	0.0601, 0.1272	0.2405, 0.2410
Residual electron density (max/min), e Å <sup>-3</sup>	1.318/–0.337	0.319/–0.235

Bian (doublets at 0.92 ppm (12H) and 1.26 ppm (12H); septet at 3.20 ppm (4H), triplet at 1.08 ppm (12H), multiplet at 4.1–3.84 ppm (8H), and singlet at 4.86 ppm (2H)).

The reaction of compound **I** with *n*-BuLi in toluene followed by the replacement of the solvent by a



Scheme 2.

Compound **II** is a linear coordination polymer in which the Dem-Bian ligand is linked with  $ZnCl_2$  by the diimine fragment, and two malonate groups bind two lithium cations. Polymer chains are formed due to the bridging DME molecules coordinated by the lithium cations. In the crystal, parallel rows of the polymer chains form layers along the crystallographic plane (010). Layers of two types with different directions of the polymer chains alternate along the *b* axis. The angle between the chain directions in the adjacent layers is  $38.5^\circ$ . The bond lengths in the diimine fragment ( $C(1)-C(2)$  1.519(4) Å,  $N(1)-C(1)$ ,  $N(2)-C(2)$  1.273(3) Å) correspond to the ordinary C–C bond and double N=C bonds, indicating the neutral form of the ligands. The  $^1H$  NMR spectrum of compound **II** (Fig. 3) exhibits signals from the protons of the isopropyl groups as doublets at  $\delta$  0.82 ppm (12H) and 1.32 ppm (12H) and a septet at 3.39 ppm (4H). The signals of the protons of the diethyl malonate substituents appear as a triplet at 1.19 ppm (12H) and a quartet at 4.04 ppm (8H). The protons of the naphthalene moiety give doublets at 6.77 ppm (2H) and 8.19 ppm (2H) and a triplet at 7.55 ppm (2H). The singlet at 7.28 ppm (4H) is attributed to the aromatic protons of the 2,6-*i*-Pr<sub>2</sub>-4-Dem-C<sub>6</sub>H<sub>2</sub> substituents. The spectrum also contains the signals from DME (at 3.28 and 3.44 ppm).

The reaction of  $[(\text{Dem-Bian})\text{CuCl}]$  with *n*-BuLi (Scheme 3) is accompanied by a change in the color of the reaction mixture from blue to dark brown with the formation of a jelly-like brown precipitate. A portion of the precipitate dissolved after toluene was replaced by DME. The remained precipitate was separated by filtration. The 1D coordination polymer  $[(\text{Dem-Bian})\text{Li}_2(\text{DME})_2]_n$  (**III**) was isolated as dark brown crystals in a yield of 39% by crystallization from the obtained solution. Product **III** was characterized by IR spectroscopy and elemental analysis. The IR spec-

THF–DME mixture gives derivative  $[\text{ZnCl}_2(\text{Dem-Bian})\text{Li}(\text{DME})_2]_n$  (**II**), which was isolated as dark brown crystals (Scheme 2). Product **II** was characterized by NMR spectroscopy, and its structure was solved by XRD (Fig. 2).

