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Coordination Polymers of Calcium with the Redox-Active Acenaphthene-1,2-diimine Ligand

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Abstract—The reactions of the calcium acenaphthene-1,2-diimine complex $[(Dpp\text{-}Bian)^{2-}Ca^{2+}(THF)_4]$ (Dpp-Bian is 1,2-bis[(2,6-diisopropylphenyl)imino]acenaphthene) with phenazine (Phz) in tetrahydrofuran (THF) and with 4,4'-bipyridine (4,4'-Bipy) in benzene proceed with the electron transfer from $Dpp\text{-}Bian^{2-}$ to the substrates to give dimer $[(Dpp\text{-}Bian)^{1-}Ca^{2+}(Phz)^{1-}(THF)]_2\cdot 6(THF)$ (**I**) and 2D coordination polymer $[(Dpp\text{-}Bian)^{-}Ca^{2+}(4,4'\text{-}Bipy)^{-}(4,4'\text{-}Bipy)_{0.5}]\cdot 3(C_6H_6)$ (**II**), respectively. The reaction of $[(Dpp\text{-}Bian)^{2-}Ca^{2+}(THF)_4]$ with 1,3-bis(4-pyridyl)propane (Bpp) in a THF/benzene mixture is not accompanied by the electron transfer and leads to the formation of 2D coordination polymer $[(Dpp\text{-}Bian)^{2-}Ca^{2+}(Bpp)_2]\cdot 2(THF)\cdot(C_6H_6)$ (**III**). Compounds **I**–**III** are characterized by elemental analysis and IR spectroscopy. The molecular structure of compound **I** is determined by XRD (CIF file CCDC no. 2176826). The quality of the XRD experimental data obtained for crystals of compounds **II** and **III** turns out to be insufficient for the determination (with a necessary accuracy) of bond lengths and angles. The XRD data make it possible to establish unambiguously the mutual arrangement of atoms in the molecules of compounds **II** and **III** and the number and mutual arrangement of solvate benzene and THF molecules. The presence of ligand-localized unpaired electrons in compounds **I**–**III** is confirmed by EPR spectroscopy. The thermal stability of coordination polymers **II** and **III** is studied by thermogravimetric analysis.

Keywords: redox-active ligands, calcium, 1,2-bis(arylamino)acenaphthene, metal-organic coordination polymers, molecular structure

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INTRODUCTION

Assembling of metal-organic frameworks (MOFs) with the formation of diverse "lace" structures is carried out using metal ions as nodal sites of polymer chains and conformationally rigid or labile organic ligands as linkers [1, 2]. Among a large variety of annually synthesized MOFs, only a minor number of them manifests redox properties. These properties appear due to the presence of redox-active metal ions or organic ligands, or guest molecules located in MOF cavities [3–6]. Redox-active MOFs provide access to numerous properties tunable inside this material by the manipulation of redox states, in particular, redox-active centers [7–12]. Since the properties of coordination polymers containing redox-active blocks depend on the oxidation states of metals and reduction states of linkers, ligands that can reversibly donate or accept electrons with the retention of coordination to the nodal metal center are of special interest. Among these ligands are, e.g., 1,2-bis[(2,6-diisopropylphenyl)imino]acenaphthene (Dpp-Bian), 4,4'-bipyridine (4,4'-Bipy), and phenazine (Phz). The first of them can act as a conformationally rigid chelating ligand and exists in metal complexes in the neutral, radical anion, or dianionic state [13, 14]. The two latter ligands, 4,4'-Bipy and Phz, can generate radical anions and dianions being treated with alkaline metals along with the capacity of acting as neutral bridging ligands [15–18]. Unlike coordination polymers of transition metals, 2D and 3D polymer networks based on alkaline and alkaline-earth metals remain poorly studied [19, 20]. Note that Ca-based MOFs attract attention of researchers in the recent years due to nontoxicity and availability [20]. We have recently synthesized the 1D and 2D coordination polymers of Group II metals with Dpp-Bian and 4,4'-Bipy [21] in which each metal center coordinates both ligands. The assembling of these polymers includes the coordination of neutral 4,4'-Bipy by the mononuclear calcium complex with the Dpp-Bian dianion and electron transfer from $Dpp\text{-}Bian^{2-}$ to 4,4'-Bipy to form heteroligand complex $[(Dpp\text{-}Bian)^{-}Ca^{2+}(4,4'\text{-}Bipy)^{-}]$, whose molecules begin to associate forming MOF. Thus, we pioneered to assemble the coordination polymer using two different radical anion ligands: terminal Dpp-Bian and bridging 4,4'-Bipy. These objects are of great interest because of a possibility to construct new bistable molecular systems important for

the development of molecular electronics. Continuing our studies of assembling coordination processes based on calcium and redox-active ligands, we carried out the reactions of [(Dpp-Bian)Ca(THF)$_4$] with Phz, 1,3-bis(4-pyridyl)propane (Bpp), and 4,4'-Bipy in benzene, which was not earlier used by us as the solvent. The products of these reactions are discussed in this article.

EXPERIMENTAL

The products of the reactions of [(Dpp-Bian)Ca(THF)$_4$] with phenazine, 4,4'-bipyridine, and 1,3-bis(4-pyridyl)propane are compounds **I**, **II**, and **III**, respectively. They are sensitive to oxygen and moisture and, hence, all manipulations concerning their synthesis, isolation, and identification were carried out in vacuo using a Schlenk technique or under an argon atmosphere in a glove box (MBraun). Tetrahydrofuran, benzene, 2-methyltetrahydrofuran, and deuterated THF (two latter purchased from Aldrich) were dried and stored above sodium diphenyl ketyl after which they were sampled by condensation in vacuo prior to use. The starting [(Dpp-Bian)Ca(THF)$_4$] was synthesized using a known procedure [22] and used in situ. 4,4'-Bipyridine and 1,3-bis(4-pyridyl)propane (Aldrich) was purified by sublimation, and phenazine (Aldrich) was used as received. The yields of the products (compounds **I**–**III**) indicated in the described methods were based on the amount of the Dpp-Bian used. IR spectra (4000–450 cm^{-1}) were recorded on an FSM-1201 spectrometer. Suspensions of the compounds in Nujol were prepared for IR spectra recording. ^{1}H NMR spectra were measured on an Avance NEO spectrometer (300 MHz). EPR spectra were recorded on a Magnettech ESR5000 spectrometer (9.48 GHz). The EPR spectrum was simulated and hyperfine coupling constants for compound **I** were calculated using the EasySpin software (version 5.2.28) [23]. Elemental analysis was carried out on a Vario EL Cube automated analyzer. Thermogravimetric analysis was conducted on a METTLER TOLEDO TGA/DSC 3+ instrument at 40–500°C in a nitrogen flow (flow rate 50 mL/min, heating rate 5 K/min). The weights of the studied samples were 16.509 and 7.397 mg for compounds **II** and **III**, respectively.

