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

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Experimental part.

General information.

Compounds **1** and **2** are sensitive to air and moisture. All manipulations concerning their preparation and identification were carried out under vacuum using glass ampoules. Toluene and THF were dried over sodium/benzophenone and condensed under vacuum into the flasks just prior to use. C_6D_6 was dried over sodium/benzophenone at ambient temperature and condensed under vacuum into the NMR tubes that contained the sample. The IR spectra were recorded on a FSM-1201 spectrometer, the ^1H NMR – on a Bruker Advance III 400 spectrometer. The ESR spectrum was recorded on Magnettech ESR5000 (9.48 GHz). Elemental analysis was performed on a Vario EL Cube analyzer. Thermal analysis in the temperature range 40-500 °C was carried out using a TGA/DSC 3+ METTLER TOLEDO instrument. The experiments were performed under N_2 flow (50 cm^3 min^{-1}) at a 5 K min^{-1} heating rate. Compound **1** [S1] and **2** [S2] were prepared and isolated according to a literature procedure. 1,3-Di(4-pyridyl)propane (Aldrich) was purified by sublimation.

[(dpp-bian)Ga–Zn(dpp-bian)(μ^2-1,3-$Py_2(CH_2)_3$)]$_n$ 3. To a solution of compound **1** (0.20 g, 0.17 mmol) in toluene (30 ml), 1,3-di(4-pyridyl)propane (0.03 g, 0.17 mmol) was added. The mixture was stirred at 50 °C for 15 min. The resulting brown solution was concentrated to 10 ml and allowed to stand at 10 °C for 24 h. Dark brown crystals of product **3** were separated by decantation, washed with cold toluene and dried in vacuum. Yield 0.13 g (68%). Anal. calcd. for $C_{92}H_{102}GaN_6Zn$ (1426.88): C, 77.44; H, 7.2; N 5.89. Found: C 77.37; H 7.15; N 5.83.

IR (Nujol): 1612 s, 1588 m, 1560 w, 1515 s, 1492 w, 1433 s, 1358 m, 1317 s, 1253 m, 1209 w, 1184 m, 1136 w, 1114 w, 1082 w, 1064 w, 1036 w, 1014 w, 925 m, 891 w, 874 w, 855 w, 836 w, 818 w, 804 w, 761 s, 732 s, 696 m, 669 w, 641 w, 619 w, 612 w, 573 w, 543 w, 523 w, 514 w, 464 w cm^{-1}.

[(dpp-bian)Zn(μ^2-1,3-$Py_2(CH_2)_3$)]$_n$ 4. To a solution of compound **2** (0.16 g, 0.13 mmol) in THF (30 ml) 1,3-di(4-pyridyl)propane (0.05 g, 0.27 mmol) was added. The resulting brown solution was left at 25 °C for 14 days. Green crystals of product **4** were separated by decantation, washed with cold THF and dried in vacuum. Yield 0.18 g (71%). Anal. calcd. for $C_{60.33}H_{76.67}N_4O_{2.83}Zn$ (968,62): C, 74.80; H, 7.97; N, 5.78. Found: C, 74.71; H, 7.89; N, 5.71.

IR (Nujol): 1671 w, 1642 w, 1619 s, 1601 s, 1559 w, 1523 m, 1495 m, 1362 m, 1337 s, 1316 s, 1275 w, 1254 m, 1219 w, 1186 m, 1177 m, 1105 w, 1068 s, 1040 w, 1028 w, 994 m, 971 w, 935 w, 924 s, 835 m, 815 w, 805 s, 787 s, 759 s, 751 s, 723 w, 622 w, 510 w cm^{-1}.

Table S1. Crystal data and structure refinement details for **3** and **4**.