Table 2. Selected bond lengths and angles in compounds **II** and **III**

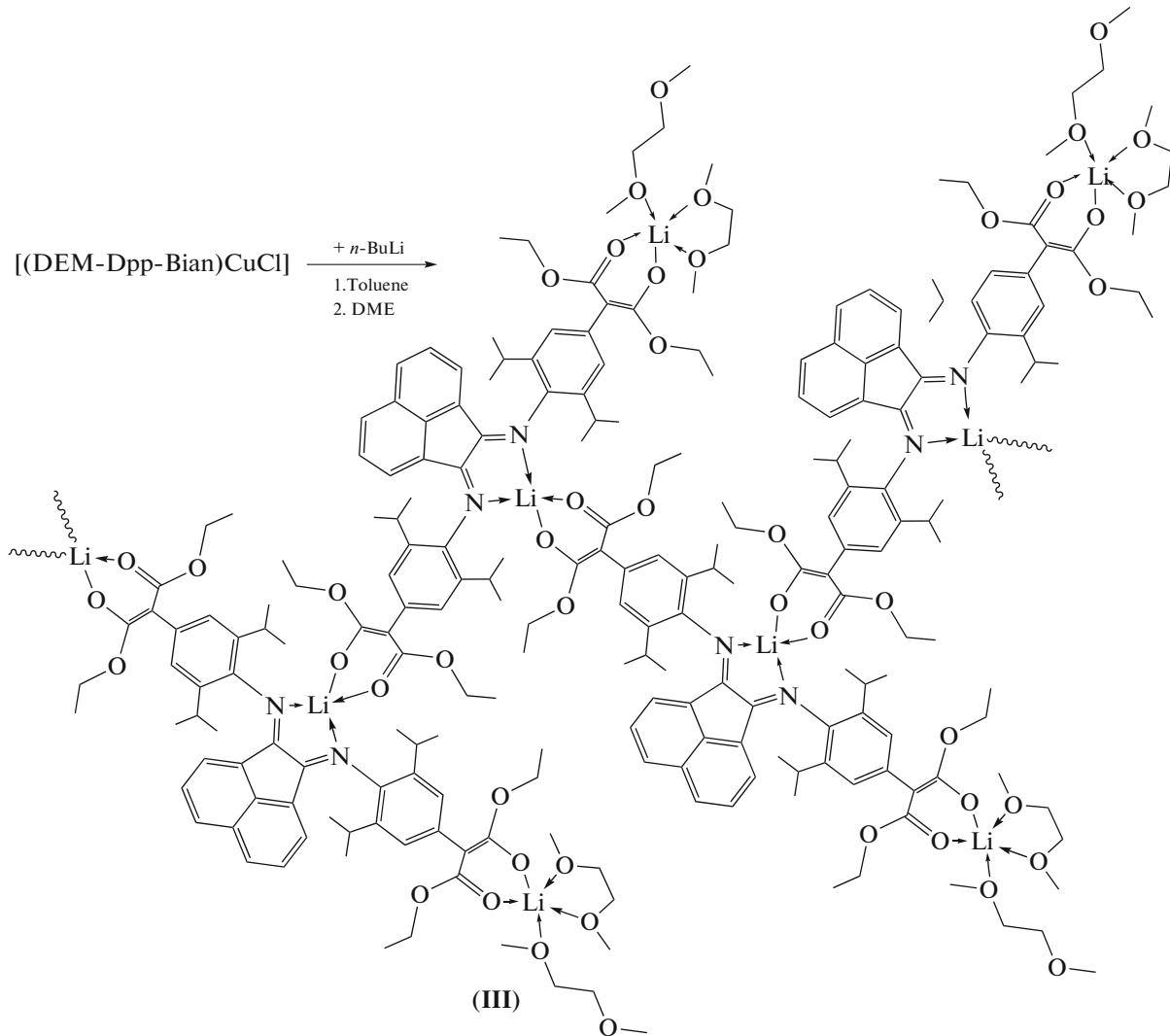
Bond	<i>d</i> , Å	
	<b>II</b> *	<b>III</b> *
M(1)–Cl(1)	2.1956(6)	
M(1)–Cl(2)	2.1956(6)	
N(1)–C(1)	1.273(3)	1.261(6)
N(2)–C(2)	1.273(3)	1.291(6)
C(1)–C(2)	1.519(4)	1.527(6)
M(1)–N(1)	2.117(2)	2.118(11)
M(1)–N(2)	2.117(2)	2.128(10)
Li(1)–O(1)	1.891(4)	1.815(10)
Li(1)–O(2)	1.914(4)	1.856(10)
Li(1)–O(3)	2.197(4)	
Li(1)–O(4)	2.072(4)	
Li(2)–O(3)		1.911(11)
Li(2)–O(4)		1.920(10)
Li(2)–O(5)		2.481(14)
Li(2)–O(6)		1.987(13)
Li(2)–O(7)		2.030(11)