Synthesis of [(Dpp-Bian)Ca(Phz)]$_2$·8(THF) (I). Phenazine (0.09 g, 0.5 mmol) was added to a solution of complex [(Dpp-Bian)Ca(THF)$_4$] prepared from Dpp-Bian (0.25 g, 0.5 mmol) in THF (30 mL). The color of the reaction mixture changed from green to red-brown. The resulting solution was concentrated to 10 mL and hold at 6°C for 24 h. Red-brown crystals of compound **I** were separated by decantation, washed with cold THF, and dried in vacuo. The yield was 0.29 g (57%).

The EPR spectrum in 2-methyltetrahydrofuran at 290 K is a superposition of two multiplets: radical anion (Dpp-Bian)$^-$, quintet, g = 2.00564, a_i(2 × ^{14}N) = 0.4706 mT; radical anion Phz$^-$, multiplet, g = 2.00571, a_i(2 × ^{14}N) = 0.2392, a_i(4 × ^{1}H) = 0.2421, a_i(4 × ^{1}H) = 0.0120 mT.

IR (ν, cm^{-1}): 1669 m, 1654 w, 1641 w, 1592 m, 1557 m, 1526 m, 1514 s, 1429 s, 1414 s, 1362 s, 1332 s, 1313 s, 1276 w, 1249 s, 1219 w, 1185 s, 1151 m, 1138 m, 1110 w, 1070 s, 1028 m, 938 w, 926 m, 897 s, 846 m, 835 m, 820 s, 795 m, 787 m, 773 m, 751 s, 733 s, 668 w, 656 w, 613 s, 604 w, 595 m, 537 w.

For $C_{128}H_{160}N_8O_8Ca_2$

Anal. calcd., %	C, 76.15	H, 7.99	N, 5.55
Found, %	C, 76.13	H, 7.95	N, 5.52

Synthesis of [(Dpp-Bian)Ca(4,4'-Bipy)$_{1.5}$]·3(C$_6$H$_6$) (II). Complex [(Dpp-Bian)Ca(THF)$_4$] (synthesized in an evacuated ampule from Dpp-Bian (0.5 g) in THF) was dissolved in benzene (40 mL), and 4,4-bipyridine (0.31 g, 2.0 mmol) in benzene (10 mL) was added. The reaction mixture immediately turned blue, and a finely crystalline precipitate formed. The ampule was sealed and heated at 100°C for 48 h. The formed dark blue, nearly black crystals of compound **II** were decanted, washed with cold benzene, and dried in vacuo at 30°C for 15 min. The yield was 0.87 g (87%). The sample designed for XRD was not dried.

IR (ν, cm^{-1}): 1670 w, 1657 w, 1642 w, 1591 s, 1531 m, 1514 m, 1478 s, 1434 s, 1434 s, 1417 s, 1408 s, 1360 s, 1315 m, 1274 m, 1252 m, 1222 m, 1200 s, 1187 s, 1104 w, 1066 w, 1057 w, 1039 m, 1014 s, 990 w, 954 s, 940 s, 926 s, 847 w, 835 w, 804 s, 786 m, 768 s, 761 s, 752 s, 734 w, 676 s, 622 m, 608 s, 572 w, 538 w, 499 w.

For $C_{57}H_{58}N_5Ca$ (monosolvate)

Anal. calcd., %	C, 80.24	H, 6.85	N, 8.21
Found, %	C, 79.61	H, 6.79	N, 8.10

Synthesis of [(Dpp-Bian)Ca(Bpp)$_2$]·2(THF)·(C$_6$H$_6$) (III). 1,3-Bis(4-pyridyl)propane (0.19 g, 1.0 mmol) was added to a benzene solution (20 mL) of complex [(Dpp-Bian)Ca(THF)$_4$] prepared from Dpp-Bian (0.25 g) in THF. The color of the reaction mixture instantly changed from green to brown, and a dark finely crystalline precipitate formed, which was dissolved after THF (10 mL) was added to the reaction mixture. Brown crystals of compound **III** were formed on the slow evaporation of the obtained solution in vacuo for 24 h. After the solution was decanted and washed with cold benzene, the crystals were dried at 30°C in vacuo for 15 min. The yield was 0.55 g (95%). The crystal for XRD was sampled without drying.

IR (ν, cm^{-1}): 1609 s, 1582 s, 1571 w, 1559 w, 1503 w, 1416 s, 1347 s, 1299 s, 1245 s, 1211 m, 1170 s,

1140 m, 1105 m, 1099 m, 1068 s, 1036 w, 1003 s, 984 w, 936 w, 917 s, 884 w, 876 w, 852 m, 838 w, 807 s, 793 s, 756 s, 739 w, 690 w, 680 m, 666 w, 621 m, 614 s, 599 m, 573 w, 543 w, 534 w, 512 s, 505 s, 436 w, 427 m.

