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Synthesis and Structural Characterization of Four Zinc Complexes Containing 3,5-Dimethylpyrazole and Carboxylate Ligands

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Abstract. Four new zinc(II) complexes $Zn_2(\mu\text{-dmpz})_2(Hdmpz)_2(L1)_2$ (**1**) (Hdmpz = 3,5-dimethylpyrazole, HL1 = 2-methyl-2-phenoxypropanoic acid), $Zn(Hdmpz)_2(L2)_2$ (**2**) [HL2 = 2-hydroxy-5-(phenyldiazenyl)benzoic acid], $Zn_2(\mu\text{-dmpz})_2(Hdmpz)_2(L3)_2$ (**3**) [HL3 = 3,4-(methylenedioxy)benzoic acid], and $Zn_2(\mu\text{-dmpz})_2(Hdmpz)_2(L4)_2$ (**4**) [HL4 = 3-(4-methoxyphenyl)acrylic acid] were prepared and structurally characterized by different techniques including elemental analysis, IR spectroscopy, and single-crystal X-ray diffraction analysis. The X-ray studies suggested that all these complexes except compound **2** are centrosymmetric dinuclear complexes with a tetrahedral arrangement around each zinc ion, whereas compound **2** is a mononuclear complex. The pyrazole ligand is coordinated in both terminal as well as a bridging fashion in the dinuclear moiety, whereas the pyrazole ligand in compound **2** is coordinated only in monodentate terminal fashion with its neutral nitrogen group. In all four complexes the carboxylate functions behave as monodentate ligands. All complexes show intramolecular hydrogen bonding of N–H···O between N–H of pyrazole and nonbonded oxygen atom of carboxylate. Furthermore, rich intermolecular weak interactions such as classical hydrogen bonds, C–H···O, C–H···N, C–H···π, and CH_3–π interactions exist and complexes **1**–**4** display a set of 3D superamolecular frameworks. In addition, the four compounds are thermally stable below 150 °C.

1 Introduction

Supramolecular assemblies with desirable topological networks of selforganized molecular building blocks have received great attention in recent years.[1–3] This is due to fundamental interest in selfassembly processes,[4] supramolecular motifs,[5] and most significantly crystal engineering about their intriguing structural topologies. However, the prediction of the final supramolecular frameworks constructed by a set of ligands and metal ions to rationalize the design of compounds with well defined structures is still a challenge. The final structures depend on many factors such as the coordination arrangement of the metal ions, the metal-ligand stoichiometric ratio, the nature of counterions, weak interactions (hydrogen bonding, aromatic π–π stacking interactions as well as van der Waals forces),[6–8] and the experimental conditions.

Furthermore, coordination polymers with functional properties, such as magnetism, catalysis, optical, and sorption properties[9,10] make up rapidly growing field of research. Up to now, a variety of metal ions or more complex metal-containing fragments have been employed, and organic ligands containing O- or N-donors have been widely used. These two markedly different chemical functionalities have also been widely coupled in the same systems.[11]

The Zn^{2+} ion with d^{10} electron configuration is particularly suitable for the construction of coordination polymers. It exhibits a variety of coordination numbers and arrangements varying from tetrahedral, trigonal bipyramidal, and square pyramidal to octahedral. Sometimes a severe distortion of the ideal polyhedron bonding set is formed. Because of the lability of zinc complexes, the formation of coordination bonds is reversible, which enables zinc ions and ligands to rearrange during the assembly process to form highly ordered structures. Consequently, zinc can readily form all kinds of architectures such as 1D, 2D, and 3D structures.

The use of pyrazole or pyrazolate derivatives has drawn strong interest in modeling biological systems.[12–14] Pyrazole has also been widely employed in polypyrazolylborates to stabilize a variety of organometallic and coordination compounds.[15,16] Up to now, a variety of complexes containing 3,5-dimethylpyrazole (Hdmpz) ligands have been synthesized and employed in coordination chemistry or organometallic chemistry.[17–19] Additionally, many complexes with simple pyrazole ligands both in terminal as well as in bridging mode are available.[20–22] But in the presence of carboxylic acids and pyrazole derivatives the complexes are not very common except a few recently reported examples.[23,24] Our research group has been investigating coordination compounds with mixed ligands of carboxylate and imidazole derivatives for a long time.[25–27] The pyrazole ligand and the carboxylate ligand appear to have similar steric requirements and, to a certain extent, similar bonding capabilities.

In order to get a better understanding of the influence of the carboxylate residue in the formation of new coordination polymers, we studied the zinc-pyrazolate-carboxylate system,

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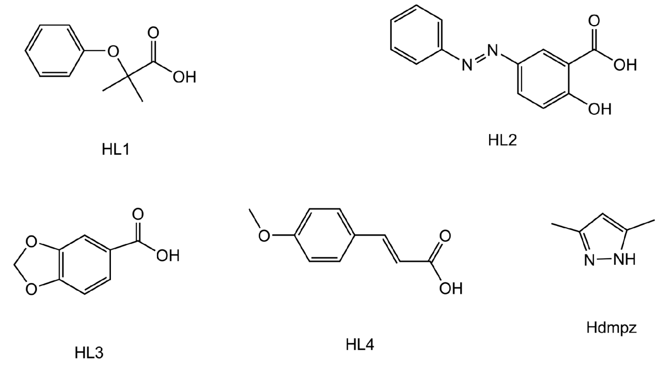
also aiming to investigate the role the weak noncovalent interactions play in forming the final supramolecular frameworks. In the following we report the synthesis, structural characterization, and thermal behavior of four stereochemically "stiffer" zinc complexes using 3,5-dimethylpyrazole (Hdmpz) and different carboxylate ligands (Scheme 1), namely $Zn_2(\mu\text{-}dmpz)_2(Hdmpz)_2(L1)_2$ (**1**) (L1 = 2-methyl-2-phenoxypropionate), $Zn(Hdmpz)_2(L2)_2$ (**2**) [L2 = 2-hydroxy-5-(phenyldiazenyl)benzoate]; $Zn_2(\mu\text{-}dmpz)_2(Hdmpz)_2(L3)_2$ (**3**) [L3 = 3,4-(methylenedioxy)benzoate], and $Zn_2(\mu\text{-}dmpz)_2(Hdmpz)_2(L4)_2$, (**4**) [L4 = 3-(4-methoxyphenyl)acrylate].



