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Non-covalently bonded 2D–3D metal–organic frameworks from the reactions of Cd(II) and Zn(II) with 3,5-dimethylpyrazole and carboxylate ligands

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ABSTRACT

Seven new complexes, namely $Cd(Hdmpz)_2(L1)_2(1)$ (Hdmpz = 3,5-dimethylpyrazole, L1 = N-phenylmaleamate), Cd(Hdmpz)₄(L2)₂ (2) (L2 = 1,3-benzodioxole-5-carboxylate), $Zn_2(\mu$ -dmpz)₂(Hdmpz)₂(L3)₂ (3) (L3 = 2-chloronicotinate), $Zn(Hdmpz)_2(L4)_2$ (4) (L4 = 3,5-dinitrobenzoate), $Zn(Hdmpz)_2(HL5)_2$ (5) $(HL5 = 5-chlorosalicylate), Cd(Hdmpz)_2(HL6)$ (6) $(HL6 = 5-sulfosalicylate) and Cd_2(Hdmpz)_4(L7)_2$ (7) (L7 = maleate), have been synthesized from the self-assembly of the Zn/Cd ions, 3,5-dimethylpyrazole and carboxylate ligands at room temperature. All the complexes were structurally characterized by different techniques, including elemental analysis, IR spectra, TG and single crystal X-ray diffraction analysis. The X-ray studies suggest that these complexes display mononuclear to dinuclear structures with a tetrahedral geometry around each zinc center, and an octahedral geometry around each cadmium center. The pyrazole ligands in all the compounds except compound **3** are coordinated only in the monodentate fashion by its neutral N group. In **2**, **3**, **4**, **5** and **6**, the carboxylate groups behave as monodentate ligands. The COO⁻ group in **1** and the SO₃⁻ group in **6** both coordinate to the metal in a chelating bidentate fashion. The carboxylates in 7 functioned as a tetradentate bridging ligand. The uncoordinated oxygen atom of the carboxylate group in all of the compounds forms intramolecular hydrogen bonds with the N-H group of the coordinated 3,5-dimethylpyrazole ligand. On the basis of the X-ray crystallographic study, the rich intra- and intermolecular non-covalent interactions, such as classical hydrogen bonds, CH-Cl, CH₃-Cl, Cl···Cl, Cl···O, C-H···O, CH₃···O, C-H··· π , CH₂··· π , CH₃- π , O- π and π - π interactions, are analyzed. The various non-bonding interactions in these compounds are responsible for different structures, such as sheet, 3D network and 3D layer structures. The thermal stabilities of 1-7 were examined and the results show that the complexes seem to be good candidates for novel hybrid inorganic-organic materials with good thermal stability.

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1. Introduction

Metal coordination polymers have attracted great current interest in coordination chemistry because of their intriguing structures and potential as functional materials [1–3]. Studies in this field have been focused on the design and construction of novel coordination frameworks and the relationships between their structures and properties. It is still a great challenge to predict the exact structures and compositions of the assembly products built by coordination bonds and/or hydrogen bonds in crystal engineering. The framework structure of the coordination polymers is primarily dependent upon the coordination preferences of the central metal ions and the functionality of the ligands. Aside from the coordination bonding interactions, hydrogen bonding, π – π stacking interactions, solvent molecules, counterions and the ratio of the metal salt to the organic ligand also influence the formation of the ultimate architectures. Therefore, systematic research on this topic is still important for understanding the roles of these factors in the formation of metal coordination frameworks.

Research on metal carboxylates has always been intriguing in that they play important roles not only in synthetic chemistry, with the essence of the labile coordination modes of the carboxylate group and having architectures such as open and porous frameworks [4,5], but also for their biologic activities [6,7] and physiological effects [8,9]. A versatile carboxylate anion can adopt a wide range of bonding modes, including monodentate, symmetric and asymmetric chelating, and bidentate and monodentate bridging [10].