Angle	$\omega$ , deg	
	<b>II</b> *	<b>III</b> *
Cl(1)Zn(1)Cl(2)	121.30(3)	
N(1)M(1)N(2)	80.05(9)	81.3(4)
O(1)Li(1)O(2)	93.08(18)	94.6(5)
O(3)Li(2)O(4)		90.9(4)
O(3)Li(1)O(4)	77.09(14)	
O(5)Li(2)O(6)		72.6(5)

\* M = Zn (**II**), M = Li (**III**).

trum of compound **III** has no bands of stretching vibrations of the C=O in the diethyl malonate substituent, which is observed, for example, in [(Dem-Bian)CuCl] (1731 cm<sup>-1</sup>) [38]. The vibrations of the C=N bonds in the IR spectrum of compound **III** are

presented by an intense band at 1649 cm<sup>-1</sup>, which corresponds to the neutral state of the ligand. A low solubility of product **III** in organic solvents did not allow us to obtain an informative <sup>1</sup>H NMR spectrum for this compound.

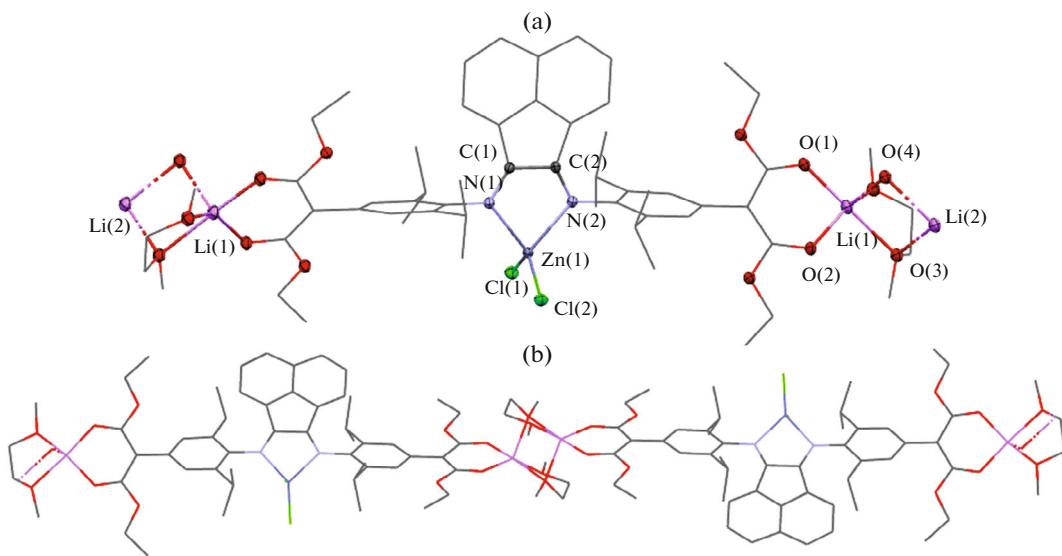


Scheme 3.

The structure of compound **III** was determined by XRD (Fig. 4). Complex **III** is a zigzag 1D coordination polymer. In the monomeric unit, the Dem-Bian ligand is connected with two lithium ions Li(1) and Li(2) by the oxygen atoms of the malonate groups. The polymer chains are formed due to the additional coordination of Dem-Bian by the diimine fragment on the Li(1) atom of the adjacent polymer unit. The Li(1) ion exists in the tetrahedral coordination environment. The Li(2) lithium ion is linked with the second malonate group of Dem-Bian and additionally with three oxygen atoms of two terminal DME molecules. Thus, no branches of the polymer chain via the Li(2)

atoms occur. The coordination number of the Li(2) cation is five, and its coordination sphere has the configuration of a distorted trigonal bipyramidal. The bond lengths in the diimine fragment (C(1)–C(2) 1.527(6) Å, N(1)–C(1) 1.261(6) Å, N(2)–C(2) 1.291(6) Å) indicate the neutral form of the ligand. The cavities of the crystal cell of compound **III** contain free 1,2-dimethoxyethane, one molecule of which falls onto two monomeric units.