	3	**4**
Empirical Formula	$C_{92}H_{102}GaN_6Zn$	$C_{60.33}H_{76.67}N_4O_{2.83}Zn$
M	1426.88	968.62
T [K]	100(2)	100(2)
Crystal system	Monoclinic	Trigonal
Space group	*C*2/*c*	*R*3
a [Å]	49.577(3)	35.042(2)
b [Å]	14.3857(7)	35.042(2)
c [Å]	22.6011(12)	11.7479(8)
α [deg]	90	90
β [deg]	110.5999(17)	90
γ [deg]	90	120
V [Å^3]	15088.4(13)	12493.1(18)
Z	8	9
d_{calc} [g/cm^3}	1.256	1.159
μ [mm^{-1}]	0.726	0.488
F_{000}	6056	4674
Crystal dimensions [mm]	0.24×0.13×0.06	0.20×0.05×0.04
θ range [deg]	2.100–27.103	2.013–25.693
HKL indices	$-63 \le h \le 63$ $-18 \le k \le 18$ $-28 \le l \le 28$	$-42 \le h \le 42$ $-42 \le k \le 42$ $-14 \le l \le 154$
Reflections collected / unique	99172 / 16637	46589 / 10560
R_{int}	0.0946	0.0724
Data / Restraints / Parameters	16637/91/917	10560 /151/695
$S(F^2)$	1.048	1.037
R_1 / wR_2 ($I > 2\sigma(I)$)	0.0621 / 0.1230	0.0464 / 0.0967
R_1 / wR_2 (all data)	0.1070 / 0.1423	0.0586 / 0.0997
Absolute structure parameter	-	-0.153(9)
Largest diff. peak and hole [e/Å^3]	1.031/-0.692	0.339 / -0.357

Table S2. Selected bond lengths (Å) and angles (°) in the complexes **3** and **4**.

3					
Bond Lengths (Å)					
Ga(1)-N(1)	1.969(3)	N(1)-C(1)	1.384(4)	N(6)-C(78)	1.341(4)
Ga(1)-N(2)	1.988(3)	N(2)-C(2)	1.383(4)	N(6)-C(82)	1.342(4)
Ga(1)-N(5)	2.193(3)	N(3)-C(37)	1.348(4)	C(1)-C(2)	1.392(4)
Zn(1)-N(4)	2.027(3)	N(4)-C(38)	1.344(4)	C(37)-C(38)	1.433(4)
Zn(1)-N(3)	2.132(3)	N(5)-C(73)	1.327(4)	Ga(1)-Zn(1A)*	2.4529(5)
Zn(1)-N(6)	2.180(3)	N(5)-C(77)	1.327(4)		
Angles (°)					
N(1)-Ga(1)-N(2)	87.91(11)		N(4)-Zn(1)-N(3)	84.11(10)	
N(1)-Ga(1)-N(5)	95.58(11)		N(4)-Zn(1)-N(6)	97.27(10)	
N(2)-Ga(1)-N(5)	94.20(10)		N(3)-Zn(1)-N(6)	93.77(10)	
N(1)-Ga(1)-Zn(1A)	135.17(8)		N(4)-Zn(1)-Ga(1B)	134.33(8)	
N(2)-Ga(1)-Zn(1A)	129.88(8)		N(3)-Zn(1)-Ga(1B)	127.94(7)	
N(5)-Ga(1)-Zn(1A)	103.25(7)		N(6)-Zn(1)-Ga(1B)	109.91(7)	
4					
Bond Lengths (Å)					
Zn(1)-N(1)	1.961(6)	N(1)-C(1)	1.372(9)	N(4)-C(44)	1.340(9)
Zn(1)-N(2)	1.957(6)	N(2)-C(2)	1.383(9)	N(4)-C(48)	1.319(9)
Zn(1)-N(3)	2.072(5)	N(3)-C(37)	1.341(8)	C(1)-C(2)	1.394(8)
Zn(1)-N(4)	2.012(5)	N(3)-C(41)	1.345(9)		
Angles (°)					
N(2)-Zn(1)-N(1)	91.06(18)		N(2)-Zn(1)-N(3)	106.0(2)	
N(2)-Zn(1)-N(4)	124.6(2)		N(1)-Zn(1)-N(3)	112.1(2)	
N(1)-Zn(1)-N(4)	120.5(2)		N(4)-Zn(1)-N(3)	102.1(2)	

