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Coordination polymers derived from gallium and zinc metal–metal bonded species

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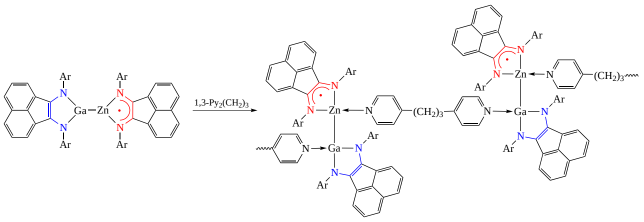
The reaction of (dpp-bian)Ga–Zn(dpp-bian) (dpp-bian is 1,2-bis[(2,6-diisopropylphenyl)imino]acenaphthene) with 1,3-di(4-pyridyl)propane results in 1D coordination polymer [(dpp-bian)Ga–Zn(dpp-bian)(μ^2-1,3-Py$_2$(CH$_2$)$_3$)]$_n$ with the retained Ga–Zn bond. In contrast, the coordination of 1,3-di(4-pyridyl)propane to Zn atoms in the (dpp-bian)Zn–Zn(dpp-bian) complex induces the cleavage of the Zn–Zn bond which is accompanied by reduction of dpp-bian radical anions to dianions. The reaction product represents 1D coordination polymer [{(dpp-bian)Zn}(μ^2-1,3-Py$_2$(CH$_2$)$_3$)]$_n$.

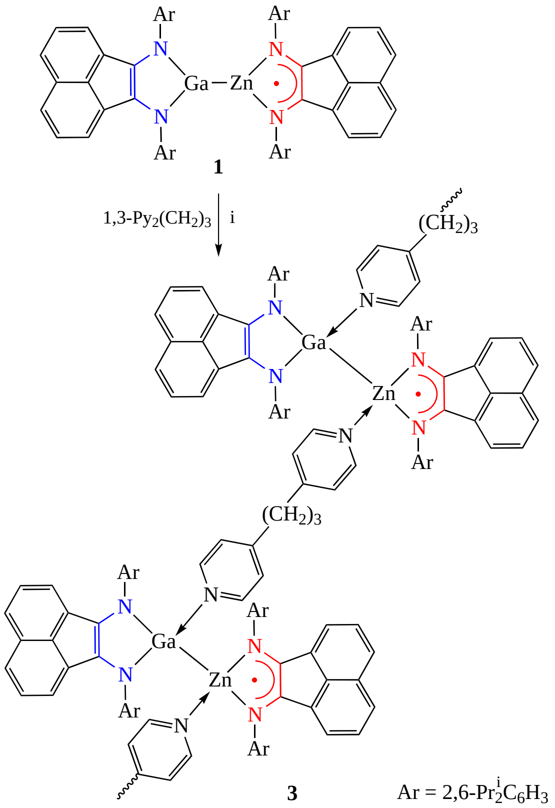


Keywords: gallium compounds, zinc compounds, redox-active ligands, metal–organic frameworks, X-ray diffraction.

Design and preparation of the metal–organic coordination polymers (MOCPs) is a rapidly developing field of coordination chemistry. The 2D and 3D metal–organic frameworks (MOFs) often display advanced properties that may be useful in catalysis,[1] gas storage,[2] magnetism,[3] *etc*. Although the principles of assembling metal–organic frameworks are well established, their controlled synthesis is still challenging due to the complex interplay of several factors. Among those are the nature of metal centres, type of terminal as well as bridging ligands.[4,5] In a majority of MOCPs or MOFs, the asymmetric unit consists of a single metal ion as a centre of propagation of the polymeric/framework structure.[6] The metal–metal bonded species[7] can find application in molecular electronics,[8] permanent magnets,[9] organometallic catalysis,[10,11] and even in enzyme-mediated transformations.[12] The presence of such reactive units could endow MOFs to acquire unexpected functions, profitable distinguishing them from traditional materials.