For $C_{70}H_{84}N_6O_2Ca$, [(Dpp-Bian)Ca(Bpp)$_2$]·2THF

Anal. calcd., %	C, 77.73	H, 7.82	N, 7.77
Found, %	C, 78.49	H, 7.56	N, 7.14

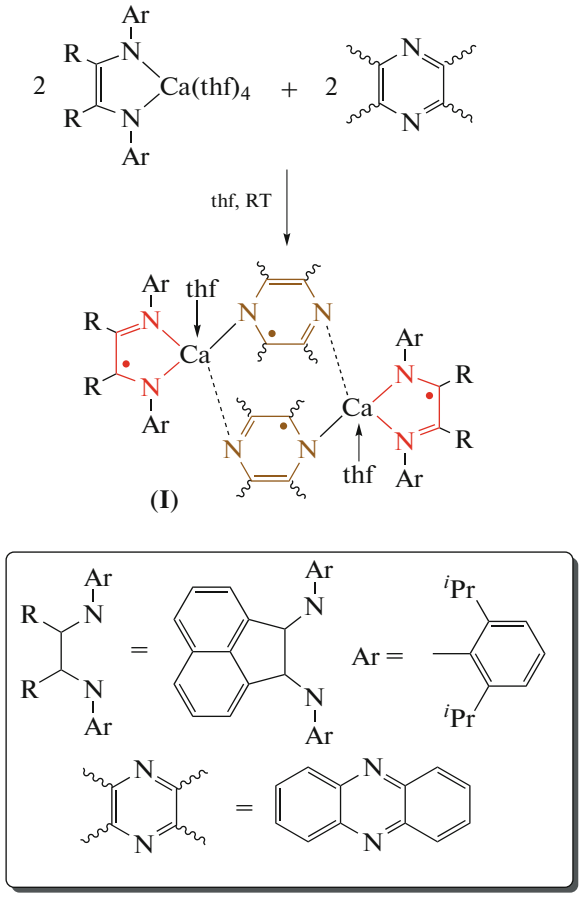
XRD of compound I. The crystals suitable for XRD were prepared from THF. The crystal under study was covered with a mineral oil (Aldrich) and fixed on a glass capillary, which was placed in a cold nitrogen jet of a Bruker D8 Quest single-crystal X-ray diffractometer. Diffraction data (ω scan mode, MoK_α radiation, λ = 0.71073 Å) were collected, initial reflection indexing was performed, and unit cell parameters were refined using the APEX3 program [24]. Experimental sets of intensities were integrated using the SAINT program [25, 26]. The structure was solved by a direct method according to the dual-space algorithm using the SHELXT software [27] and refined by least squares for F^2_{hkl} using the SHELXTL software [28, 29] in the anisotropic approximation for non-hydrogen atoms. Hydrogen atoms were placed in the geometrically calculated positions and refined isotropically. An absorption correction was applied using the SADABS program [30]. The revealed solvate THF molecules were in the general positions. The ratio of the solvate THF molecules and calcium complex was 6 : 1. The crystallographic data and XRD experimental parameters are given in Table 1. Selected bond lengths and bond angles are listed in Table 2.

The structure was deposited with the Cambridge Crystallographic Data Centre (CIF file CCDC no. 2176826; ccdc.cam.ac.uk/getstructures).

RESULTS AND DISCUSSION

The reaction of [(Dpp-Bian)Ca(THF)$_4$] with phenazine occurs in THF at room temperature for 1–2 min. The reaction product is dimer **I** (Scheme 1) isolated as dark red crystals (57%) after the reaction mixture was hold at 6°C for 24 h. According to the EPR spectroscopy and XRD data, dimer **I** contains the Dpp-Bian and Phz radical cations coordinated by the calcium ion.

The EPR spectrum of a crystalline sample of complex **I** exhibits a single line (g = 2.0045) confirming the presence of unpaired electrons in the compound. In a 2-methyltetrahydrofuran solution at 290 K, compound **I** demonstrates the isotropic multiplet EPR spectrum (Fig. 1). The simulation using the EasySpin program [23] shows that the best correspondence of the experimental and calculated EPR spectra is achieved in the case of superimposing the EPR signals of the Dpp-Bian and Phz radical anions present in equal amounts. One of two unpaired electrons in each monomer fragment interacts with two equivalent nuclei of the nitrogen atoms of the Dpp-Bian ligand, and another electron interacts with two equivalent nuclei of nitrogen and two groups of four equivalent protons of the phenazine fragment. Thus, the observed EPR signal is a superposition of signals from two paramagnetic species and probably indicates the dissociation of compound **I** to [(Dpp-Bian)Ca]$^+$ and (Phz)$^-$ in the solution. Compound **I** exhibits no signals in the half and zero fields, which are characteristic of biradicals, in either the crystalline state, or 2-methyltetrahydrofuran matrix. Probably, the intermolecular antiferromagnetic exchange between spins of the adjacent molecules occurs in the crystalline state.



Scheme 1.