The thermal stability of synthesized coordination polymers **II** and **III** was studied by thermogravimetric analysis (Figs. 5 and 6). Compound **II** is stable to 140°C. The coordination polymer decomposes above

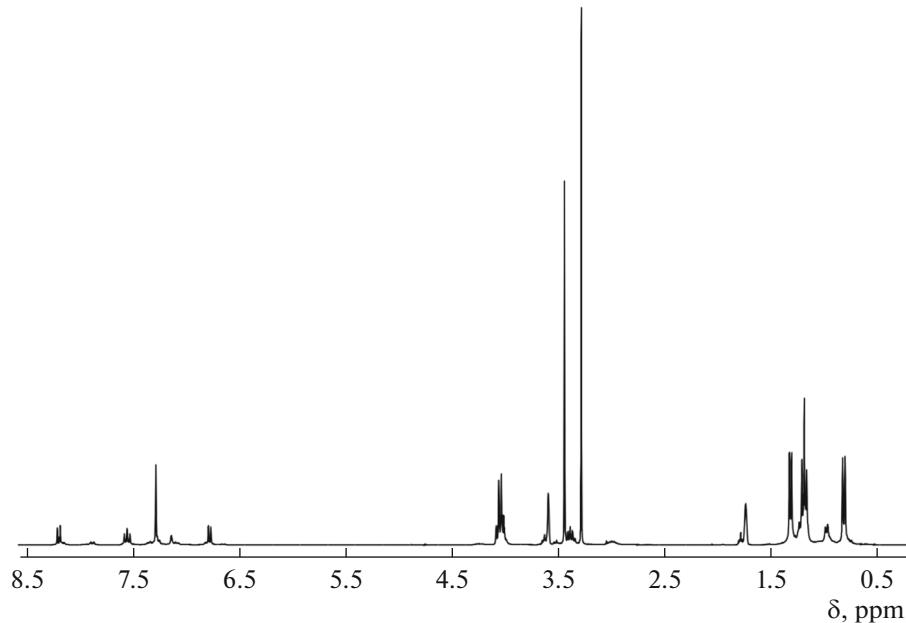


**Fig. 2.** Structure of compound **II**: (a) monomeric unit (hydrogen atoms are omitted, thermal ellipsoids for the key atoms are of 30% probability, and the Li(2) atoms of the adjacent monomeric unit are shown) and (b) fragment of the polymer chain.