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Pyrazole and its derivatives have been widely employed in polypyrazolylborates to stabilize a variety of organometallic and coordination compounds [11,12]. Up until now, a variety of complexes containing pyrazole (Hdmpz) ligands have been synthesized and employed in coordination chemistry or organometallic chemistry [13–15]. Many complexes with simple pyrazole ligand, both in the terminal as well as the bridging mode, are also available [16–18], but complexes with the presence of both carboxylic acids and pyrazole derivatives are not very common, except for some recently reported examples in the literature [19]. We have been working on coordination compounds with mixed carboxylate and pyrazole derivative ligands [20]. The pyrazole ligand and the carboxylate ligand appear to possess similar steric requirements and, to a certain extent, similar bonding capabilities. In order to understand the influence of the carboxylate residue in the formation of new complexes and the role weak non-covalent interactions play in forming the final supramolecular frameworks, we selected carboxylic acids bearing the NH, CONH, OH, Cl, NO₂ and SO₃H units, which are good groups for forming hydrogen bonds and some other non-bonding interactions [21]. Thus, in the following we report the synthesis, structural characterization and thermal behavior of Zn and Cd complexes of a combination of 3,5-dimethylpyrazole (Hdmpz) and different carboxylate ligands (Scheme 1), namely $Cd(Hdmpz)_2(L1)_2$ (1) (Hdmpz = 3,5-dimethylpyrazole, L1 = N-phenylmaleamate), Cd(Hdmpz)₄(L2)₂ (**2**) (L2 = 1,3-benzodioxole-5-carboxylate), $Zn_2(\mu$ -dmpz)₂(Hdmpz)₂(L3)₂ (**3**) (L3 = 2chloronicotinate), Zn(Hdmpz)₂(L4)₂ (4) (L4 = 3,5-dinitrobenzoate), $Zn(Hdmpz)_2(HL5)_2$ (**5**) (HL5 = 5-chlorosalicylate), $Cd(Hdmpz)_2(-$ HL6) (6) (HL6 = 5-sulfosalicylate) and $Cd_2(Hdmpz)_4(L7)_2$ (7) (L7 = maleate).

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 they were used without further purification. The FT-IR spectra were recorded from KBr pellets in the range 4000–400 cm⁻¹ on a Mattson Alpha-Centauri spectrometer. Microanalytical (C, H, N and S) 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 N₂ atmosphere between room temperature and 800 °C (heating rate10 °C min⁻¹) using Al crucibles.

2.2. Synthesis of the complexes

2.2.1. Synthesis of $Cd(Hdmpz)_2(L1)_2$ (1)

A solution of Cd(CH₃COO)₂·2H₂O (0.0270 g, 0.1 mmol) in 6 mL of MeOH was added to a MeOH solution (12 mL) containing Hdmpz (0.0192 g, 0.2 mmol) and N-phenylmaleamic acid (HL1) (0.0765 g, 0.4 mmol), under continuous stirring. The solution was stirred for about 2 h at room temperature, the solution became turbid, then a few drops of conc. ammonia were added until the solution became completely clear. The clear solution was filtered into a test tube and after several days colorless crystals formed, which were filtered off, washed with MeOH and dried under vacuum to afford 0.0510 g of the product. Yield: 74.45% (Based on Hdmpz). Elemental analysis performed on crystals exposed to the atmosphere: Calc. for C₃₀H₃₂CdN₆O₆ (685.02): C, 52.55; H, 4.67; N, 12.26. Found: C, 52.49; H, 4.61; N, 12.22%. IR (KBr disc, cm^{-1}): 3421w ($v_{as}(NH)$), 3267m (v_s(NH)), 3097m, 2986m, 2876m, 1662s (C=O), 1623s (v_{2s}(-COO)), 1494s (v_s(COO)), 1446m, 1390m, 1333m, 1276m, 1235m, 1171m, 1085m, 1024m, 969m, 888m, 814m, 756m, 712m, 663m, 619m.

2.2.2. Synthesis of $Cd(Hdmpz)_4(L2)_2(\mathbf{2})$

A solution of Cd(CH₃COO)₂·2H₂O (0.0270 g, 0.1 mmol) in 6 mL of MeOH was added to an EtOH solution (8 mL) containing Hdmpz (0.0192 g, 0.2 mmol) and 1,3-benzodioxole-5-carboxylic acid (HL2) (0.0664 g, 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 a test tube and after several days colorless crystals were formed, which were filtered off, washed with EtOH and dried under vacuum to afford 0.0330 g of the product. Yield 79.79% (based on Hdmpz). Elemental analysis performed on crystals exposed to the atmosphere: Calc for C₃₆H₄₂CdN₈O₈ (827.18): C, 52.23; H, 5.08; N, 13.54. Found: C, 52.19; H, 4.99; N, 13.45%. IR (KBr): 3417w (vas(NH)), 3243w (vs(-NH)), 2932m, 2668m, 2554m, 2519m, 2335m, 1716m, 1623s (v_{as}(-COO)), 1575m, 1534m, 1476m, 1440m, 1415s (v_s(COO)), 1372m, 1313m, 1258m, 1155m, 1095m, 1027m, 888m, 849m, 806m, 767m, 668m, 622m.

2.2.3. Synthesis of $Zn_2(\mu - dmpz)_2(Hdmpz)_2(L3)_2$ (3)

A solution of $Zn(CH_3COO)_2 \cdot 2H_2O$ (0.0220 g, 0.1 mmol) in 5 mL of EtOH was added to a MeOH solution (10 mL) containing Hdmpz (0.0192 g, 0.2 mmol) and 2-chloronicotinic acid (HL3) (0.0628 g,



Scheme 1. The ligands used in this paper.