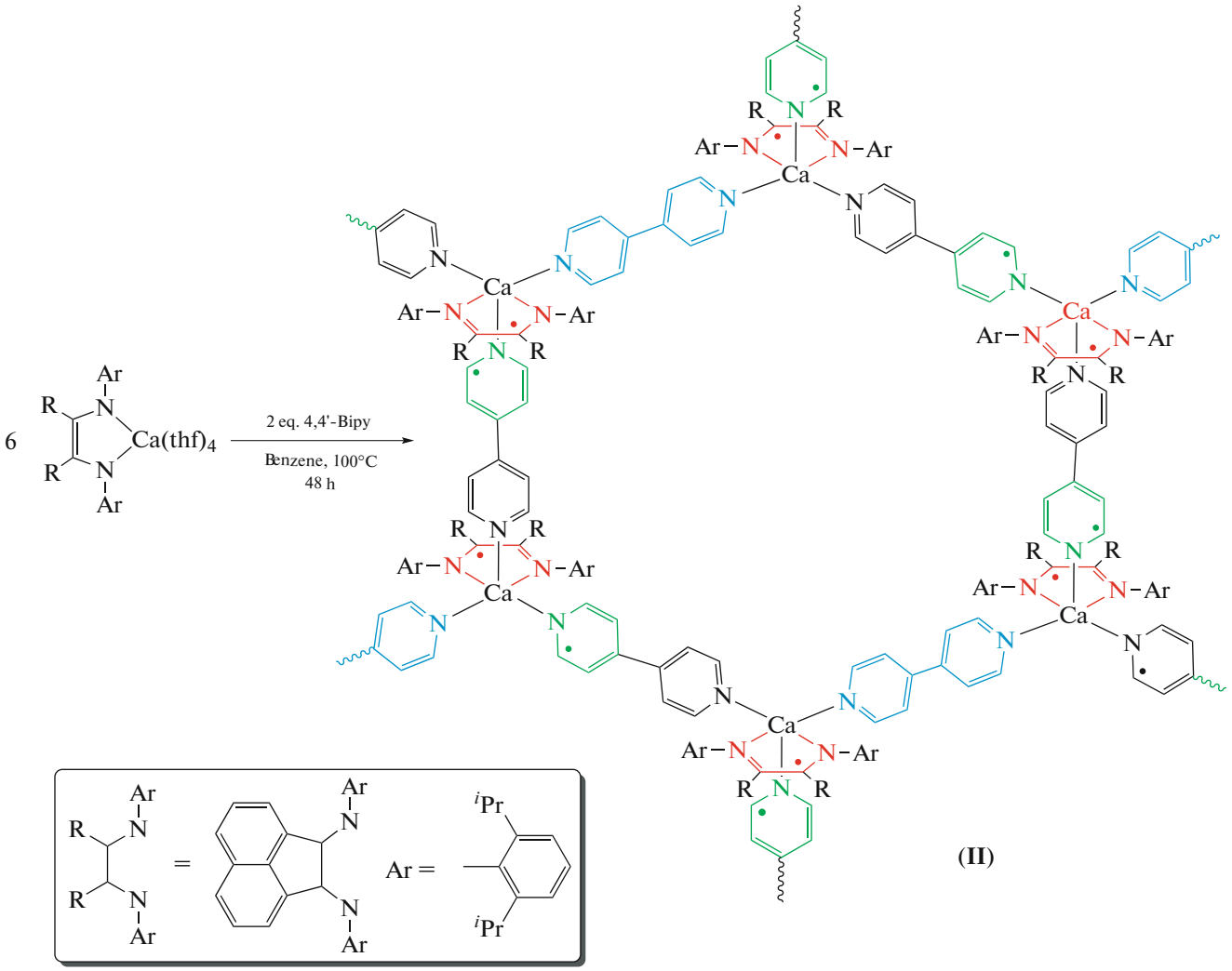
According to the XRD data, compound **I** in the crystalline state is the centrosymmetric dimer (Fig. 2) in which two [(Dpp-Bian)Ca(THF)]$^+$ radical cations are bound to each other by two phenazine radical anions lying in parallel planes. The pentacoordinated calcium atoms in compound **I** have a distorted trigonal bipyramidal environment. The bond lengths in the diimine fragment of the Dpp-Bian ligand (N(1)–C(1) 1.335(3), N(2)–C(2) 1.332(4), and C(1)–C(2) 1.452(4) Å) confirm its radical anion state. For comparison, the N(1)–C(1), N(2)–C(2), and C(1)–C(2) distances in the bis(ligand) derivative [(Dpp-

Table 1. Crystallographic data and experimental and structure refinement parameters for compound **I**

Parameter	Value
Empirical formula	$C_{128}H_{160}N_8O_8Ca_2$
FW	2018.79
Crystal system	Monoclinic
Space group	$P2_1/n$
Temperature, K	100(2)
Radiation wavelength, Å	0.71073
a, Å	12.7110(5)
b, Å	15.5771(6)
c, Å	27.8184(11)
α, deg	90
β, deg	90.678(1)
γ, deg	90
V, Å^3	5507.7(4)
Z	2
ρ_{calc}, g/cm^3	1.217
μ, mm^{-1}	0.166
F(000)	2176
Crystal size, mm	0.47 × 0.22 × 0.19
Measurement range over θ, deg	2.19–27.00
Index ranges	$-16 \le h \le 16$, $-19 \le k \le 19$, $-35 \le l \le 35$
Number of measured reflections	125145
Number of independent reflections R_{int}	11951 0.049
Number of reflections with $I > 2\sigma(I)$	9918
Absorption correction (max/min)	0.9705/0.9087
Data/restraints/parameters	11951/120/685
GOOF	1.067
R_1, wR_2 ($I > 2\sigma(I)$)	0.0782, 0.1945
R_1, wR_2 (for all reflections)	0.0944, 0.2018
Residual electron density (min/max), e Å^{-3}	–0.779/0.736

Bian)$_2$Ca] are 1.334(4), 1.342(4), and 1.442(5) Å, respectively [31]. The Ca–N(1) and Ca–N(2) bond lengths in complex **I** (2.381(2) and 2.432(2) Å) are comparable with the Ca–N distances in [(Dpp-Bian)$_2$Ca] (2.371(3) and 2.378(3) Å). The nitrogen–carbon distance in the radical anion phenazine ligand of compound **I** (1.366(3)–1.370(3) Å) is shorter than the corresponding distances in [AlMe$_2$]$_2$(μ-η^1:η^1-Phz)$_2$ (1.388(5)–1.396(5) Å) but is longer than that in the neutral ligand in [AlMe$_3$]$_2$(μ-η^1:η^1-Phz) (1.349(5)–1.359(5) Å) [17].

The reaction of [(Dpp-Bian)Ca(THF)$_4$] with two molar equivalents of 4,4'-bipyridine in benzene affords 2D coordination polymer **II** in a yield of 87% (Scheme 2). Blue crystals of compound **II** were obtained by the solvothermal method on heating the reaction mixture in an evacuated sealed ampule at 100°C for 48 h (*attention, excessive pressure!*) followed by slow cooling to room temperature (10°C/h). The presence of radical ligands in compound **II** is confirmed by the EPR signal from its crystalline sample (singlet, g = 2.00447).



Scheme 2.