Scheme 1. Ligands used in this article.

2 Experimental Section

2.1 Materials and Physical Measurements

The chemicals and solvents used in this work are of analytical grade and available commercially and were used without further purification. The FT-IR spectra were recorded from KBr pellets in range 4000–400 cm^{-1} with a Mattson Alpha-Centauri spectrometer. Microanalytical (C, H, N) data were obtained with a Perkin–Elmer Model 2400II elemental analyzer. Thermogravimetric analyses (TGA) were studied by a Delta Series TA-SDT Q600 in a nitrogen atmosphere between room temperature and 800 °C (heating rate 10 $°C\cdot min^{-1}$) using Al crucibles.

2.2 Synthesis of Complexes

$Zn_2(\mu\text{-}dmpz)_2(Hdmpz)_2(L1)_2$ (1): A solution of $Zn(CH_3COO)_2\cdot 2H_2O$ (22 mg, 0.1 mmol) in MeOH (5 mL) was added to a MeOH solution (5 mL) containing Hdmpz (19.2 mg, 0.2 mmol) and 2-methyl-2-phenoxypropanoic acid (HL1) (72 mg, 0.4 mmol), under continuous stirring. The solution was stirred for about 2 h at room temperature and a small amount of precipitate formed. Afterwards, a few drops of conc. ammonia were added until the precipitate dissolved completely. The clear solution was filtered into a test tube, after several days colorless crystals were formed, which were filtered off, washed with MeOH and dried under vacuum to afford 70 mg of the product. Yield 80.31 % (based on Hdmpz). Elemental analysis performed on crystals exposed to the atmosphere: $C_{40}H_{52}N_8O_6Zn_2$: calcd. C 55.07; H 5.97; N 12.85 %; found: C 54.91; H 5.91; N 12.74 %. **IR** (KBr): $\tilde{\nu}$ = 3440 m, 3236 w, 3120 s, 2960 s, 2920 s, 2830 m, 2776 m, 1640 s, 1620 s, 1560 s, 1480 s, 1450 m, 1400 s, 1360 m, 1270 m, 1230 m, 1150 s, 1030 m, 980 m, 890 m, 820 m, 780 m, 740 m, 710 m, 680 m, 610 m cm^{-1}.

$Zn(Hdmpz)_2(L2)_2$ (2): A solution of $Zn(CH_3COO)_2\cdot 2H_2O$ (22 mg, 0.1 mmol) in MeOH (5 mL) was added to a MeOH solution (10 mL) containing Hdmpz (19.2 mg, 0.2 mmol) and 2-hydroxy-5-(phenyldiazenyl)benzoic acid (HL2) (96.8 mg, 0.4 mmol), under continuous stirring. The solution was stirred for about 2 h at room temperature and the solution became turbid. Afterwards, a few drops of conc. ammonia were added until the solution became clear. The red solution was filtered into a test tube, after several days dark red crystals were formed, which were filtered off, washed with MeOH and dried under vacuum to afford 52 mg of the product. Yield 70.26 % (based on Hdmpz). Elemental analysis performed on crystals exposed to the atmosphere: $C_{36}H_{34}N_8O_6Zn_2$: calcd. C 58.37; H 4.59; N 15.13 %; found: C 58.34; H 4.56; N 15.10 %. **IR** (KBr): $\tilde{\nu}$ = 3732 w, 3441 w, 3402 w, 3294 w, 3134 m, 3062 m, 3035 m, 2978 m, 2856 m, 2360 s, 2270 m, 1662 m, 1648 m, 1622 s, 1557 s, 1480 s, 1430 s, 1384 s, 1310 m, 1255 s, 1168 m, 1050 m, 1016 m, 907 m, 860 m, 780 m, 688 m, 606 m cm^{-1}.

$Zn_2(\mu\text{-}dmpz)_2(Hdmpz)_2(L3)_2$ (3): A solution of $Zn(CH_3COO)_2\cdot 2H_2O$ (22 mg, 0.1 mmol) in EtOH (5 mL) was added to an EtOH solution (8 mL) containing Hdmpz (19.2 mg, 0.2 mmol) and 1,3-benzodioxole-5-carboxylic acid (HL3) (66.4 mg, 0.4 mmol), under continuous stirring. The solution was stirred for about 2 h at room temperature and the solution became turbid. Afterwards, a few drops of conc. ammonia were added until the solution became clear. The solution was filtered into the test tube, after several days colorless crystals were formed, which were filtered off, washed with EtOH and dried under vacuum to afford 63 mg of the product. Yield 74.69 % (based on Hdmpz). Elemental analysis performed on crystals exposed to the atmosphere: $C_{36}H_{40}N_8O_8Zn_2$: calcd. C 51.22; H 4.74; N 13.28 %; found: C 51.20; H 4.71; N 13.18 %. **IR** (KBr): $\tilde{\nu}$ = 3405 m, 3240 w, 2920 m, 2660 m, 2540 s, 2520 m, 2320 m, 1725 m, 1638 s, 1580 m, 1540 m, 1460 m, 1442 s, 1408 m, 1380 s, 1300 s, 1260 s, 1140 m, 1096 m, 1020 s, 895 m, 852 m, 816 m, 774 m, 672 m, 620 m cm^{-1}.