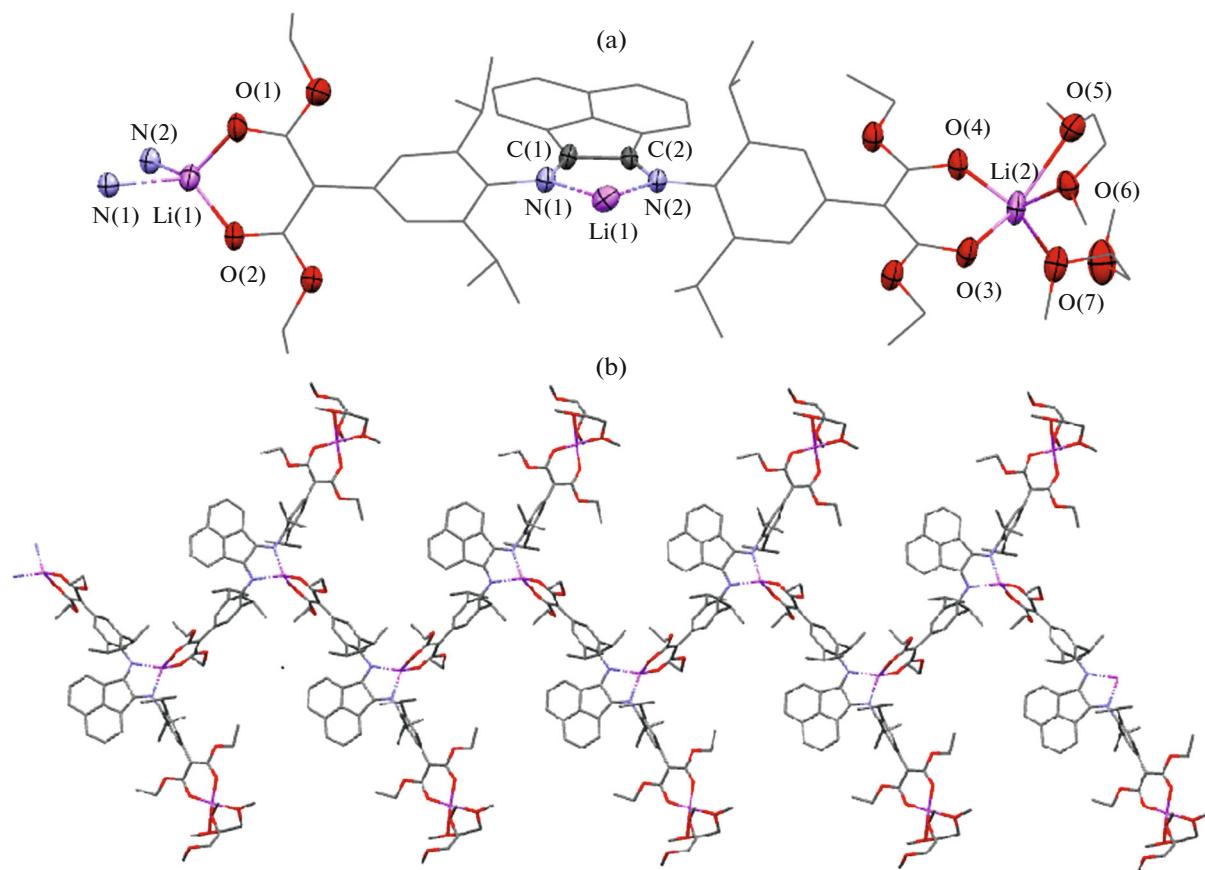
this temperature because of the loss of coordinated DME molecules. The mass loss is 16% (maximum rate at 160°C), which corresponds to the removal of two DME molecules. The next mass loss stages correspond to the destruction of the [(Dem-BianZnCl<sub>2</sub>)] fragment. For compound **III**, the solvate DME molecule and the DME molecule bound to the lithium ion

via one oxygen atom (mass loss 12%) are removed at the first stage (40–85°C). The last DME molecule is detached at the next stage (150–210°C) with a mass loss of 9%. The [(Dem-BianLi<sub>2</sub>(DME)] fragment decomposes at  $T > 210^\circ\text{C}$ .

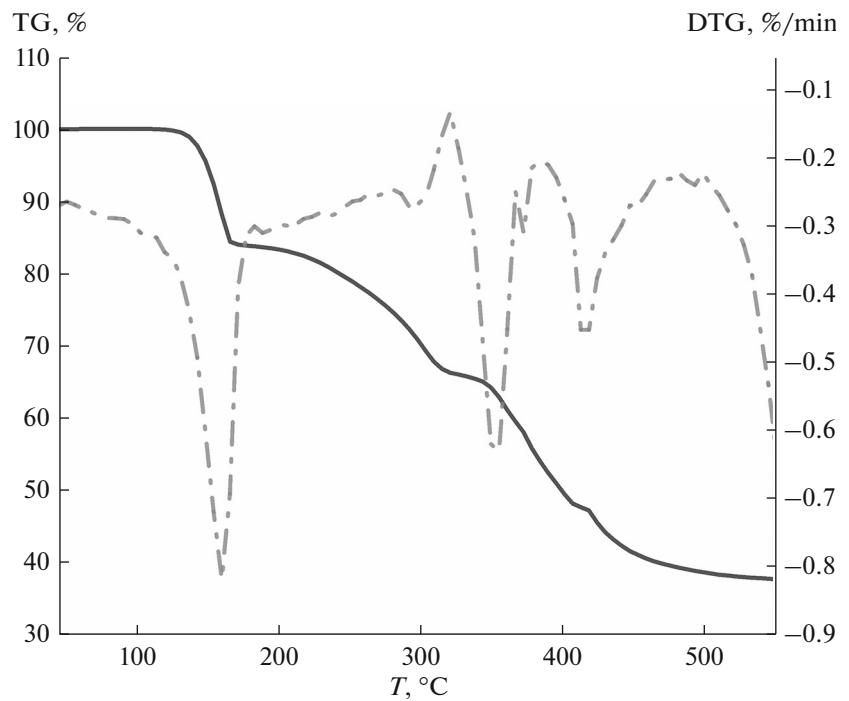
Thus, two new lithium coordination polymers (metal-organic frameworks) with the 1,2-bis[2,6-