The mixture formed due to the oxidation/hydrolysis of compound **II** in air contains, according to the ^{1}H NMR spectral data, free Dpp-Bian and 4,4'-Bipy in a ratio of 1 : 1.5. The elemental and XRD analyses data are consistent with this observation. Thus, the charge distribution between the metal and ligands in compound **II**, probably, is as follows: [(Dpp-Bian)-Ca^{2+}(4,4'-Bipy)$^-$(4,4'-Bipy)$_{0.5}$]; i.e., six Dpp-Bian and six 4,4'-Bipy radical anions, as well as three neutral 4,4'-bipyridine ligands, fall onto six calcium atoms. The 2D coordination network can be considered as numerous parallel 1D coordination polymer chains [(Dpp-Bian)$^-$$Ca^{2+}$(4,4'-Bipy)$^-$] crosslinked by

Table 2. Selected bond lengths and angles in compound **I**

Bond	*d*, Å
Ca(1)–N(1)	2.381(2)
Ca(1)–N(2)	2.432(2)
Ca(1)–N(3)	2.421(2)
Ca(1)–N(4)	2.446(2)
Ca(1)–O(1)	2.393(2)
N(1)–C(1)	1.335(3)
N(2)–C(2)	1.332(4)
C(1)–C(2)	1.452(4)
Angle	**ω, deg**
N(1)Ca(1)O(1)	91.25(8)
N(3)Ca(1)N(2)	115.96(8)
N(1)Ca(1)N(3)	99.48(8)
O(1)Ca(1)N(3)	149.55(8)
N(1)Ca(1)N(2)	72.62(7)
O(1)Ca(1)N(2)	94.41(8)
N(1)Ca(1)N(4)	149.04(8)
O(1)Ca(1)N(4)	80.52(7)
N(3)Ca(1)N(4)	75.66(8)
N(2)Ca(1)N(4)	137.38(8)

the neutral 4,4'-Bipy ligands (blue fragments in Scheme 2).

Compound **II** is a new illustration of the solvent nature effect on the compositions and structures of the coordination polymers based on calcium and redox-active Dpp-Bian and 4,4'-Bipy. We have previously shown that the reaction of [(Dpp-Bian)Ca(THF)$_4$] with 4,4'-Bipy in THF affords 1D polymer [(Dpp-Bian)$^{-}$Ca^{2+}(4,4'-Bipy)$^{-}$(THF)$_2$]·4THF, whereas crosslinked 2D polymer [(Dpp-Bian)$^{-}$Ca^{2+}(4,4'-Bipy)(4,4'-Bipy)$^{-}$]·2THF·2C$_6$H$_6$ is formed in a THF/benzene mixture [21]. As found quite recently, the reaction of [(Dpp-Bian)Ca(THF)$_4$] with 4,4'-Bipy occurs readily in 1,2-dimethoxyethane (DME). This reaction product is highly soluble in DME and, probably, has a dimeric structure similar to those of the related magnesium and barium complexes [{(Dpp-Bian)M(DME)$_n$}$_2$(4,4'-Bipy)] (M = Mg, n = 1; M = Ba, n = 2) [32]. Evidently, donor solvents do not favor the formation of coordination polymers, since they compete with donor ligands. On the contrary, in non-solvating media without steric hindrances, bidentate donor ligands are easily coordinated by metal atoms to form coordination chains.

Prior to performing TG and elemental analyses of compound **II**, its crystals were dried at room temperature in vacuo for 15 min. This was accompanied by the removal of some solvate benzene molecules. The TG curve of compound **II** demonstrates three mass loss stages (Fig. 3). Residual solvate molecules of the solvent are released at the first stage (40–90°C). The maximum rate is observed at 66°C. The overall mass loss at this stage is 9%, which corresponds to one benzene molecule. At the next stage (100–220°C), the mass loss is 25% (calcd. 27%), which is related to the thermal decomposition of the framework and release of 4,4'-Bipy. The third stage (220–350°C) is associated with the destruction of the [(Dpp-Bian)Ca] fragment.

A low quality of crystals of complex **II** did not allow us to determine bond lengths and bond angles by XRD. However, the data obtained are sufficient for the unambiguous determination of the mutual arrangement of atoms in the crystal (Fig. 4), including solvate benzene molecules. The structural unit of the infinite 2D network in compound **II** is the [(Dpp-Bian)Ca(4,4'-Bipy)$_{1.5}$] fragment. The network has the topology (6,3) and consists of alternating 4,4'-Bipy ligands and calcium ions coordinating the terminal Dpp-Bian ligands. The calcium atoms have a distorted trigonal bipyramidal environment formed by five nitrogen atoms. Three benzene molecules fall onto one metallocomplex fragment.

The reaction of [(Dpp-Bian)Ca(THF)$_4$] with two molar equivalents of Bpp in benzene affords a dark finely crystalline precipitate, which is dissolved upon the addition of THF to the reaction mixture. The evaporation of the obtained solution for 24 h results in product **III**, which was isolated as brown needles in a yield of 95% (Scheme 3). Compound **III** gives no EPR signals in either the solution, or crystalline state. The ^{1}H NMR spectrum of compound **III** is poorly informative because of a low solubility in benzene. Nevertheless, the whole body of spectral data indicates diamagnetism of compound **III**. Therefore, the charge distribution in this compound is probably as follows: [(Dpp-Bian)$^{2-}$Ca^{2+}(Bpp)$_2$]·2(THF)·(C$_6$H$_6$). Thus, the coordination of Bpp by the [(Dpp-Bian)Ca(THF)$_4$] complex does not result in the electron transfer from the Dpp-Bian dianion to 1,3-bis(4-pyridyl)propane.