* – Symmetry transformations used to generate equivalent atoms (A): x, -y+1, z+1/2; (B): x, -y+1, z-1/2

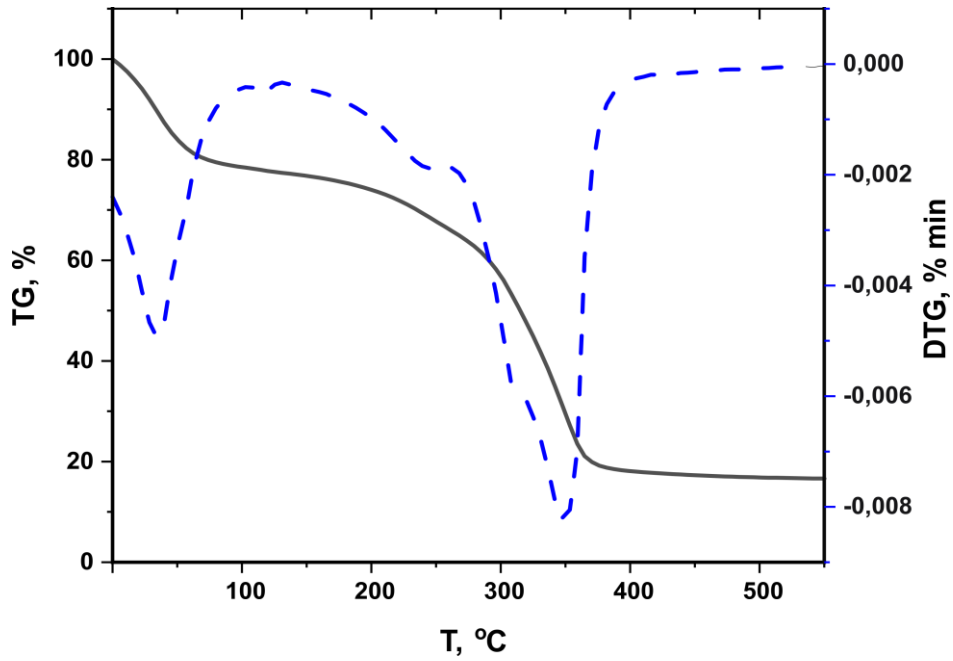

Figure S1. TGA and DTG diagrams for complex **3**.