0.4 mmol), under continuous stirring. The solution was stirred for about 2 h at room temperature, a small amount of precipitate formed, then a few drops of conc. ammonia were added until the precipitate dissolved completely. The clear solution was filtered into a test tube and after several days colorless block crystals formed, which were filtered off, washed with MeOH and dried under vacuum to afford 0.0320 g of the product. Yield: 77.45% (Based on Hdmpz). Elemental analysis performed on crystals exposed to the atmosphere: Calc. for $C_{32}H_{36}Cl_2N_{10}O_4Zn_2$ (826.35): C, 46.47; H, 4.36; N, 16.94. Found: C, 46.41; H, 4.27; N, 16.89%. IR (KBr disc, cm⁻¹): 3435w (v_{as} (NH)), 3269w (v_{s} (NH)), 3146m, 3062m, 2953m, 2874m, 1617s (v_{as} (COO)), 1582m, 1551m, 1503m, 1456m, 1426s (v_{s} (COO)), 1375m, 1293m, 1235m, 1178m, 1064m, 1013m, 969m, 856m, 798m, 753m, 698m, 647m, 610m.

2.2.4. Synthesis of $Zn(Hdmpz)_2(L4)_2$ (4)

A solution of Zn(CH₃COO)₂·2H₂O (0.0220 g, 0.1 mmol) in 5 mL of EtOH was added to a MeOH solution (12 mL) containing Hdmpz (0.0192 g, 0.2 mmol) and 3,5-dinitrobenzoic acid (HL4) (0.0848 g, 0.4 mmol), under continuous stirring. The solution was stirred for about 2 h at room temperature, the solution became turbid, then a few drops of conc. ammonia were added until the solution became completely clear. The clear solution was filtered into a test tube and after several days colorless crystals formed, which were filtered off, washed with EtOH and dried under vacuum to afford 0.0540 g of the product. Yield: 79.43% (Based on Hdmpz). Elemental analysis performed on crystals exposed to the atmosphere: Calc. for C₂₄H₂₂N₈O₁₂Zn (679.87): C, 42.36; H, 3.24; N, 16.47. Found: C, 42.29; H, 3.18; N, 16.45%. IR (KBr disc, cm⁻¹): 3462br (v_{as}(NH)), 3273m (v_s(NH)), 3154m, 3076m, 2993m, 2975w, 2871m, 1621s (v_{as}(COO)), 1583m, 1525s (v_{as}(NO₂)), 1464m, 1422s (v_s(COO)), 1381m, 1319s (v_s(NO₂)), 1283m, 1242m, 1173m, 1112m, 1066m, 975m, 891m, 843m, 790m, 738m, 677m, 636m, 604m.

2.2.5. Synthesis of Zn(Hdmpz)₂(HL5)₂ (5)

A solution of $Zn(CH_3COO)_2 \cdot 2H_2O$ (0.0220 g, 0.1 mmol) in 5 mL of EtOH was added to an EtOH solution (4 mL) containing Hdmpz (0.0192 g, 0.2 mmol) and 5-chlorosalicylic acid (H_2L5) (0.0690 g, 0.0000 g)0.4 mmol), under continuous stirring. The solution was stirred for about 2 h at room temperature, the solution became turbid, then a few drops of conc. ammonia were added until the solution became completely clear. The clear solution was filtered into a test tube and after several days colorless crystals formed, which were filtered off, washed with EtOH and dried under vacuum to afford 0.0490 g of the product. Yield: 81.57% (Based on Hdmpz). Elemental analysis performed on crystals exposed to the atmosphere: Calc. for C₂₄H₂₄Cl₂N₄O₆Zn (600.74): C, 47.94; H, 3.99; N, 9.32. Found: C, 47.89; H, 3.92; N, 9.22%. IR (KBr disc, cm⁻¹): 3497m (v_{as}(NH)), 3286m (v_s(NH)), 3089m, 2947m, 2869m, 1604s (v_{as}(COO)), 1553m, 1400s (v_s(COO)), 1331m, 1274m, 1211m, 1167m, 1075m, 986m, 912m, 842m, 768m, 716m, 668m, 605m.

2.2.6. Synthesis of Cd(Hdmpz)₂(HL6) (6)

A solution of Cd(CH₃COO)₂·2H₂O (0.0270 g, 0.1 mmol) in 6 mL of MeOH was added to a MeOH solution (7 mL) containing Hdmpz (0.0192 g, 0.2 mmol) and 5-sulfosalicylic acid dihydrate (H₃L6) (0.1016 g, 0.4 mmol), under continuous stirring. The solution was stirred for about 2 h at room temperature, the solution became turbid, then a few drops of conc. ammonia were added until the solution became completely clear. The clear solution was filtered into a test tube and after several days colorless block crystals formed, which were filtered off, washed with MeOH and dried under vacuum to afford 0.0450 g of the product. Yield: 86.40% (Based on Hdmpz). Elemental analysis performed on crystals exposed to the atmosphere: Calc. for $C_{17}H_{20}CdN_4O_6S$ (520.83): C, 39.17; H, 3.84; N, 10.75; S, 6.14. Found: C, 39.13; H, 3.78; N, 10.67; S, 6.07%. IR

(KBr disc, cm⁻¹): 3584s (ν (OH)), 3466m (ν _{as}(NH)), 3257m (ν _s(NH)), 3139m, 2951m, 2867m, 1669s (ν (C=O)), 1539m, 1488m, 1361m, 1297s (ν (C=O)), 1267m, 1226m, 1165m, 1093m, 1036m, 936v, 889m, 823v, 749m, 677m, 611v.