$Zn_2(dmpz)_2(Hdmpz)_2(L4)_2$ (4): A solution of $Zn(CH_3COO)_2\cdot 2H_2O$ (22 mg, 0.1 mmol) in MeOH (5 mL) was added to a MeOH solution (3 mL) containing Hdmpz (19.2 mg, 0.2 mmol) and 3-(4-methoxyphenyl)acrylic acid (HL4) (71.2 mg, 0.4 mmol), under continuous stirring. The solution was stirred for about 2 h at room temperature and a small amount of precipitate was formed. Afterwards, a few drops of conc. ammonia were added until the precipitate dissolved completely. The clear solution was filtered into the test tube, after several days colorless block crystals formed, which were filtered off, washed with MeOH and dried under vacuum to afford 63 mg of the product. Yield 72.61 % (based on Hdmpz). Elemental analysis performed on crystals exposed to the atmosphere: $C_{40}H_{48}N_8O_6Zn_2$: calcd. C 55.33; H 5.53; N 12.91 %; found: C 55.32; H 5.51; N 12.89 %. **IR** (KBr): $\tilde{\nu}$ = 3570 m, 3429 m, 3237 w, 2880 s, 2782 m, 2360 s, 2320 s, 1950 m, 1880 m, 1680 m, 1645 s, 1624 m, 1598 s, 1550 m, 1520 s, 1448 m, 1408 m, 1360 m, 1296 m, 1260 s, 1220 m, 1180 s, 1056 m, 1014 m, 940 m, 902 m, 828 m, 728 m, 662 m, 628 m cm^{-1}.

2.3 X-ray Crystallography

Suitable crystals were mounted on a glass fiber and were investigated with a Bruker SMART 1000 CCD diffractometer operating at 50 kV and 40 mA using Mo-K_α radiation (0.71073 Å). Data collection and reduction were performed using the SMART and SAINT software.[28] The structures were solved by direct methods, and the non-hydrogen atoms were subjected to anisotropic refinement by full-matrix least-squares on F^2 using SHELXTL package.[29] Hydrogen atom positions for all structures were located in a difference map. Further details of the structural analysis are summarized in Table 1. Selected bond lengths and angles for complexes **1**–**4** are listed in Table 2, and the relevant hydrogen bond parameters are provided in Table 3.

Table 1. Summary of X-ray crystallographic data for complexes **1**, **2**, **3**, and **4**.

	1	**2**	**3**	**4**
Formula	$C_{40}H_{52}N_8O_6Zn_2$	$C_{36}H_{34}N_8O_6Zn$	$C_{36}H_{40}N_8O_8Zn_2$	$C_{40}H_{48}N_8O_6Zn_2$
Fw	871.64	740.08	843.50	867.60
T /K	298(2)	298(2)	298(2)	298(2)
Wavelength /Å	0.71073	0.71073	0.71073	0.71073
Crystal system	triclinic,	triclinic	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a /Å	8.7662(11)	11.0730(13)	9.0247(11)	8.3860(10)
b /Å	9.5918(12)	12.5171(14)	10.0554(13)	8.6601(11)
c /Å	14.1033(16)	14.7395(15)	11.1835(17)	14.8002(16)
α /°	104.370(2)	106.7940(10)	95.7440(10)	82.9470(10)
β /°	98.7190(10)	109.197(2)	101.943(2)	89.967(2)
γ /°	105.345(2)	93.3510(10)	102.757(2)	86.2250(10)
V /Å^3	1077.4(2)	1820.2(3)	957.0(2)	1064.4(2)
Z	1	2	1	1
D_{calcd} /Mg·m^3	1.343	1.350	1.464	1.354
Absorption coefficient / mm^{-1}	1.166	0.730	1.314	1.180
F(000)	456	768	436	452
Crystal size /mm	0.50 × 0.48 × 0.30	0.26 × 0.18 × 0.13	0.35 × 0.19 × 0.16	0.41 × 0.37 × 0.26
θ range /deg	1.53–25.02	1.72–25.02	1.88–25.02	2.37–25.02
Limiting indices	$-10 \le h \le 9$	$-13 \le h \le 13$	$-9 \le h \le 10$	$-9 \le h \le 9$
	$-11 \le k \le 9$	$-12 \le k \le 14$	$-11 \le k \le 11$	$-10 \le k \le 6$
	$-14 \le l \le 16$	$-17 \le l \le 17$	$-13 \le l \le 13$	$-17 \le l \le 17$
Reflections collected	5509	9652	5068	5339
Reflections independent (R_{int})	3718 (0.0262)	6342 (0.0371)	3319 (0.0364)	3678 (0.0192)
Goodness-of-fit on F^2	1.051	0.833	0.950	1.042
R indices [$I > 2\sigma I$]	$R_1 = 0.0392$, $wR_2 = 0.0900$	$R_1 = 0.0487$, $wR_2 = 0.0896$	$R_1 = 0.0512$, $wR_2 = 0.1173$	$R_1 = 0.0417$, $wR_2 = 0.0933$
R indices (all data)	$R_1 = 0.0610$, $wR_2 = 0.1033$	$R_1 = 0.1243$, $wR_2 = 0.1095$	$R_1 = 0.0764$, $wR_2 = 0.1285$	$R_1 = 0.0700$, $wR_2 = 0.1100$
Largest diff. peak and hole /e·Å^{-3}	0.483, –0.352	0.375, –0.427	0.666, –0.419	0.529, –0.301

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained on quoting the depository numbers CCDC-746309 (**1**), -746312 (**2**), -746310 (**3**), and -746311 (**4**). (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

3 Results and Discussion

3.1 Preparation and General Characterization

Most compounds based on pyrazole derivatives reported previously were prepared by conventional solution approach. Thus, all of the title compounds have already been prepared by the conventional solution method. The reaction between $Zn(CH_3COO)_2 \cdot 2H_2O$, carboxylic acids, and Hdmpz carried out in MeOH or EtOH solvents with ratios of 1:2:4 yields pure $Zn_2(\mu\text{-dmpz})_2(Hdmpz)_2(L)_2$ or $Zn(Hdmpz)_2(L)_2$ upon addition of a few drops of conc. ammonium solution. During the process the acetate was substituted by the corresponding carboxylate ions, and some Hdmpz ligands remain their NH groups, and some Hdmpz ligands are deprotonated. Crystal of all compounds, suitable for X-ray diffraction, were grown in yields of over 70 %. These compounds are insoluble in almost all common solvents. The IR spectra of **1**, **2**, **3**, and **4** display the characteristic carboxylate bands in the range 1560–1622 cm^{-1} for $\nu_{as}(CO_2)$ and at 1400–1430 cm^{-1} for $\nu_s(CO_2)$.[30] The frequency differences between $\nu_{as}(CO_2)$ and $\nu_s(CO_2)$ are 160, 192, 172, and 190 cm^{-1} for **1**, **2**, **3**, and **4**, respectively. This suggests a monodentate coordination mode for the carboxylate ligands in all four compounds. Coordinated neutral Hmdpz molecules are present in all four compounds, which is further confirmed by the presence of the characteristic NH band in the region 3400–3000 cm^{-1}.[31] The compositions of these compounds were determined by elemental analysis, and their structures were fully characterized by X-ray diffraction analysis. Hydrogen atoms connected to oxygen or nitrogen atoms were located from the difference electron density map.