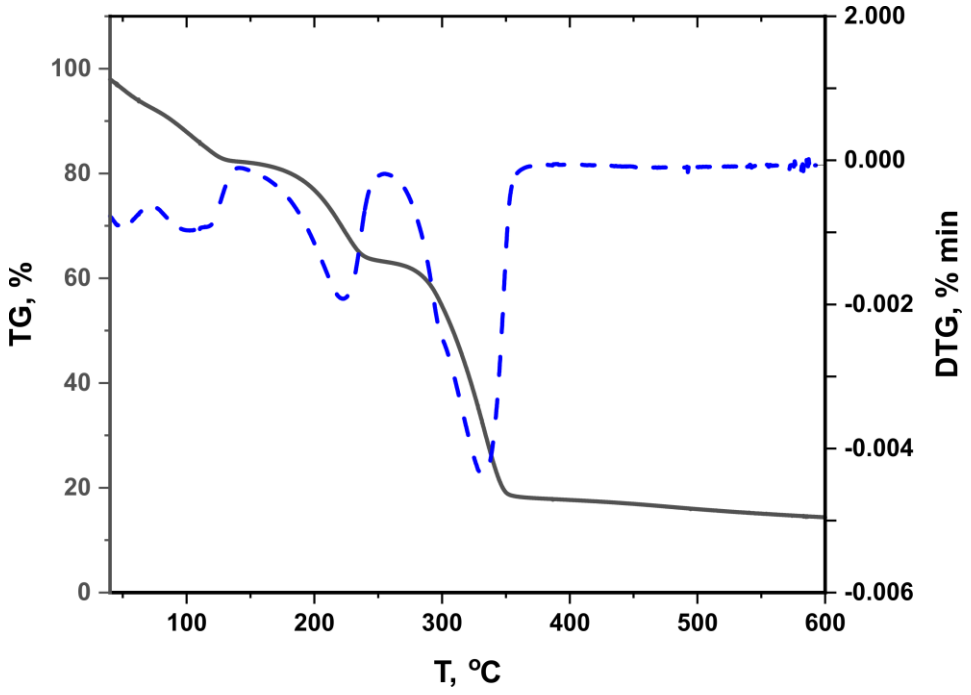

Figure S2. TGA and DTG diagrams for complex **4**.

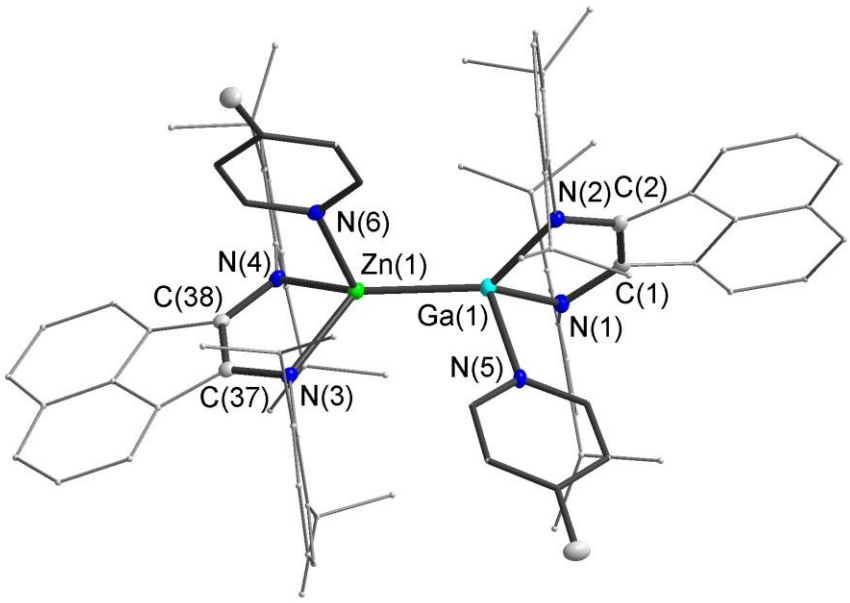

Figure S3. View of polymer fragment of **3**. Thermal ellipsoids with a 30% probability.

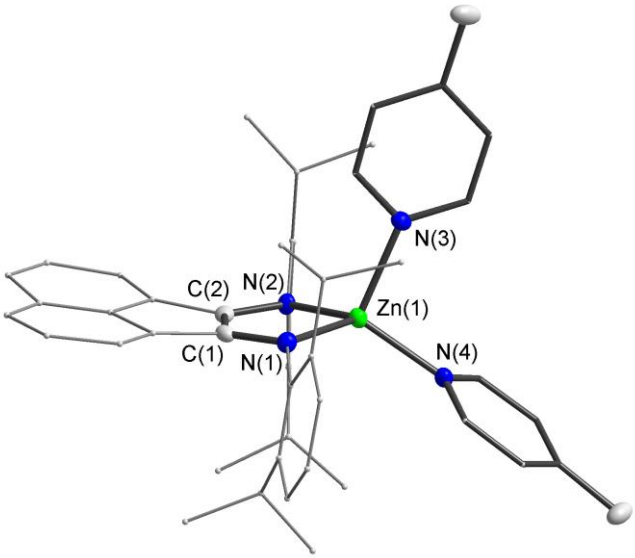

Figure S4. View of polymer fragment of **4**. Thermal ellipsoids with a 30% probability.