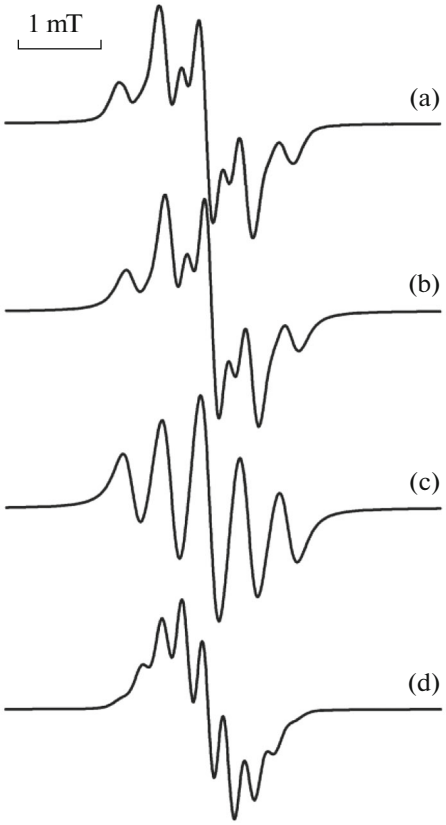
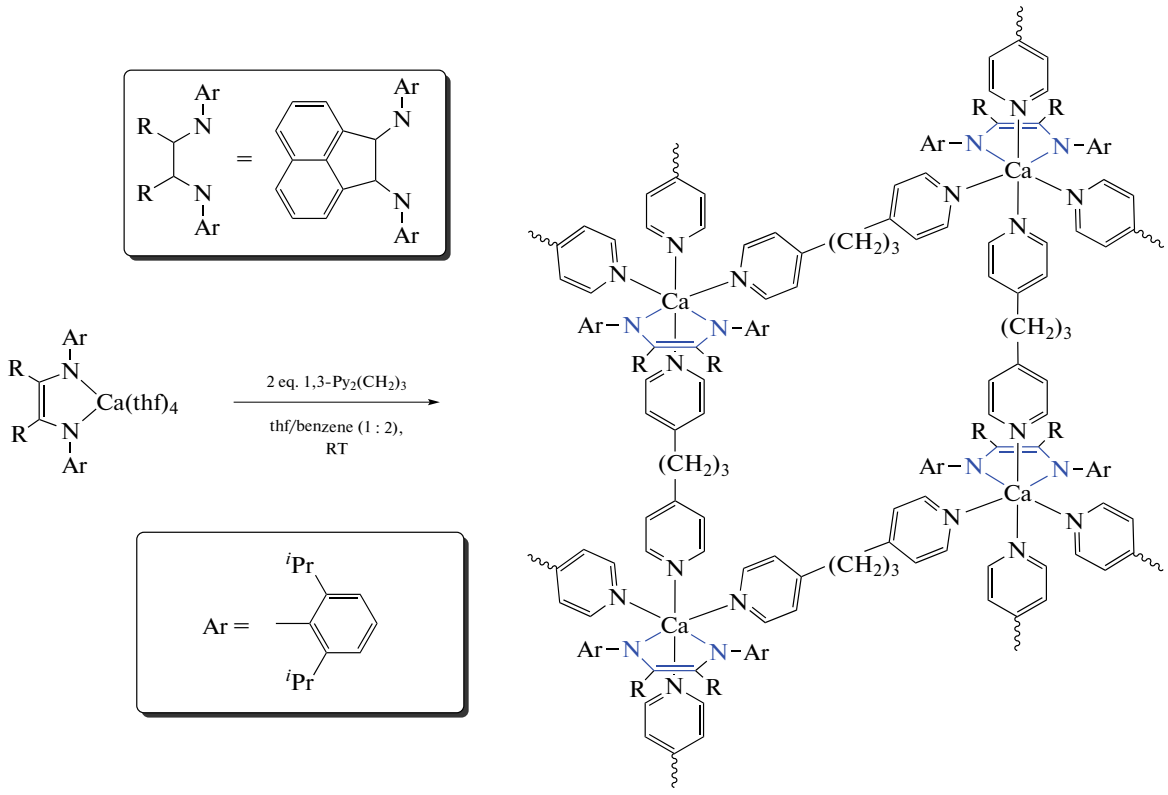


Fig. 1. (a) EPR spectrum of compound **I** in 2-methyltetrahydrofuran (290 K); (b) calculated spectrum for an equimolar mixture of $(Dpp\text{-}Bian)^-$ and Phz^-; (c) calculated spectrum for the radical anion $(Dpp\text{-}Bian)^-$, $g = 2.00564$, $a_i(2 \times {}^{14}N) = 0.4706$ mT; and (d) calculated spectrum for the radical anion Phz^-, $g = 2.00571$, $a_i(2 \times {}^{14}N) = 0.2392$, $a_i(4 \times {}^{1}H) = 0.2421$, $a_i(4 \times {}^{1}H) = 0.0120$ mT.



Scheme 3.

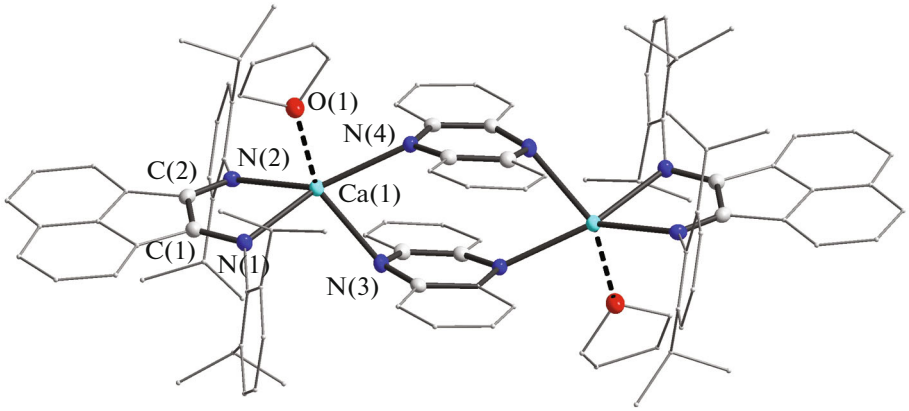


Fig. 2. Molecular structure of compound **I**. Thermal ellipsoids of 50% probability. Hydrogen atoms are omitted.