3.2 Crystal Structure Description

3.2.1 Crystal and Molecular Structure of 1

The structural determination revealed that complex **1** crystallizes in triclinic system with space group $P\bar{1}$. As illustrated in Figure 1, the asymmetric unit consists of one Zn^{II} cation, one pyrazole molecule, one pyrazolate unit, and one carboxylate ligand. The pyrazolate unit acts as a *N*,*N*'-exobidentate ligand, keeping the two zinc ions at a non-bonding distance of ca. 3.567 Å. The complex molecule is dinuclear and consists of a Zn^{II} atom positioned at the center of a planar six-membered $[Zn(\mu\text{-dmpz})_2Zn]$ unit; each single unit has a four-coordinate zinc ion with three Zn–N bonds (one Zn–N$_{pyrazole}$, two

Table 2. Selected bond lengths /Å and angles /° for **1**, **2**, **3**, and **4**.

1			
Zn(1)–O(1)	1.954(2)	Zn(1)–N(1)	1.974(3)
Zn(1)–N(2)#1	1.999(2)	Zn(1)–N(3)	2.031(3)
O(1)–Zn(1)–N(1)	112.92(10)	O(1)–Zn(1)–N(2)#1	104.96(10)
N(1)–Zn(1)–N(2)#1	113.17(10)	O(1)–Zn(1)–N(3)	111.21(10)
N(1)–Zn(1)–N(3)	110.70(10)	N(2)#1–Zn(1)–N(3)	103.36(10)
2			
Zn(1)–O(4)	1.914(3)	Zn(1)–O(1)	1.921(3)
Zn(1)–N(7)	1.986(3)	Zn(1)–N(5)	1.997(3)
N(1)–N(2)	1.236(4)	N(1)–C(6)	1.431(5)
N(2)–C(8)	1.447(5)	N(3)–N(4)	1.24(6)
N(3)–C(19)	1.51(3)	N(4)–C(21)	1.46(5)
N(3')–N(4')	1.25(18)	N(3')–C(19)	1.49(11)
N(4')–C(21)	1.53(11)	O(4)–Zn(1)–O(1)	106.04(13)
O(4)–Zn(1)–N(7)	114.58(13)	O(1)–Zn(1)–N(7)	112.22(13)
O(4)–Zn(1)–N(5)	102.75(12)	O(1)–Zn(1)–N(5)	112.88(13)
N(7)–Zn(1)–N(5)	108.09(13)		
3			
Zn(1)–O(1)	1.924(3)	Zn(1)–N(2)#1	1.969(3)
Zn(1)–N(1)	1.970(3)	Zn(1)–N(3)	1.997(4)
O(1)–Zn(1)–N(2)#1	108.01(14)	O(1)–Zn(1)–N(1)	107.49(14)
N(2)#1–Zn(1)–N(1)	112.79(13)	O(1)–Zn(1)–N(3)	110.77(14)
N(2)#1–Zn(1)–N(3)	111.76(14)	N(1)–Zn(1)–N(3)	105.97(15)
4			
Zn(1)–O(1)	1.923(3)	Zn(1)–N(2)#1	1.972(2)
Zn(1)–N(1)	1.981(2)	Zn(1)–N(3)	2.004(3)
O(1)–Zn(1)–N(2)#1	106.87(11)	O(1)–Zn(1)–N(1)	109.22(11)
N(2)#1–Zn(1)–N(1)	113.36(10)	O(1)–Zn(1)–N(3)	114.13(12)
N(2)#1–Zn(1)–N(3)	109.73(11)	N(1)–Zn(1)–N(3)	103.68(11)

Symmetry codes for **1**: #1 –*x* + 2, –*y*, –*z*. Symmetry code for **3**: #1 –*x* + 1, –*y*, –*z* + 1. Symmetry code for **4**: #1 –*x* + 1, –*y* + 1, –*z* + 1.

Table 3. Hydrogen bond lengths and angles in studied structures of **1**, **2**, **3**, and **4**.

D–H···A	*d*(D–H) /Å	*d*(H···A) /Å	*d*(D···A) /Å	<(DHA) /°
1				
N(4)–H(4)···O(2)	0.86	1.97	2.751(3)	150.1
2				
O(6)–H(6A)···O(5)	0.82	1.88	2.596(3)	146.0
O(3)–H(3)···O(2)	0.82	1.85	2.570(4)	146.6
N(8)–H(8)···O(5)	0.86	1.99	2.790(4)	153.7
N(6)–H(6)···O(2)	0.86	1.98	2.741(4)	146.2
3				
N(4)–H(4)···O(2)	0.86	1.89	2.695(5)	156.0
4				
N(4)–H(4)···O(2)	0.86	1.93	2.712(5)	150.1

Zn–N$_{pyrazolato}$) and one Zn–O$_{carboxylate}$ bond. The bridging Zn–N distance of 1.976 Å (average) is shorter than the terminal Zn–N distance of 2.031(3) Å, which are similar to the reported values.[24] The carboxylate groups coordinate in monodentate manner with a Zn(1)–O(1) distance of 1.954(2) Å. The distance (3.268 Å) between the nonbonded oxygen atom and zinc ions is too large for oxygen to coordinate with the metal ion. The coordination arrangement around zinc in complex **1** is a distorted tetrahedron with coordination angles in the range 103.36(10)°–113.17(10)°. The geometrical parameters of this species closely match those recently reported for the analogous [{Zn(μ-C_2H_5COO)(μ-pz*)(Hpz*)}$_2$][32] (Hpz* = 4-acetyl-3-amino-5-methylpyrazole) and [{Zn(μ-C_2H_5COO)(μ-pz)-(Hpz)}$_2$][24] complexes.