2.2.7. Synthesis of $Cd_2(Hdmpz)_4(L7)_2$ (7)

A solution of Cd(CH₃COO)₂·2H₂O (0.0270 g, 0.1 mmol) in 6 mL of MeOH was added to a MeOH solution (10 mL) containing Hdmpz (0.0192 g, 0.2 mmol) and maleic acid (H₂L7) (0.0232 g, 0.2 mmol), under continuous stirring. The solution was stirred for 2 h at room temperature, the solution became turbid, then a few drops of conc. ammonia were added until the solution became clear. The clear solution was filtered into a test tube and after several days colorless block crystals formed, which were filtered off, washed with MeOH, and dried under vacuum to afford 0.0320 g of the product. Yield: 76.42% (based on Hdmpz). Elemental analysis performed on crystals exposed to the atmosphere: Calc. for C28H36Cd2N8O8 (837.45): C, 40.12; H, 4.30; N, 13.37. Found: C, 40.06; H, 4.26; N, 13.31%. IR (KBr disk, cm^{-1}): 3456m ($v_{as}(NH)$), 3254w ($v_{s}(NH)$), 3161w, 3067w, 2983m, 2864m, 2575m, 2519m, 2328m, 1625m, 1570s (v_{as}(COO⁻)) 1547m, 1513m, 1463m, 1416m, 1383s (v_s(-COO⁻)), 1275m, 1229m, 1163w, 1120w, 1047m, 1006m, 945m, 888m, 834m, 791w, 714m, 692m, 644m, 604m.

2.3. X-ray crystallography

Suitable crystals were mounted on a glass fiber on 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 SMART and SAINT software [22]. 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 the SHELXTL package [23]. Hydrogen atom positions for all of the structures were found in a difference map. Further details of the structural analysis are summarized in Tables 1 and 2. Selected bond lengths and angles for complexes **1–7** are listed in Table 3, and the relevant hydrogen bond parameters are provided in Table 4.

3. Results and discussion

3.1. Preparation and general characterization

Complexes **1–7** were prepared in MeOH or EtOH at room temperature via the combination of the metalate acetate, Hdmpz, and the corresponding carboxylic acid. The corresponding crystals suitable for X-ray crystallography analysis were grown upon addition of a few drops of conc. ammonia solution, giving yields of 74.45–86.40%.

During the reaction, the acetate ligand has been substituted by the corresponding carboxylate ions. In 1, 2, 4, 5, 6 and 7 only the pyrazole group exists, while 3 possesses both the pyrazole and the pyrazolate units. These compounds are not soluble in most common solvents. The infrared spectra of 1-7 were consistent with their molecular compositions. Compound 1 contains a carboxyl group with the chelating bidentate coordination mode, with $v_{as}(CO_2$) and $v_s(CO_2)$ bands at 1623 and 1494 cm⁻¹ respectively (with a Δ value of 129 cm⁻¹). The IR spectra of **2–5** display characteristic carboxylate bands in the range 1604–1623 cm⁻¹ for $v_{as}(CO_2)$ and 1400–1426 cm⁻¹ for $v_s(CO_2)$ [24]. The frequency differences between $v_{as}(CO_2)$ and $v_s(CO_2)$ are in the range 191–208 cm⁻¹ for compounds 2–5. This suggests a unidentate coordination mode for the carboxylate ligands infs compounds 2-5. Compound 6 displays strong IR peaks for COOH groups. There are coordinated neutral Hmdpz ligands in all of the seven compounds, which is further

Table 1

Summar	v of	X-ray	crysta	llographic	data	for co	mplexes	1-3.