As expected, free Dpp-Bian and Bpp in the molar ratio 1 : 2 were found by ^{1}H NMR spectroscopy in the products of oxidation of compound **III** with air oxygen. Prior to thermogravimetric (TG) and elemental analyses, the crystals of compound **III** were dried at room temperature in vacuo for 15 min accompanied by the removal of the solvate benzene molecule. The TG curve of compound **III** (Fig. 5) demonstrates three stages of mass loss. Two solvate THF molecules are removed (mass loss 13%) at the first stage (36–120°C). At the next stage (150–233°C), the mass loss is 34%, which is due to the decomposition of the polymer and detachment of two Bpp molecules. The maximum rate of the process is observed at 191°C. The third mass loss stage (220–340°C) is associated with the destruction of the [(Dpp-Bian)Ca] fragment. Thus, the thermal decomposition of related compounds **II** and **III** proceeds via the same stage in close temperature ranges.

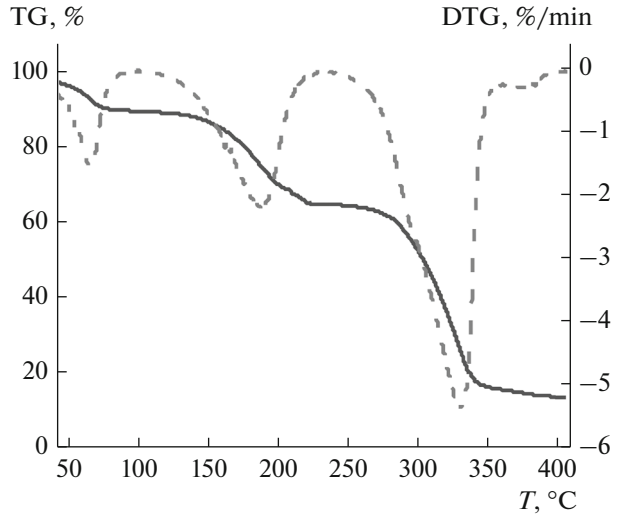


Fig. 3. TG and DTG curves for complex **II**.

Unfortunately, only the mutual arrangement of atoms in the crystals of complex **III** was determined by XRD. A low quality of the crystal is caused, most likely, as in the case of compound **II**, by the distortion of the crystal structure because of the partial removal of the solvate solvent when the crystals were selected for XRD experiments. According to the XRD data, compound **III** is the 2D coordination polymer (Fig. 6) in which the Bpp ligands and calcium ions alternate and coordinate terminal Dpp-Bian. The asymmetric structural unit in compound **III** is presented by the [(Dpp-Bian)Ca(Bpp)$_2$] fragment. The octahedral coordination environment of the calcium atom is formed by six nitrogen atoms: two atoms from the Dpp-Bian ligand and four atoms from two Bpp ligands. The cavities of the crystalline cell of compound **III** contain two THF molecules and one benzene molecule.

Compounds **II** and **III** are poorly soluble in non-coordinating solvents because of their polymer nature. Their dissolution in THF leads to the decomposition of both compounds to the starting reagents: [(Dpp-Bian)Ca(THF)$_4$] and 4,4'-Bipy and Bpp, respectively. The same was observed earlier for the calcium and strontium complexes with 4,4'-Bipy [21]. In the case of compound **II**, the decomposition is accompanied by the backward electron transfer from 4,4'-Bipy to the Dpp-Bian ligand.

Thus, we synthesized and characterized two new crosslinked metal-organic coordination polymers of calcium. One of them contains only redox-active ligands: terminal Dpp-Bian and bridging 4,4'-Bipy. Unlike the previously published 2D coordination polymer [(Dpp-Bian)Ca(4,4'-Bipy)$_2$]·2(C_6H_6)·2(THF) in which each calcium atom is bound to four bridging 4,4'-bipyridine ligands and forms the network with the topology (4,4), in compound [(Dpp-Bian)Ca(4,4'-Bipy)$_{1.5}$]·3C_6H_6 (**II**) described in this work each calcium atom is linked to three 4,4'-Bipy linkers and forms the network with the topology (6,3). Therefore, the polymer structure based on calcium and redox-