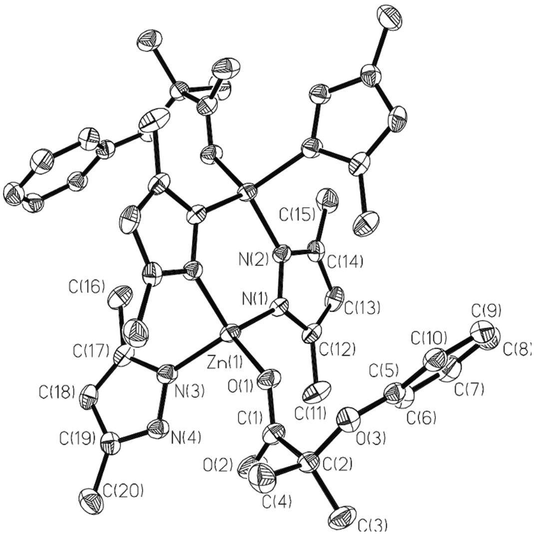


Figure 1. Molecular structure of complex **1** showing the atomic numbering scheme at 30 % ellipsoid probability level.

In complex **1**, the nonbonded oxygen atom of the carboxylate forms an intramolecular hydrogen bonding of N(4)–H(4)···O(2) with N(4)–O(2) and H(4)···O(2) distances of 2.751(3) and 1.97 Å, respectively. The adjacent dinuclear moieties are connected through C–H···π interaction between the 4-CH on pyrazole rings and the adjacent pyrazolato rings (with the distance of the carbon atom to the pyrazolato ring of 3.612 Å) to form a one dimensional chain along the *a* axis. Additionally, interchain C–H···π interactions (with the distance of 4-C on pyrazolato rings to the pyrazole ring of 3.761 Å) exist between the 4-CH on pyrazolato rings and the pyrazole rings in parallel chains along the *b* axis. The combined hydrogen bonds cause that compound **1** displays a 3D network structure, as shown in Figure 2.

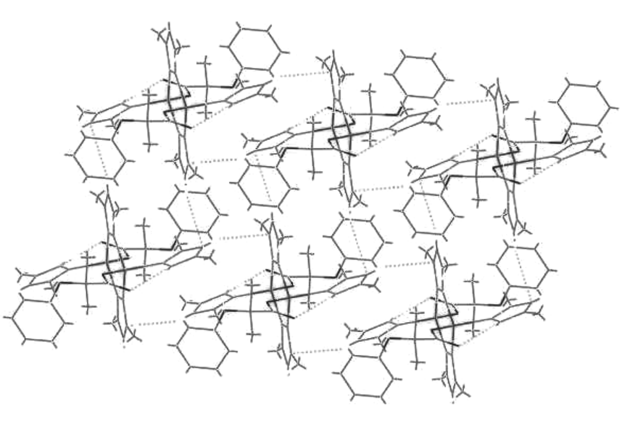


Figure 2. Packing diagram of compound **1** showing the three dimensional network structure viewed along the *b* axis. Dashed lines represent the intramolecular N–H···O, and intermolecular CH–π interactions.

3.2.2 Crystal and Molecular Structure of 2

Compound **2** of the formula $Zn(Hdmpz)_2(L2)_2$ crystallizes as triclinic dark red crystals in the centrosymmetric space group $P\bar{1}$ with two formula units in the unit cell. Each zinc ion is tetrahedrally coordinated by two oxygen atoms of two monodentate L2 ligands and by two nitrogen atoms, of two different monodentate pyrazole ligands (Figure 3). The molecular structure of **2** resembles the related $[Zn(CH_3COO)_2(ML)_2]$ monomers (ML = a monodentate nitrogen ligand), like the bis-imidazole[33] and bis-pyridine[34] complexes. The nitrogen atoms of the azo group in one L2 molecule are disordered over two positions with equal occupancies.

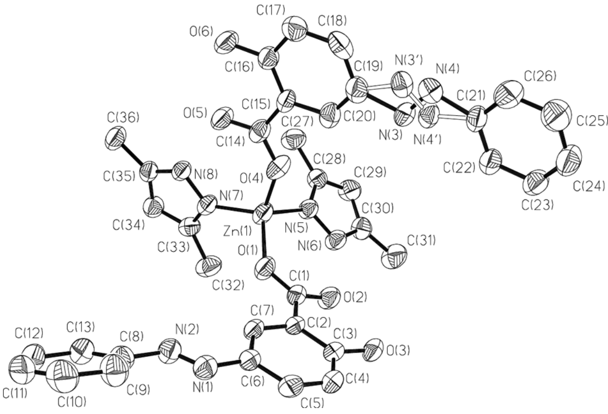


Figure 3. Molecular structure of complex **2** showing the atomic numbering scheme at 30 % ellipsoid probability level.