	1	2	3
Formula	$C_{30}H_{32}CdN_6O_6$	C ₃₆ H ₄₂ CdN ₈ O ₈	$C_{32}H_{36}Cl_2N_{10}O_4Zn_2$
Formula weight	685.02	827.18	826.35
T (K)	298(2)	298(2)	298(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	monoclinic	triclinic	monoclinic
Space group	C2	ΡĪ	P2(1)/n
a (Å)	18.4619(17)	9.0250(8)	8.6544(8)
b (Å)	7.9510(5)	10.6849(9)	14.5510(16)
c (Å)	12.0791(11)	10.9631(11)	14.6941(14)
α (°)	90	74.4380(10)	90
β (°)	120.123(2)	85.208(2)	91.9380(10)
γ (°)	90	74.6380(10)	90
V (Å ³)	1533.6(2)	981.95(16)	1849.4(3)
Z	2	1	2
$D_{\text{calc.}}$ (Mg/m ³)	1.483	1.399	1.484
Absorption coefficient, mm ⁻¹	0.764	0.615	1.492
F(000)	700	426	848
Crystal size (mm)	$0.40 \times 0.39 \times 0.32$	$0.45 \times 0.37 \times 0.22$	$0.25\times0.19\times0.12$
θ (°)	2.55-25.00	2.34-25.02	2.69-25.02
Limiting indices	$-21\leqslant h\leqslant 21,-8\leqslant k\leqslant 9,$	$-10\leqslant h\leqslant 10,-12\leqslant k\leqslant 12,$	$-10\leqslant h\leqslant 10$, $-17\leqslant k\leqslant 16$,
	$-14 \leqslant l \leqslant 10$	$-13 \leqslant l \leqslant 9$	$-17 \leq l \leq 13$
Reflections collected	3830	4941	9311
Reflections independent (R_{int})	2130 (0.0292)	3418 (0.0236)	3253 (0.0661)
Goodness-of-fit (GOF) on F^2	1.058	1.070	0.893
R indices $[I > 2\sigma(I)]$	0.0204, 0.0519	0.0308, 0.0763	0.0473, 0.0955
R indices (all data)	0.0205, 0.0519	0.0327, 0.0786	0.0898, 0.1106
Largest difference in peak and hole $(e \text{ Å}^{-3})$	0.259 and -0.302	0.377 and -0.652	0.406 and -0.302

Table 2

Summary of X-ray crystallographic data for complexes 4-7.

	4	5	6	7
Formula	C ₂₄ H ₂₂ N ₈ O ₁₂ Zn	$C_{24}H_{24}Cl_2N_4O_6Zn$	C ₁₇ H ₂₀ CdN ₄ O ₆ S	C ₂₈ H ₃₆ Cd ₂ N ₈ O ₈
Formula weight	679.87	600.74	520.83	837.45
Т (К)	298(2)	298(2)	298(2)	298(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Crystal system	triclinic	triclinic	orthorhombic	triclinic
Space group	ΡĪ	ΡĪ	Cmc2(1)	ΡĪ
a (Å)	11.4450(10)	10.236(3)	14.7358(13)	8.2815(7)
b (Å)	11.6569(11)	11.906(3)	9.3354(11)	13.8825(14)
c (Å)	12.4901(13)	12.380(3)	14.3430(12)	15.7906(16)
α (°)	77.755(2)	115.277(3)	90	90.8640(10)
β (°)	78.377(2)	98.918(3)	90	92.9230(10)
γ (°)	61.9900(10)	92.119(3)	90	94.187(2)
V (Å ³)	1427.6(2)	1338.8(6)	1973.1(3)	1807.9(3)
Ζ	2	2	4	2
$D_{\text{calc.}}$ (Mg/m ³)	1.582	1.490	1.753	1.538
Absorption coefficient (mm ⁻¹)	0.938	1.162	1.256	1.230
F(000)	696	616	1048	840
Crystal size (mm)	$0.45 \times 0.41 \times 0.32$	$0.49 \times 0.41 \times 0.39$	$0.41 \times 0.40 \times 0.40$	$0.34 \times 0.12 \times 0.10$
θ (°)	2.37-25.02	2.62-25.02	2.58-24.99	2.47-25.02
Limiting indices	$-11\leqslant h\leqslant 13$, $-13\leqslant k\leqslant 13$,	$-12\leqslant h\leqslant 12$, $-14\leqslant k\leqslant 11$,	$-17\leqslant h\leqslant 17$, $-8\leqslant k\leqslant 11$,	$-9\leqslant h\leqslant 9$, $-16\leqslant k\leqslant 11$,
	$-10 \leqslant l \leqslant 14$	$-10 \leqslant l \leqslant 14$	$-14 \leqslant l \leqslant 17$	$-18 \leqslant l \leqslant 18$
Reflections collected	7173	6680	4745	8521
Reflections independent (R_{int})	4942 (0.0237)	4627 (0.0246)	1728 (0.0354)	6150 (0.0540)
Goodness-of-fit (GOF) on F^2	1.054	1.023	1.076	1.050
<i>R</i> indices $[I > 2\sigma(I)]$	0.0378, 0.0874	0.0389, 0.0964	0.0198, 0.0486	0.0817, 0.1935
R indices (all data)	0.0547, 0.0968	0.0597, 0.1118	0.0204, 0.0490	0.1573, 0.2495
Largest difference in peak and hole (e $Å^{-3}$)	0.243 and -0.461	0.413 and -0.419	0.412 and -0.352	2.647 and –1.859

confirmed by the presence of characteristic NH bands in the region $3500-3200 \text{ cm}^{-1}$ [25]. Weak absorptions observed in the range $3000-2800 \text{ cm}^{-1}$ can be attributed to aromatic C-H and the ole-finic CH group of the anions in **1** and **7**.