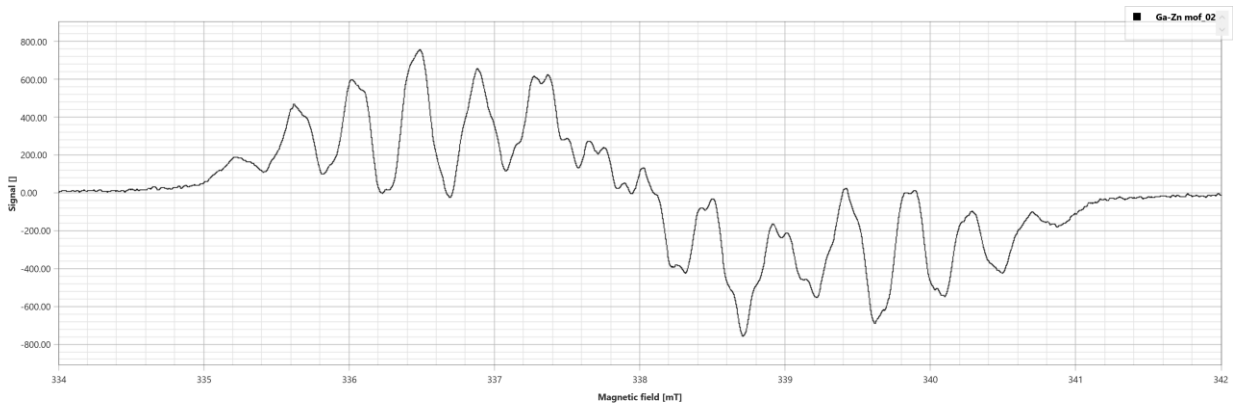

Figure S5. ESR spectrum of compound **3** (toluene, 298 K).