The difference between complexes **1** and **2** lies in the fact that in **2** bridging pyrazolate ligands do not exist, complex **2** only bears neutral nitrogen ligands. The observance that the hydrogen atoms H6 and H8 in **2** are bound to nitrogen and not to oxygen atoms, is in agreement with the different acidic characters of pyrazole and 2-hydroxy-5-(phenyldiazenyl)benzoic acid,[23] which is also confirmed by the difference electron density map in which the hydrogen atoms are found. The ZnN_2O_2 moiety has coordination distances and angles in the ranges of 1.914(3)–1.997(3) Å and 102.75(12)–114.58(13)°, respectively; thus, the overall coordination arrangement resembles that found in compounds $[Zn(Hpz)_2(Me_3NCH_2CO_2)](ClO_4)_2$[24] and $\{[Zn(CH_3COO)_2(Hpz_2]\cdot CH_3COOH\}$ (Hpz = pyrazole).[23a] Although the distortion in the ZnN_2O_2 moiety is differently oriented in the latter two compounds, the angles around the zinc atoms are in the range of 98.94(19)–117.30(18)° and 95.73(7)–118.34(8)°, respectively. Moreover, complex **2** is not an ionic species, it consists of monocationic zinc(II) complex and carboxylate counterions. In **2**, the non-bonded oxygen atoms, far away enough from the zinc ions with distances 3.312 and 3.338 Å, respectively, are involved in two intramolecular hydrogen bonds [N(6)–H(6)···O(2), and N(8)–H(8)···O(5)] with N–O distances in the range from 2.741(4)–2.790(4) Å and H–O distances of 1.98–1.99 Å. In addition to the intramolecular N–H···O hydrogen bonds, intramolecular O–H···O hydrogen bonds (Table 3) also exist between the phenol OH group and the non-bonded oxygen atoms to produce a $S_1^1(6)$ loop motif, thus the non-bonded oxygen atoms form two hydrogen bonds in bifurcate mode. In compound **2** the ligand L2 [2-hydroxy-5-(phenyldiazenyl)benzoate] adopts *E* conformation about the N=N bond. The two pairs of C–N bond lengths related with the azo groups in the two anions are in the range of 1.431(5)–1.53(11) Å [(N(1)–C(6), 1.431(5) Å; N(2)–C(8), 1.447(5) Å, (N(3)–C(19), 1.51(3) Å; N(4)–C(21), 1.46(5) Å; N(3')–C(19), 1.49(11) Å; N(4')–C(21), 1.53(11) Å]. The differences in bond lengths of the pair of C–N bonds within the two L2 ligands are 0.016(5), 0.05(3), and 0.04(11) Å, respectively For the pair of C–N bonds [N(1)–C(6), 1.431(5) Å; N(2)–C(8), 1.447(5) Å], the N–C bond concerning the azo group and the salicylate moieties [N(1)–C(6)] is the shorter in the two C–N bonds. Whereas the corresponding distances between N(3)–C(19) [1.51(3) Å] and N(4)–C(21) [1.46(5) Å] do not agree with the same results [contrary to the above results herein the N–C bond concerning the azo group and the salicylate moieties N(3)–C(19) is the larger in the two C–N bonds], which may be caused by the fact that N(4) forms an additional intermolecular C–H···N hydrogen bond whereas the N(1) atom is not involved in such interaction. These effects are also reflected in the dihedral angle between the two rings in the same ligand of L2.

The arene rings and the pyrazole rings are almost planar with the largest deviation from mean plane of 0.009 Å. The dihedral angles between two phenyl rings in the ligands L2 are 6.5 (containing N3 and N4) and 30.1° (containing N1 and N2), respectively, which suggest that the ligand L2 containing N3 and N4 is essentially planar but neither is the ligand containing N1 and N2, whereas the dihedral angles between two phenyl rings in two distinct ligands L2 are 64.7, 63.2, 80.1, and 75.8°, respectively. The two pyrazole ligands are almost perpendicular with each other with a dihedral angle of 88.8°. The mononuclear units are connected through C–H···N interactions (with a C–N distance of 3.386 Å, and a N–H distance of 2.498 Å) between 4-CH of the pyrazole molecule and the diazenyl nitrogen atom to form 1D zig-zag chain structure along the *a* axis. The Zn···Zn distance along the chain is 11.073 Å, whereas the Zn···Zn distances between two adjacent chains are 15.249 and 14.740 Å, respectively. The adjacent chains were further connected through C–H···O (between the benzene CH and the phenol OH group with C–O distance of 3.502 Å), CH_3–O (between the 5-CH_3 on pyrazole ring and the OH group with C–O distance of 3.376 Å), and C–H···π (with the separation between the carbon atom in one L2 and the benzene ring in another L2 of 3.614 Å) interactions to form a 3D network structure, which is shown in Figure 4.

3.2.3 Crystal and Molecular Structure of 3

Compound **3** also crystallizes in the triclinic space group $P\bar{1}$. It contains a dinuclear complex of the formula $[Zn_2(\mu\text{-}dmpz)_2(Hdmpz)_2(L3)_2]$, with the zinc atom located at a crystallographic inversion center (Figure 5). Each zinc ion is tetrahedrally coordinated by one oxygen atom of a monodentate L3 ligand and by three nitrogen atoms, of one monodentate pyrazole molecule and two different bridging pyrazolate ligands.

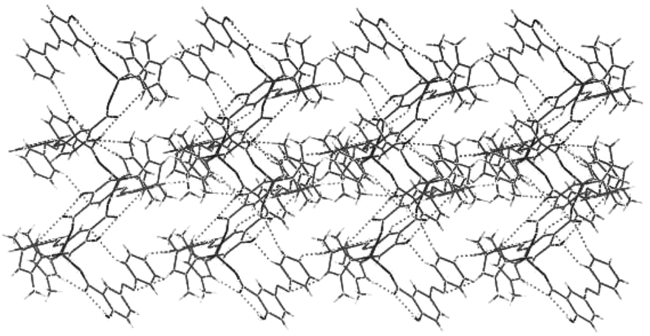


Figure 4. Packing diagram of compound **2** showing the three-dimensional network structure viewed along the *c* axis. Dashed lines represent the intramolecular O–H···O, N–H···O, intermolecular CH–N, and interchain C–H···O, CH_3–O, CH–π interactions.