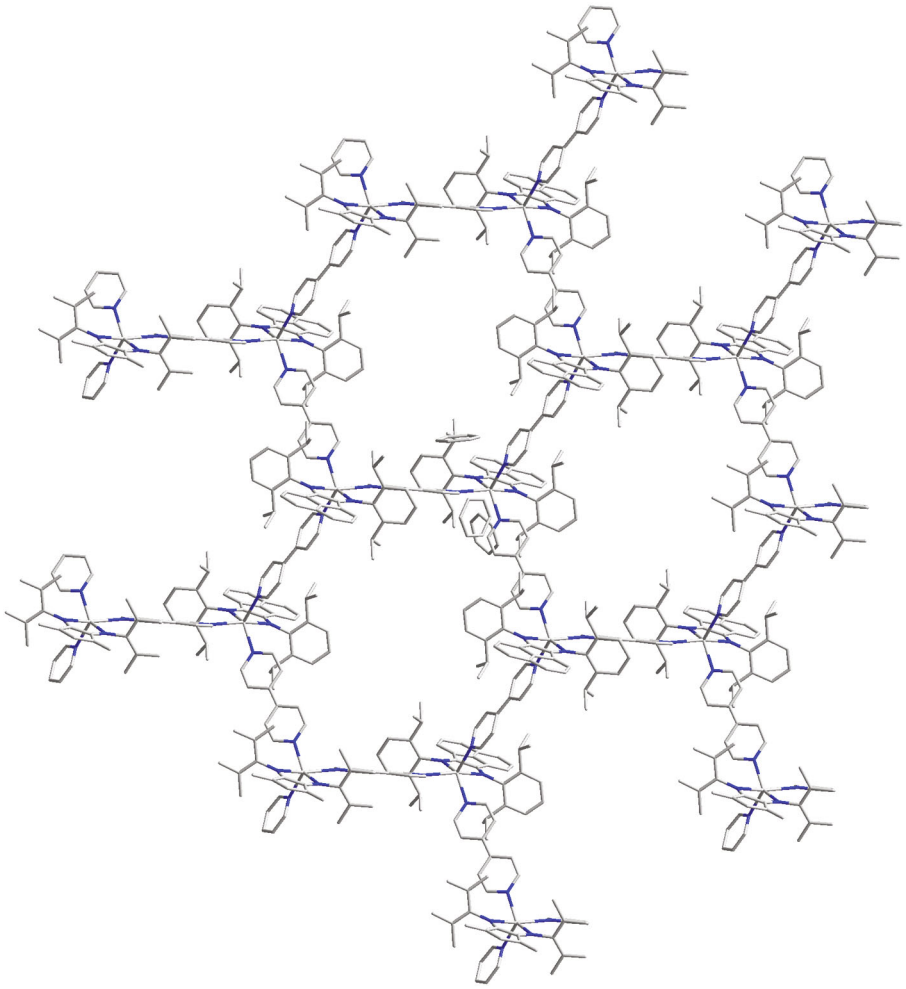


Fig. 4. Fragment of the crystal structure of compound **II**. Hydrogen atoms are omitted.

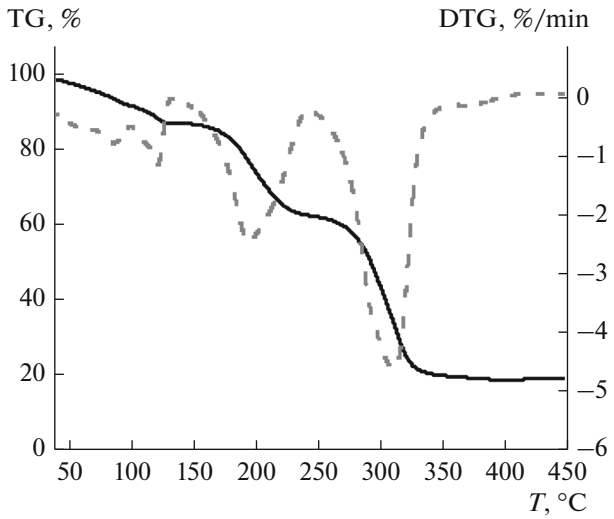


Fig. 5. TG and DTG curves for complex **III**.

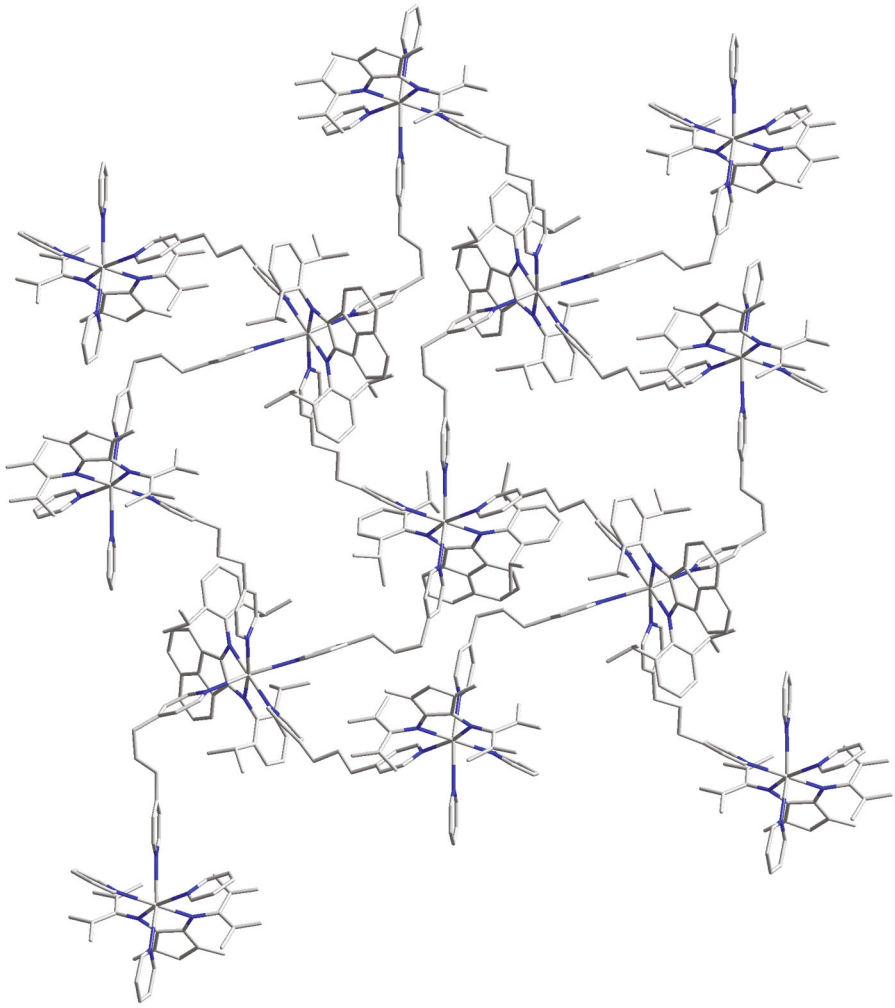


Fig. 6. Fragment of the crystal structure of compound **III**. Hydrogen atoms are omitted.

active ligands Dpp-Bian and 4,4'-Bipy can be controlled by the solvent used. The formation of coordination polymers in solvating solvents is difficult because of the competition with donor ligands. On the contrary, the use of aromatic solvents makes it possible to prepare crosslinked structures in high yields. Another crosslinked coordination polymer, compound **III**, consists of alternating 1,3-bis(4-pyridyl)propane and calcium ions. Unlike compound **II**, its terminal Dpp-Bian exists in the dianionic state rather than in the form of radical anion. Steric factors prevent the formation of a coordination polymer in the reaction of [(Dpp-Bian)Ca(THF)$_4$] with phenazine. The product of this reaction is a dimer with two bridging phenazine ligands: [(Dpp-Bian)$^{-}$Ca^{2+}(Phz)-(THF)]$_2$·6(THF) (**I**). Four radical anion ligands fall onto two calcium atoms in this dimer. Compounds **I** and **II** synthesized in this work are heterospin systems and can be used for the construction of molecular magnets with exchange interactions of different types.

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CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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