Only few coordinative assemblies having a metal–metal bond and redox-active diimine ligands have been reported. Among them are one-dimensional (1D) chain complexes containing Ga–Fe,[13] Ga–Ni,[14] Ga–V,[15] and In–In[16] fragments. Several years ago we became interested in main group metal complexes of redox-active ligands able to emulate the reactivity of transition metal complexes associated with a shuttle like exchange between two oxidation states of a metal centre. Such processes are often impossible with main group metals because of a sole oxidation state. On the other hand, M–M bonded species for the group 13 and especially group 14 metals are not rare. The variability of the chemical behaviour of M–M bonded species supported with redox-active ligands[17] offers prospects for the construction of coordination polymers. Recently we prepared a coordination polymer by reacting of digallane (dpp-bian)Ga–Ga(dpp-bian) with 1,3-bis(4-pyridyl)propane 1,3-Py$_2$(CH$_2$)$_3$.[18]

In continuation of our research, herein we reacted two other M–M bonded compounds, (dpp-bian)Ga–Zn(dpp-bian)[19,20] **1** and (dpp-bian)Zn–Zn(dpp-bian)[21] **2** with 1,3-di(4-pyridyl)-propane 1,3-Py$_2$(CH$_2$)$_3$. The reaction of equimolar amounts of compound **1** and 1,3-Py$_2$(CH$_2$)$_3$ in toluene at ambient temperature gives polymer [(dpp-bian)Ga–Zn(dpp-bian)(μ^2-1,3-Py$_2$(CH$_2$)$_3$)]$_n$



Scheme 1 *Reagents and conditions*: i, toluene, 50 °C, 15 min, then 10 °C, 24 h.

3 (Scheme 1). Product **3** was isolated in 68% yield as brown crystals.

In toluene product **3** dissociates to ‘monomeric’ species, which allows for registration of the EPR spectrum being identical to that of the starting **1**.[19] At 293 K, the absorption maximum for **3** is located at 520 nm that also corresponds to the original complex **1**. The TGA study of product **3** (see Online Supplementary Materials, Figure S1) revealed two steps of a mass loss. The first step (60 °C, 20.5% weight loss) is associated with a destruction of the polymeric chains and release of free 1,3-$Py_2(CH_2)_3$ and toluene present in the crystal cell. The second step of the weight loss takes place at 220 °C and reflects decomposition of (dpp-bian)Ga–Zn(dpp-bian).

In contrast to **1,** paramagnetic zinc–zinc-bonded compound (dpp-bian)Zn–Zn(dpp-bian) **2** reacts with 1,3-di(4-pyridyl)-propane to afford diamagnetic coordination polymer $[\{(\text{dpp-bian})\text{Zn}\}(\mu^2\text{-}1,3\text{-Py}_2(\text{CH}_2)_3)]_n$ **4** (Scheme 2). Compound **4** is resulted from the intramolecular electron transfer from the Zn−Zn bond to two dpp-bian ligands in complex **2**. Product **4** was isolated as green crystals in 71% yield. Its low solubility precludes its characterization by the NMR spectroscopy, however the ^{1}H NMR spectrum of the substance obtained by oxidation of **4** consists of free dpp-bian and 1,3-$Py_2(CH_2)_3$ in a molar ratio 1 : 1.

The TGA study of complex **4** (see Online Supplementary Materials, Figure S2) revealed three thermal processes accompanied with a weight loss. The first one in the range 30–140 °C is associated with release of THF present in the crystal cell (19%). The second one at 180–240 °C indicates the release of 1,3-bis(4-pyridyl)propane. The total weight loss at this step is 16%. Further heating to 270 °C leads to decomposition of remaining (dpp-bian)Zn and yields amorphous products.