The latter act in the common *N*,*N*'-exobidentate mode, to keep the two zinc ions at a non-bonding distance of ca. 3.544 Å. The ZnN_3O units has coordination distances and angles in the ranges 1.924(3)–1.997(4) Å and 105.97(15)–112.79(13)°, respectively; the geometrical parameters of this species are similar to those recently reported for the analogous [{Zn(μ-C_2H_5COO)(μ-pz*)(Hpz*)}$_2$][32] (Hpz* = 4-acetyl-3-amino-5-methylpyrazole, Zn···Zn 3.62 Å) and [{Zn(μ-C_2H_5COO)(μ-pz)(Hpz)}$_2$][24] (Hpz = pyrazole, Zn···Zn 3.62 Å) complexes. However, in our species, where the L3 ligands simply substitute the propionate ligands present in [{Zn(μ-C_2H_5COO)(μ-pz*)(Hpz*)}$_2$] or [{Zn(μ-C_2H_5COO)(μ-pz)(Hpz)}$_2$], the zinc ions do not have any bonding interaction with the "second" oxygen atom of each carboxylate, which is found at distance of 3.364 Å from the zinc ion. In **3**, the non-bonded oxygen atoms, which are far away enough from the zinc ions, form an intramolecular hydrogen bond [N4–H4···O2 with N4–O2 and H4–O2 distances of 2.695(5) and 1.89 Å, respectively]. The dihedral angle between the monodentate coordinated pyrazole and the terminal pyrazolate ligands is 74.0°. The angle between the five-membered ring of 1,3-dioxole and the benzene ring in the same L3 molecule amounts to 4.6°. The carboxylate groups are roughly coplanar with the benzene ring of L3 in a dihedral angle of 4.5°. The adjacent dinuclear moieties are connected through CH_3-π (the distance between 5-CH_3 of the pyrazole molecule and the benzene ring amounts to 3.731 Å), C–H···π (including two kinds of C–H···π interactions one is between the 4-CH of pyrazole and the benzene ring with a C···C_g distance of 3.751 Å, the other is between the 4-CH of pyrazole and the pyrazolate ring, in which the corresponding distance is 3.792 Å) to form a 3D network structure when viewed along the *c* axis (Figure 6). There also exist CH_2–π interactions between O–CH_2–O and the pyrazolate ring with a C···C_g distance of ca. 3.641 Å. Furthermore, weak CH_3···CH_3 interactions of van der Waals type are observed between two methyl groups of two adjacent dinuclear moieties with a C···C distance of 2.981 Å and a H···H distance of 2.299 Å. Obviously, these weak interactions contribute to the stabilization of the 3D framework.

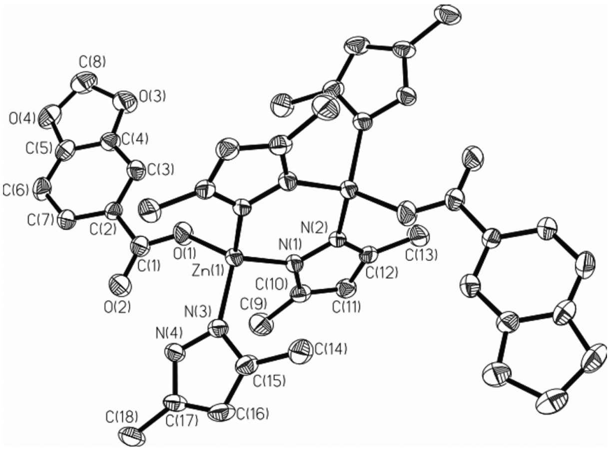


Figure 5. Molecular structure of complex **3** showing the atomic numbering scheme at 30 % ellipsoid probability level.

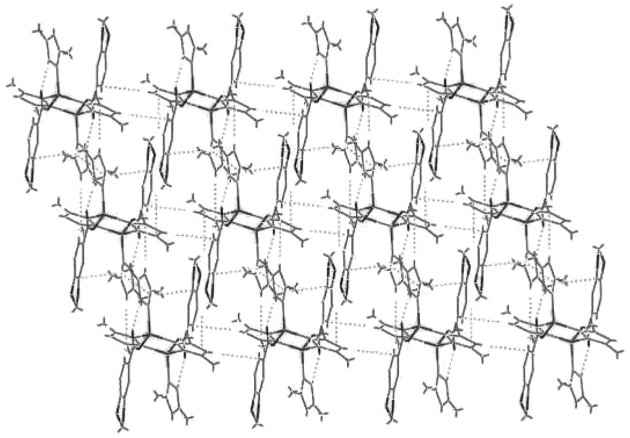


Figure 6. Packing diagram of compound **3** showing the three dimensional network structure viewed from the *c* axis. Dashed lines represent the intermolecular CH–π, CH_2–π, CH_3–π, and intramolecular N–H···O interactions.

3.2.4 Crystal and Molecular Structure of 4

Similar to compounds **2** and **3**, complex **4** of the formula [Zn_2(μ-dmpz)$_2$(Hdmpz)$_2$(L4)$_2$] crystallizes in the triclinic space group $P\bar{1}$ with one formula unit in the unit cell. Compound **4** is also a dinuclear complex consisting of a planar six-membered [Zn(μ-dmpz)$_2$Zn] core and an inversion center located in the center of the six-membered [Zn(μ-dmpz)$_2$Zn] ring (Figure 7). Each zinc ion is tetrahedrally coordinated by two bridging pyrazolate ligands, one monodentate pyrazole molecule, and one monodentate L4 ligand to complete a bonding set of N_3O. The bridging pyrazolate ligands coordinate with the zinc ions in *N*,*N*'-exobidentate fashion, keeping the two zinc ions at a non-bonding distance of ca. 3.543 Å.

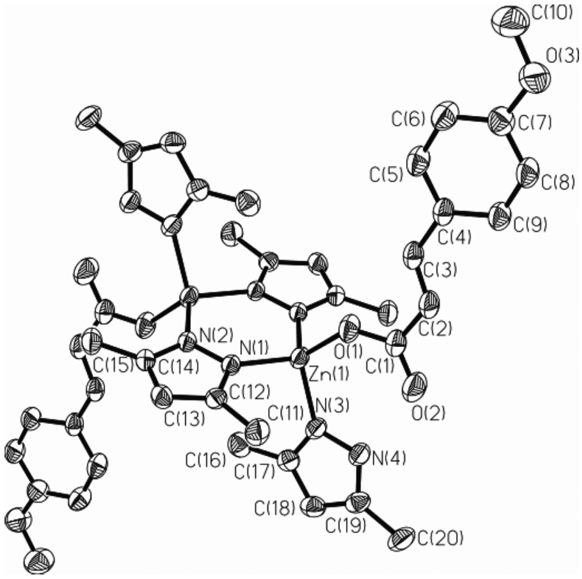


Figure 7. Molecular structure of complex **4** showing the atomic numbering scheme at 30 % ellipsoid probability level.