**Fig. 3.** <sup>1</sup>H NMR spectrum of compound **II** (300 MHz, THF-d<sub>8</sub>, 300 K).



**Fig. 4.** Structure of compound III: (a) monomeric unit (hydrogen atoms are omitted, thermal ellipsoids for the key atoms are of 30% probability, and the  $\text{Li}(1)$  atom on the  $\text{N}(1)$  and  $\text{N}(2)$  atoms of the diimine fragment of the Dem-Bian ligand at the center from the adjacent monomeric unit is shown) and (b) fragment of the polymer unit.



**Fig. 5.** TG and DTG curves for complex II.

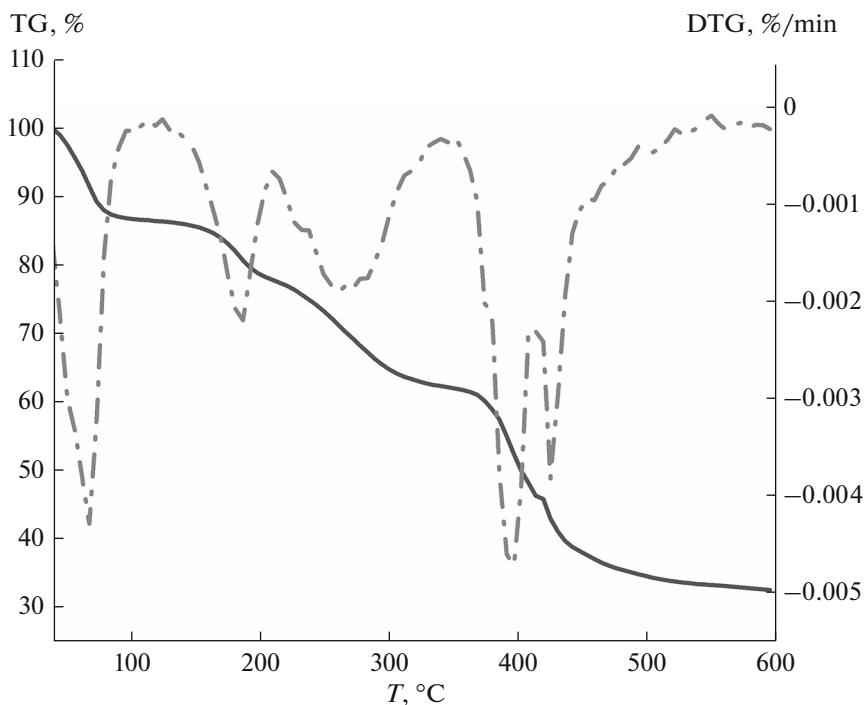


Fig. 6. TG and DTG curves for complex III.

diisopropyl-4-diethylmalonophenyl)imino]acenaphthene ligand were synthesized and characterized.

#### ACKNOWLEDGMENTS

This work was carried out using the equipment of the Center for Collective Use “Analytical Center of Razuvayev Institute of Organometallic Chemistry of Russian Academy of Sciences” supported by the grant “Provision of Development of Material Technical Infrastructure of Centers for Collective Use of Scientific Equipment” (unique identifier RF-2296.61321X0017, agreement no. 075-15-2021-670).

#### FUNDING

This work was supported by the Russian Science Foundation, project no. 19-13-00336-Π.

#### CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

#### REFERENCES

- Bernauer, J., Pölker, J., and von Wangelin, A.J., *Chem. Cat. Chem.*, 2022, vol. 14, no. 1, p. e202101182.
- Marreiros, J., Diaz-Couce, M., Ferreira, M.J., et al., *Inorg. Chim. Acta*, 2019, vol. 486, p. 274.
- Beltrani, M., Carfagna, C., Milani, B., et al., *Adv. Synth. Catal.*, 2016, vol. 358, no. 20, p. 3244.
- Moskalev, M.V., Skatova, A.A., Chudakova, V.A., et al., *Russ. Chem. Bull.*, 2015, vol. 64, no. 12, p. 2830.
- Moskalev, M.V., Yakub, A.M., Morozov, A.G., et al., *Eur. J. Org. Chem.*, 2015, vol. 2015, no. 26, p. 5781.
- Rumble, S.L., Page, M.J., Field, L.D., et al., *Eur. J. Inorg. Chem.*, 2012, vol. 2012, no. 13, p. 2226.
- Li, L., Lopes, P.S., Rosa, V., et al., *Dalton Trans.*, 2012, vol. 41, no. 17, p. 5144.
- Fedushkin, I.L., Moskalev, M.V., Lukyanov, A.N., et al., *Chem.-Eur. J.*, 2012, vol. 18, no. 36, p. 11264.
- Fedushkin, I.L., Nikipelov, A.S., Morozov, A.G., et al., *Chem.-Eur. J.*, 2012, vol. 18, no. 1, p. 255.
- Viganó, M., Ragagni, F., Buonomenna, M.G., et al., *ChemCatChem*, 2010, vol. 2, no. 9, p. 1150.
- Alonso, J.C., Neves, P., Pires da Silva, M.J., et al., *Organometallics*, 2007, vol. 26, no. 23, p. 5548.
- Gottumukkala, A.L., Teichert, J.F., Heijnen, D., et al., *J. Org. Chem.*, 2011, vol. 76, no. 9, p. 3498.
- de Fremont, P., Clavier, H., Rosa, V., et al., *Organometallics*, 2011, vol. 30, no. 8, p. 2241.
- Yu, X., Zhu, F., Bu, D., et al., *RSC Adv.*, 2017, vol. 7, no. 25, p. 15321.
- Sndl, S., Maier, T.M., van Leest, N.P., et al., *ACS Catal.*, 2019, vol. 9, no. 8, p. 7596.
- Soshnikov, I.E., Bryliakov, K.P., Antonov, A.A., et al., *Dalton Trans.*, 2019, vol. 48, no. 23, p. 7974.
- Wang, F., Tanaka, R., Li, Q., et al., *Organometallics*, 2018, vol. 37, no. 9, p. 1358.
- Liu, Z.W.Q., Solan, G.A., and Sun, W.-H., *Coord. Chem. Rev.*, 2017, vol. 350, p. 68.
- Guo, L., Liu, W., and Chen, C., *Mater. Chem. Front.*, 2017, vol. 1, no. 12, p. 2487.