New complexes **3** and **4** have been characterized by the single crystal X-ray analysis (Figures 1, 2 and Tables S1, S2 of the Online Supplementary Materials).[†] Complexes **3** and **4** crystallize as infinite 1D coordination polymers whose infinite chains are assembled *via* 1,3-$Py_2(CH_2)_3$ linkers. Complex **3** contains four-coordinate gallium and zinc centres. According to τ_4'[22,23] values both atoms adopt distorted tetrahedral geometry [τ_4' = 0.66 and 0.67 for Ga(1) and Zn(1), respectively]. In compound **3**, the Ga(1) atom is chelated by dianionic dpp-bian ligand [C(1)–C(2) 1.392(4), N(1)–C(1) 1.384(4), N(2)–C(2) 1.383(4) Å], while the Zn(1) atom is chelated by radical-anionic dpp-bian ligand [C(37)–C(38) 1.433(4), N(3)–C(37) 1.348(4), N(4)–C(38) 1.344(4) Å]. Both metal atoms coordinate neutral pyridyl rings of 1,3-$Py_2(CH_2)_3$ ligands. Due to rise of the coordination number from three to four on going from **1** to **3** the metal–metal bond length in **3** [2.4529(5) Å] is longer compared to that in **1** [2.3531(8) Å].[19]

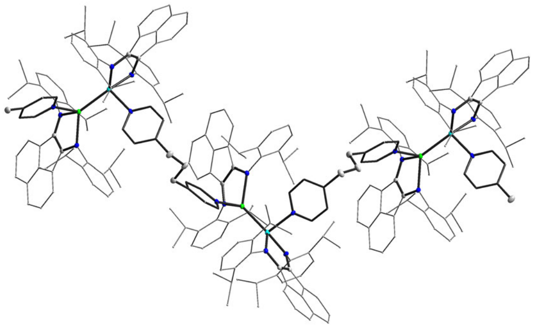


Figure 1 Molecular structure of complex **3**.

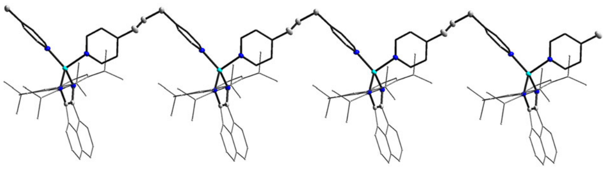
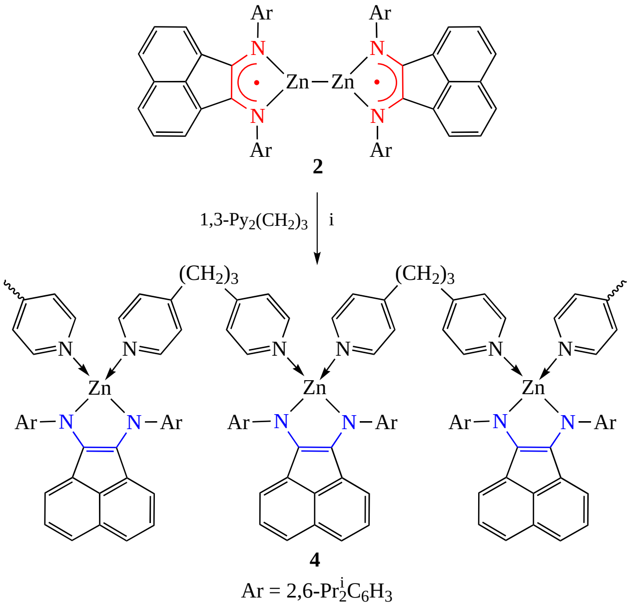


Figure 2 Molecular structure of complex **4**.



Scheme 2 *Reagents and conditions*: i, THF, 25 °C, 14 days.

[†] *Crystal data for* **3**. $C_{92}H_{102}GaN_6Zn$, M = 1426.88, monoclinic, space group $C2/c$, 100(2) K, a = 49.577(3), b = 14.3857(7) and c = 22.6011(12) Å, β = 110.5999(17)°, Z = 8, V = 15088.4(13) Å^3, d_{calc} = 1.256 g cm^{-3}, F_{000} = 6056. A black plate-shaped single crystal with dimensions of 0.24 × 0.13 × 0.06 mm was selected, and the intensities of 99172 reflections were measured using a Bruker D8 Quest diffractometer (ω-scans technique, $\lambda[\text{Mo}K_\alpha]$ = 0.71073 Å, μ = 0.726 mm^{-1}, $2\theta_{max}$ = 57.206°). After merging of equivalents and absorption corrections, 16637 independent reflections (R_{int} = 0.0946) were used for the structure solution and refinement. Final R factors: R_1 = 0.0621 [10896 reflections with $I > 2\sigma(I)$], wR_2 = 0.1423 (all reflections), GOF = 1.048.