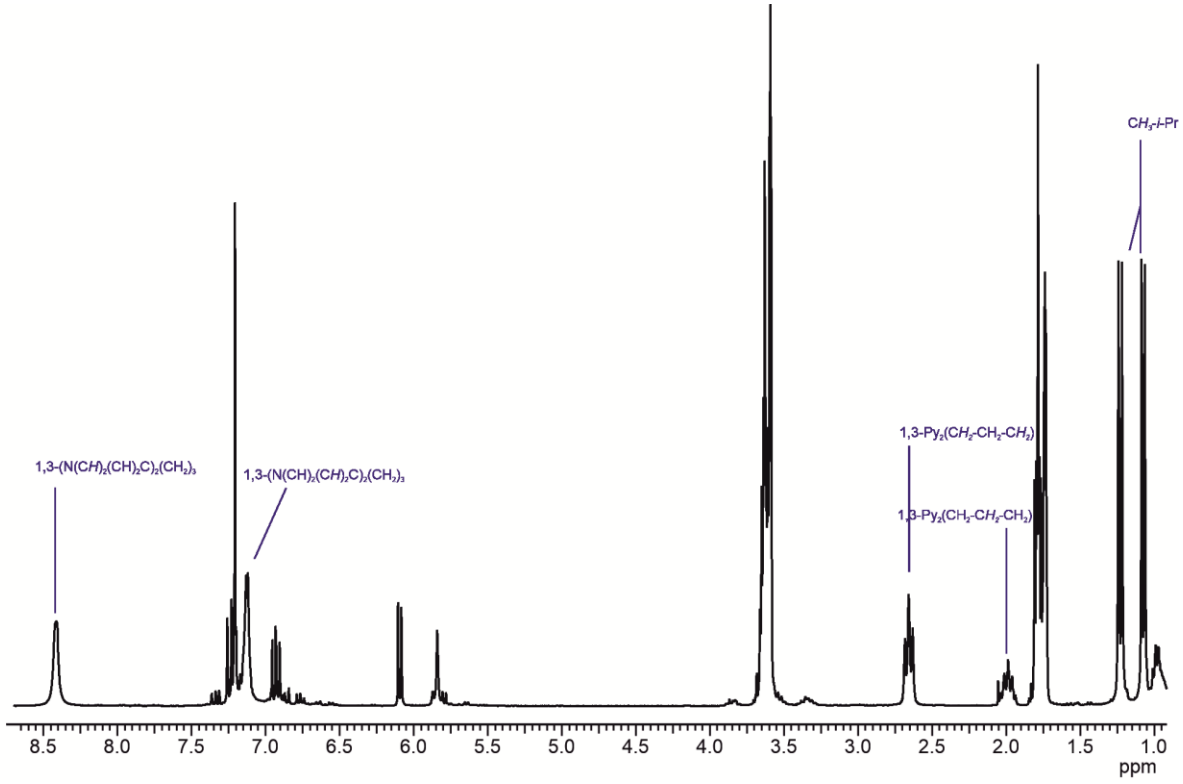

Figure S6 ^{1}H NMR spectrum of the mixture resulted from oxidation of **4** (293 K, 300 MHz, THF-d_8).

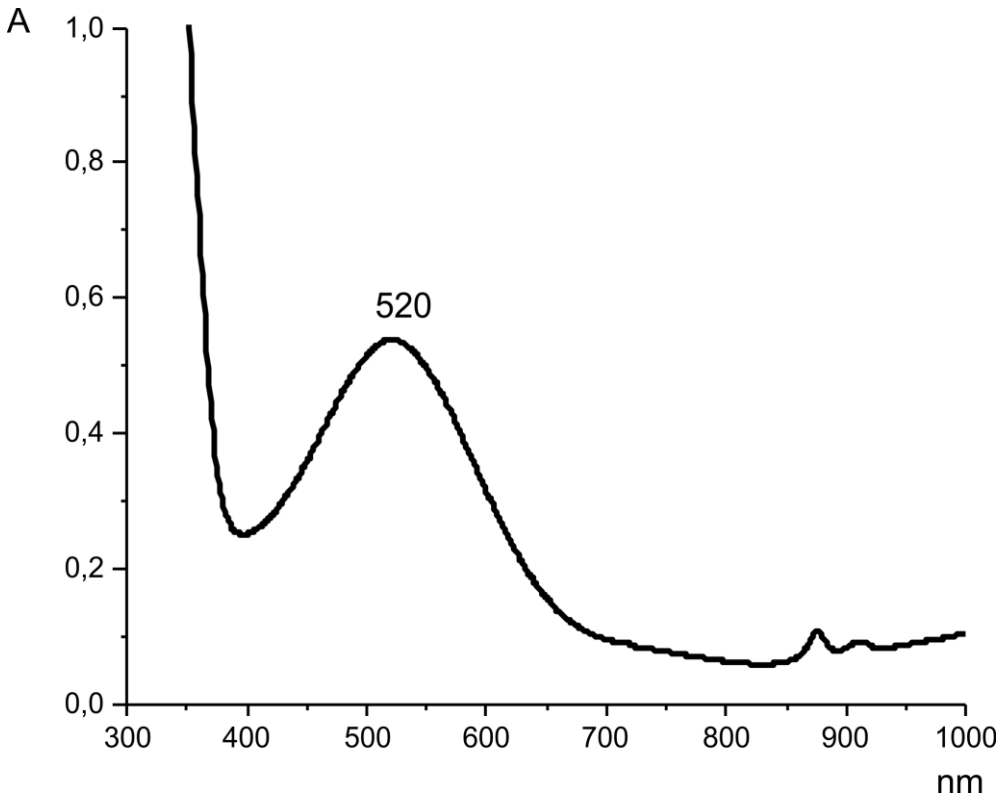

Figure S7. Uv-vis spectrum of compound **3** (293 K, toluene).

References

[S1] I. L. Fedushkin, A. N. Lukoyanov, A. N. Tishkina, M. O. Maslov, S. Yu. Ketkov, *Organometallics*, 2011, **30**, 3628.

[S2] I. L. Fedushkin, A. A. Skatova, S. Y. Ketkov, O. V. Eremenko, A.V. Piskunov, G. K. Fukin, *Angew. Chem. Int. Ed.* 2007, **46**, 4302.