The ZnN_3O unit has coordination distances and angles in the ranges of 1.923(3)–2.004(3) Å and 103.68(11)–114.13(12)°, respectively; the geometrical parameters of this species are similar to the above results presented in this paper. In this case, the zinc ions do not interact with the non-bonded oxygen atom of each carboxylate function, which is found at a distance of 3.272 Å from the metal. In **4**, the non-bonded oxygen atoms, far away from the zinc ions, are involved in an intramolecular hydrogen bond of N4–H4···O2 with N4–O2 and H4–O2 distances of 2.712(5) Å and 1.93 Å respectively. The dihedral angle between the monodentately coordinated pyrazole molecule and the bridging pyrazolate unit is 108.5°. Ligand L4 adopts *trans* conformation. The adjacent dinuclear moieties are connected through C–H···O (between CH from benzene ring and the non-bonded oxygen atom of L4 with a C–O distance of 3.479 Å), CH_3–O (between the CH_3 of the pyrazole and the methoxyl group of the ligand L4, in which the C–O distance is 3.390 Å) to form a 1D chain structure viewed along the *c* axis. The adjacent chains are further connected through C–H···π (between the 4-CH of pyrazole and the pyrazolate ring) and CH_3–π (between the 3-CH_3 of one pyrazole and the other pyrazole ring) interactions to form a 3D layer network structure, which is shown in Figure 8.

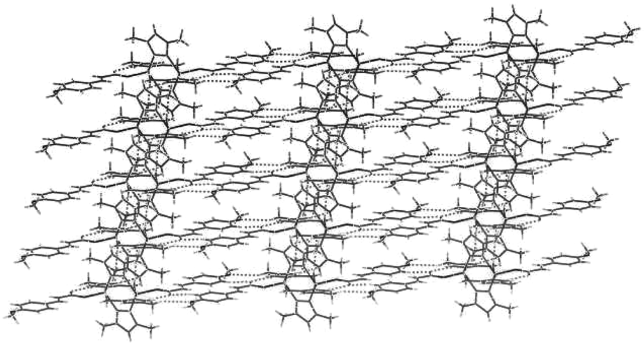


Figure 8. Packing diagram of compound **4** showing the three dimensional layer structure viewed along the *c* axis. Dashed lines represent the intramolecular N–H···O hydrogen bonds and intermolecular C–H···O, CH_3–O, and interchain CH–π, CH_3–π interactions.

3.3 Thermogravimetry (TG)

The thermal decomposition process of the complexes **1**–**4** can be divided into three stages according to the temperature range, which is listed in Table 4. The first weight loss between 153.2 °C and 255.6 °C corresponds to the release of two neutral pyrazoles. The monodentate carboxylate ligands are lost in the second stage in the temperature range of 259.3–418.1 °C. In the third stage the bridging pyrazolates were decomposed with the temperature of 418.8–613.9 °C.

4 Summary

Four zinc complexes with 3,5-dimethylpyrazole and different carboxylate ligands were synthesized and characterized by X-ray diffraction analysis, IR spectroscopy, and thermal analysis. Crystallographic studies demonstrated that in these complexes, the zinc ions are coordinated by 3,5-dimethylpyrazole. In addition, each metal ion is coordinated by carboxylate ligands in a

Table 4. TGA data for complexes **1**–**4**.

	Stage	Temperature range /°C	Weight loss /% obsd.	calcd.	Probable composition of removed molecules
1	I	153.2–251.5	21.96	22.03	two terminal pyrazoles
	II	259.3–410.4	40.98	41.07	two 2-methyl-2-phenoxypropionates
	III	420.1–608.0	21.72	21.79	two bridging pyrazolates
2	I	161.5–250.6	25.91	25.94	two pyrazole molecules
	II	278.2–402.0	65.02	65.13	two 2-hydroxy-5-(phenyldiazenyl)benzoates
3	I	154.6–248.2	22.67	22.76	two terminal pyrazole molecules
	II	282.6–418.1	39.02	39.12	two 3,4-(methylenedioxy)benzoates
	III	430.7–613.9	22.46	22.52	two bridging pyrazolates
4	I	166.2–255.6	22.05	22.13	two terminal pyrazole molecules
	II	260.4–401.6	40.69	40.80	two 3-(4-methoxyphenyl)acrylates
	III	418.8–602.4	21.82	21.90	two bridging pyrazolates

slightly distorted tetrahedral arrangement with the mean *trans* angles in the range 112.3–113.7°. The carboxylate functions act as monodentate ligands. The strong structural propensity toward tetracoordination seems to disfavor the formation of "paddlewheel" dimeric complexes.[34,35] The terminally bonded carboxylate ligands are also involved in the formation of intramolecular hydrogen bonds with the N–H group of 3,5-dimethylpyrazole. It is noteworthy that for compounds **2** and **3**, even though both contain the aromatic acid ligand, the structures of the metal coordination complexes are obviously different, one is mononuclear containing a [Zn(Hdmpz)$_2$] unit, and the other is dinuclear containing a [Zn$_2$(μ-dmpz)$_2$(Hdmpz)$_2$] moiety. The presence of the {Zn(μ-dmpz)}$_2$ core in the species **1**, **3**, and **4** indicates the propensity of pyrazolate ligands to form well-defined dinuclear entities with Zn···Zn contacts in the narrow range of 3.543–3.567 Å. Complexes **1**–**4** have abundant intra- and weak intermolecular interactions (including classical hydrogen bonds, C–H···O, C–H···N, C–H···π, and CH$_3$–π interactions) in their crystals, which lead to the formation and stabilization of these 3D network structures.

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