3.2. Crystal structure description

3.2.1. Crystal and molecular structure of $Cd(Hdmpz)_2(L1)_2$ (1)

Compound **1** was prepared by the reaction of $Cd(CH_3COO)_2 \cdot 2H_2$. O, N-phenylmaleamic acid (HL1) and Hdmpz in MeOH solvent in a ratio of 1:2:4, yielding pure Cd(Hdmpz)₂(L1)₂ upon addition of a few drops of conc. ammonia solution. The structural determination revealed that Cd, L1 and Hdmpz are present in a 1:2:2 ratio in the molecular complex **1**, and the asymmetric unit is shown in Fig. 1. Complex **1** crystallizes as monoclinic colorless crystals in the space group C2 with two formula units in the unit cell. Each Cd ion is octahedrally coordinated by four oxygen atoms of two L1 ligands and by two nitrogen atoms of two different monodentate pyrazole ligands, generating a distorted trigonal prismatic geometry (Fig. 1). Herein the L1 ligand is coordinated to the Cd ion in a chelating

Table 3

Selected bond lengths [Å] and angles [°] for 1-7.

1			
	2 259(2)	$C_{1}(1) O(1)$	2 270(2)
Cd(1) = N(1)	2.238(2)	C(1) = O(1)	2.379(2)
C(1) = O(2)	2.579(2) 1 242(4)	O(1) - C(0)	1.207(5)
U(2) - U(0)	1.245(4)	O(3) - C(9)	1.251(4)
N(1) = Cd(1) = N(1) # 1	108.4(1)	N(1) - Cd(1) - O(1)	96.86(8)
N(1)#1-Cd(1)-O(1)	102.31(8)	N(1) - Cd(1) - O(2)	89.30(8)
O(1)#1-Cd(1)-O(2)	98.17 (8)	O(2)-Cd(1)-O(2)#1	81.8(1)
2			
Cd(1) - O(1)	2.348(2)	Cd(1) - N(1)	2.364(2)
Cd(1) - N(3)	2.373(2)	O(1) - C(11)	1.247(3)
O(2) - C(11)	1 269(3)	O(3) - C(14)	1 382(3)
O(3) - C(18)	1.233(3) 1.421(4)	O(4) - C(15)	1 378(3)
O(4) - C(18)	1.412(4)	O(1) #1 - Cd(1) - N(1)	90.05(7)
O(1) Cd(1) N(1)	80.05(7)	O(1)#1 Cd(1) N(2)	00.00(7)
O(1) - Cd(1) - N(1)	89.93(7)	N(1) = Cd(1) = N(3)	90.89(7)
N(1) = Cd(1) = N(3)	03.11(7)	N(1) = Cu(1) = N(3)	07.44(7)
N(1) # 1 - Cu(1) - N(3)	92.50(7)		
3			
Zn(1)-O(1)	1.947(3)	Zn(1)-N(3)	1.956(3)
Zn(1)-N(2)	1.964(4)	Zn(1)-N(4)	2.010(4)
O(1) - C(1)	1.242(5)	O(2) - C(1)	1.221(5)
O(1) - Zn(1) - N(3)	106.7(1)	O(1) - Zn(1) - N(2)	109.6(1)
N(3) - Zn(1) - N(2)	112.9(1)	O(1) - Zn(1) - N(4)	109.6(1)
N(3) - Zn(1) - N(4)	107.5(1)	N(2) - Zn(1) - N(4)	1105(1)
	107.5(1)	(2) 2n(1) n(1)	110.5(1)
4			
Zn(1)-O(7)	1.951(2)	Zn(1) - O(1)	1.951(2)
Zn(1)-N(1)	1.983(2)	Zn(1) - N(3)	1.989(2)
O(1)-C(11)	1.278(3)	O(2)-C(11)	1.232(3)
O(7)-C(18)	1.275(3)	O(8)-C(18)	1.230(3)
O(7) - Zn(1) - O(1)	95.81(9)	O(7)vZn(1)-N(1)	112.48(9)
O(1)-Zn(1)-N(1)	110.24(9)	O(7) - Zn(1) - N(3)	112.21(9)
O(1)-Zn(1)-N(3)	117.00(9)	N(1)-Zn(1)-N(3)	108.71(9)
F			