20. Small, B.L., Rios, R., Fernandez, E.R., et al., *Organometallics*, 2010, vol. 29, no. 24, p. 6723.
21. Popeney, C.S. and Guan, Z., *Macromolecules*, 2010, vol. 43, no. 9, p. 4091.
22. Miyamura, Y., Kinbara, K., Yamamoto, Y., et al., *J. Am. Chem. Soc.*, 2010, vol. 132, no. 10, p. 3292.
23. Romain, C., Rosa, V., Fliedel, C., et al., *Dalton Trans.*, 2012, vol. 41, no. 12, p. 3377.
24. Liu, J., Li, Y., Li, Y., et al., *J. Appl. Pol. Sci.*, 2008, vol. 109, no. 2, p. 700.
25. Wang, F. and Chen, C., *Polym. Chem.*, 2019, vol. 10, no. 19, p. 2354.
26. Brown, L.A., Wekesa, F.S., Unruh, D.K., et al., *J. Pol. Sci. A*, 2017, vol. 55, no. 17, p. 2824.
27. Kazarina, O.V., Gourlaouen, C., Karmazin, L., et al., *Dalton Trans.*, 2018, vol. 47, no. 39, p. 13800.
28. Morozov, A.G., Markelova, E.S., Fedyushkin, I.L., et al., *Russ. J. Appl. Chem.*, 2018, vol. 1, no. 6, p. 1044.
29. Fedushkin, I.L., Morozov, A.G., Chudakova, V.A., et al., *Eur. J. Inorg. Chem.*, 2009, no. 33, p. 4995.
30. Bazyakina, N.L., Makarov, V.M., Ketkov, S.Yu., et al., *Inorg. Chem.*, 2021, vol. 60, p. 3238.
31. Koptseva, T.S., Bazyakina, N.L., Moskalev, M.V., et al., *Eur. J. Inorg. Chem.*, 2021, vol. 60, p. 3238.
32. Bazyakina, N.L., Moskalev, M.V., Cherkasov, A.V., et al., *CrystEngComm*, 2022, vol. 24, p. 2297.
33. Koptseva, T.S., Bazyakina, N.L., Rumyantcev, R.V., et al., *Mendeleev Commun.*, 2022, vol. 32, p. 780.
34. Bazyakina, N.L., Makarov, V.M., Moskalev, M.V., et al., *Mendeleev Commun.*, 2022, vol. 32, p. 759.
35. Su, J., Yuan, S., Li, J., et al., *Chem.-Eur. J.*, 2021, vol. 27, p. 622.
36. Bigdeli, F., Lollar, C.T., Morsali, A., et al., *Angew. Chem., Int. Ed. Engl.*, 2020, vol. 59, p. 4652.
37. Calbo, J., Golomb, M.J., and Walsh, A., *J. Mater. Chem. A*, 2019, vol. 7, p. 16571.
38. Su, J., Yuan, S., Li, J., et al., *Chem.-Eur. J.*, 2021, vol. 27, p. 622.
39. Li, B., Zhao, Y.M., Kirchon, A., et al., *J. Am. Chem. Soc.*, 2019, vol. 141, p. 6822.
40. Sokolov, V.G., Moskalev, M.V., Koptseva, T.S., et al., *Russ. Chem. Bull.*, 2021, vol. 69, no. 1, p. 125.
41. Bazhina, E.S., Aleksandrov, G.G., Kiskin, M.A., et al., *Russ. J. Coord. Chem.*, 2020, vol. 46, no. 2, p. 89. <https://doi.org/10.1134/S1070328420020025>
42. Bazhina, E.S., Shmelev, M.A., Babeshkin, K.A., et al., *Russ. Chem. Bull.*, 2021, vol. 70, no. 11, p. 2130.
43. Blinou, D.O., Zorina-Tikhonova, E.N., Voronina, Yu.K., et al., *Russ. J. Coord. Chem.*, 2022, vol. 48, no. 8, p. 487. <https://doi.org/10.1134/S1070328422080012>
44. *APEX3. Bruker Molecular Analysis Research Tool. Version 2018.7-2*, Madison: Bruker AXS Inc., 2018.
45. *Data Collection, Reduction and Correction Program. CrysAlisPro 1.171.40.67a – Software Package*, Rigaku OD, 2019.
46. *SAINT. Data Reduction and Correction Program. Version 8.38A*, Madison (WI): Bruker AXS Inc., 2017.
47. Krause, L., Herbst-Irmer, R., Sheldrick, G.M., and Stalke, D., *J. Appl. Crystallogr.*, 2015, vol. 48, p. 3.
48. Sheldrick, G.M., *Acta Crystallogr., Sect. A: Found. Adv.*, 2015, vol. 71, p. 3.
49. Sheldrick, G.M., *Acta Crystallogr., Sect. C: Struct. Chem.*, 2015, vol. 71, p. 3.
50. Sheldrick, G.M., *SHELXTL. Version 6.14. Structure Determination Software Suite*, Madison (WI): Bruker AXS, 2003.
51. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J., et al., *J. Appl. Crystallogr.*, 2009, vol. 42, p. 339.
52. Sheldrick, G.M., *SADABS. Version 2016/2. Bruker/Siemens Area Detector Absorption Correction Program*, Madison: Bruker AXS Inc., 2016.
53. *SCALE3 ABSPACK: Empirical Absorption Correction. CrysAlisPro 1.171.40.67a – Software Package*, Rigaku OD, 2019.

Translated by E. Yablonskaya