Crystal data for **4**. $C_{60.33}H_{76.67}N_4O_{2.83}Zn$, M = 968.62, trigonal, space group $R3$, 100(2) K, $a = b$ = 35.042(2), c = 11.7479(8) Å, Z = 9, V = 12493.1(18) Å^3, d_{calc} = 1.159 g cm^{-3}, F_{000} = 4674. A black stick-shaped single crystal with dimensions of 0.20 × 0.05 × 0.04 mm was selected, and the intensities of 46589 reflections were measured using a Bruker D8 Quest diffractometer (ω-scans technique, $\lambda[\text{Mo}K_\alpha]$ = 0.71073 Å, μ = 0.488 mm^{-1}, $2\theta_{max}$ = 51.386°). After merging of equivalents and absorption corrections, 10560 independent reflections (R_{int} = 0.0724) were used for the structure solution and refinement. Final R factors: R_1 = 0.0464 [9327 reflections with $I > 2\sigma(I)$], wR_2 = 0.0997 (all reflections), GOF = 1.037.

The X-ray diffraction data were collected using the APEX3 software packages. The intensity data were integrated by SAINT[25] program. SADABS[26] was used to perform area-detector scaling and absorption corrections. The both compounds were solved by dual method[27] and refined on F_{hkl}^2 using SHELXTL package.[28] All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed in calculated positions and were refined using a riding model [U_{iso}(H) = 1.5U_{eq}(C) for CH_3-group and U_{iso}(H) = 1.2U_{eq}(C) for other groups]. The structure of complex **4** was refined as a 2-component twin with matrix [0 1 0 1 0 0 0 0 -1] and BASF 0.46556. The asymmetric units of **3** and **4** contain one toluene molecule and 2.833 molecules of THF, respectively. The toluene molecule in crystal **3** and two solvent molecules in crystal **4** are disordered over two positions. For refinement of disordered fragments we used EADP, ISOR, SADI and DFIX instructions.

CCDC 2167120 (**3**) and 2167121 (**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.

A distribution of the bond lengths in the NCCN fragment of the dpp-bian ligands in **4** (Table S2) indicates the dianionic nature of the ligand. In complex **4**, each zinc cation is bound to two nitrogen atoms of one dpp-bian ligand and two nitrogen atoms of two 1,3-$Py_2(CH_2)_3$ moieties. The Zn(1) atom in complex **4** adopts a less distorted tetrahedral geometry compared to complex **3** ($\tau_4' = 0.80$). All bond lengths in the coordination sphere of gallium and zinc atoms in **3** and **4** (Table S2) are in good agreement with related complexes.[19–21]

In summary, compound **1** easily coordinates 1,3-di(4-pyridyl)-propane to afford the coordination polymer that contains redox-active organic ligand and Ga–Zn bond. In contrast to **1**, the reaction of Zn–Zn-bonded compound **2** towards 1,3-$Py_2(CH_2)_3$ is accompanied by the cleavage of M–M bond with simultaneous transfer of an electron from zinc to the redox-active dpp-bian ligand. In this case, the metal atoms coordinate two 1,3-$Py_2(CH_2)_3$ moieties of two separate 1,3-di(4-pyridyl)propane molecules. Previously[24] we observed similar behaviour in the system (dpp-bian)(I)Ga–Ga(I)(dpp-bian)–pyridine when dissolution of that digallane in pyridine resulted in monomeric compound [(dpp-bian)GaI(Py)].

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2022.11.024.

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