\mathbf{J}	1.025(2)	$7_{-}(1) O(4)$	1 022(2)
$Z\Pi(1) = O(1)$	1.925(2)	ZII(1) = O(4)	1.933(2)
Zn(1) - N(1)	1.977(3)	Zn(1) - N(3)	2.004(3)
O(1) - C(11)	1.275(4)	O(2) - C(11)	1.247(4)
O(3) - C(13)	1.357(4)	O(4) - C(18)	1.268(3)
O(5) - C(18)	1.250(4)	O(6) - C(20)	1.337(4)
O(1) - Zn(1) - O(4)	102.0(1)	O(1) - Zn(1) - N(1)	113.6(1)
O(4) - Zn(1) - N(1)	113.5(1)	O(1) - Zn(1) - N(3)	105.4(1)
O(4) - Zn(1) - N(3)	117.6(1)	N(1)-Zn(1)-N(3)	104.8(1)
6			
Cd(1) = N(1)	2278(3)	Cd(1)=O(1)#2	2 293(3)
Cd(1) - O(3)#3	2.276(3)	Cd(1) = O(4)	2.233(3)
O(1) - C(6)	1.455(5)	O(2) - C(6)	1.269(5)
O(2) = C(0)	1.240(5)	O(2) = C(0)	1.203(3) 1.452(3)
O(5) - C(8)	1.349(3)	V(4)=3(1)	1.433(2)
U(3)=3(1)	102 5 6 (8)	N(1) # 1 - Cd(1) - N(1)	110.2(1)
N(1)#1-Cd(1)-O(1)#2	102.56(8)	N(1) # 1 - Cd(1) - O(3) # 3	84.09(8)
N(1)#1-Cd(1)-O(4)#1	90.99(9)	O(1)#2-Ca (1) -O(4)#1	87.02(9)
U(3)#3-Ca(1)-U(4)#1	81.07(8)		
7			
Cd(1)-O(4)#1	2.363(9)	Cd(1)-O(3)	2.365(8)
Cd(1)-O(5)	2.371(9)	Cd(1) - N(3)	2.407(12)
Cd(1) - N(1)	2.41(1)	Cd(1) - O(1)	2.437(9)
Cd(2) = O(7)	2.33(1)	Cd(2) - N(5)	2.36(1)
Cd(2) = O(8)#2	2.36(1)	Cd(2) = O(2)	2,383(9)
Cd(2) = N(7)	2.44(1)	Cd(2) = O(6)	2.44(1)
O(1) - C(1)	131(2)	O(2) - C(1)	128(2)
O(3) - C(4)	1.31(2) 1 31(1)	O(4) - C(4)	1.28(1)
O(5) - C(5)	1.31(1)	O(6) - C(5)	1.20(1)
O(7) - C(8)	1 22(2)	O(8) - C(8)	1 29(2)
O(4) = 1 - Cd(1) - O(2)	1.32(2) 88 7(2)	$O(4) \pm 1 - Cd(1) = O(5)$	80 1(2)
O(3) = Cd(1) = O(3)	86 5(2)	O(4) # 1 - Cu(1) - U(3)	05.4(3) 05.6(A)
O(3) = Cu(1) = O(3)	00.3(3)	O(4) # 1 - Cu(1) - IN(3)	93.0(4)
O(4) = I - O(1) - IN(1)	90.1(4)	U(3) = U(1) = IV(3)	δδ.0(4)
U(3) - U(1) - N(1)	93.1(4)	N(3) = Ca(1) = N(1)	91.8(4)
U(3) - Ca(1) - U(1)	83.5(3)	U(5) - Ca(1) - U(1)	93.3(3)
N(3) - Cd(1) - O(1)	92.4(4)	N(1) - Cd(1) - O(1)	87.0(4)
U(7) - Cd(2) - O(8) #2	93.3(4)	N(5)-Cd(2)-O(8)#2	92.4(4)
O(7)-Cd(2)-O(2)	85.4(4)	N(5)-Cd(2)-O(2)	88.3(4)
O(8)#2-Cd(2)-O(2)	86.2(3)	O(7)-Cd(2)-N(7)	94.3(4)
N(5)-Cd(2)-N(7)	92.0(4)	O(8)#2-Cd(2)-N(7)	93.8(4)

Symmetry transformations used to generate equivalent atoms for 1: #1 -x + 1, y, -z.

Symmetry transformations used to generate equivalent atoms for **2**: #1 -x, -y + 2, -z + 1.

Symmetry transformations used to generate equivalent atoms for **6**: #1 - x + 1, *y*, *z*; #2 - x + 1, -y + 1, z + 1/2; #3 x, y - 1, *z*.

Symmetry transformations used to generate equivalent atoms for **7**: #1 - x + 1, -y + 2, -z; #2 - x + 1, -y + 2, -z + 1.

Table 4	
Hydrogen bond distances and angles in the studied structures of 1–7.	

	D-H···A	d(D-H) [Å]	d(H…A) [Å]	d(D…A) [Å]	<(DHA) [°]
	1	-()[]	-()[]	-()[]	()[]
	I = N(3) - H(3) - O(1) = 2	0.86	2.12	2 942(3)	161 1
	$N(2)-H(2)\cdots O(3)$	0.86	1.99	2.815(3)	161.2
	2				
	- N(2)-H(2)···O(2)#1	0.86	1.95	2.751(3)	154.9
	$N(4)-H(4)\cdots O(2)$	0.86	1.93	2.749(3)	159.1
	3				
	$N(5)-H(5)\cdots O(2)$	0.86	1.88	2.693(5)	156.5
	4				
	$N(4)-H(4)\cdots O(2)$	0.86	2.09	2.838(3)	145.6
	$N(2)-H(2)\cdots O(8)$	0.86	1.97	2.756(3)	150.9
	5				
	O(6)−H(6)···O(5)	0.82	1.83	2.555(3)	147.1
	$O(3)-H(3)\cdots O(2)$	0.82	1.88	2.603(3)	145.7
	$N(4)-H(4)\cdot \cdot \cdot O(5)$	0.86	2.07	2.821(4)	145.3
	$N(2)-H(2)\cdots O(2)$	0.86	1.96	2.767(4)	154.9
	6				
	$O(2)-H(2A)\cdots O(3)$	0.82	1.71	2.485(5)	156.1
	$N(2)-H(2)\cdots O(2)#2$	0.86	2.40	2.929(3)	120.2
	N(2)−H(2)···O(5)#6	0.86	2.15	2.956(4)	155.0
	7				
	$N(8)-H(8)\cdots O(7)#2$	0.86	1.99	2.809(15)	159.4
	$N(6)-H(6)\cdot \cdot \cdot O(1)$	0.86	2.16	2.882(16)	141.6
	$N(4)-H(4)\cdots O(6)$	0.86	2.12	2.870(15)	146.1
	$N(2)-H(2)\cdots O(3)#1$	0.86	1.97	2.797(16)	161.8
_					

Symmetry transformations used to generate equivalent atoms for 1: #2 -x + 1/2, y - 1/2, -z.

Symmetry transformations used to generate equivalent atoms for **2**: #1 - x, -y + 2, -z + 1.

Symmetry transformations used to generate equivalent atoms for **6**: #1 - x + 1, *y*, *z*; #2 - x + 1, -y + 1, z + 1/2; #3 x, y - 1, *z*; #4 - x + 1, -y + 1, z - 1/2; #5 x, y + 1, *z*; #6 - x + 1, -y, z + 1/2.

Symmetry transformations used to generate equivalent atoms for **7**: #1 -x + 1, -y + 2, -z; #2 -x + 1, -y + 2, -z + 1.

bidentate fashion, whilst the pyrazole ligand is coordinated only in the monodentate terminal fashion with its neutral nitrogen group bonding to the Cd ion. The coordination mode of Cd is similar to the reported compounds $[Cd(La)_2(Hdmpz)_2]$ where $La = R-C_6H_{4-}$ COO- [R = H, 2-Cl, 4-OH, 2-OH] [26].

The location of H2 in **1**, bound to nitrogen and not to oxygen atoms, is consistent with the different acidic characters of pyrazole and N-phenylmaleamic acid [27], and is also confirmed by the difference electron density map with which to find the H atoms. The Cd–N and Cd–O distances are 2.258(2) and 2.379(2) Å, respectively, indicating that the cadmium atom belongs to the inner coordination sphere [28]. The angles around the Cd atom range from $55.13(7)^{\circ}$ to $153.71(8)^{\circ}$.

Moreover **1** is not an ionic species consisting of a monocationic Cd(II) complex and carboxylate counterions. In **1**, the oxygen atom



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

of the CONH moiety of L1, far from the Cd ion at a distance of 4.585 Å, is involved in intramolecular hydrogen bonding (N(2)– $H(2)\cdots O(3)$) with an N–O distance of 2.815(3) Å and H–O distance of 1.99 Å.

The root mean square (rms) deviations of the phenyl ring in the anion with the C10–C15 atoms and the pyrazole ring with N1, and N2 atoms are 0.0036 and 0.0059 Å, respectively, and the above two rings intersected at an angle of 138.3°. The dihedral angle between the phenyl ring and the plane defined by the amide group (– NHCO–) in the same anion is 149.6° (for the amide group H1– N1–C4=O3). The conformations of the N–H and C=O bonds in the amide segment of the structure are *anti* to each other. Further, the conformation of the amide O atom is anti to the H atom attached to the adjacent C atom (Fig. 1).

The C(7)=C(8) bond distance (1.325(4) Å) is appropriate for a simple C=C double bond, due to the significant non-coplanarity of the carboxyl group and the olefinic group (the plane defined by the carboxylate group is almost perpendicular to the plane defined by the amide and the olefinic groups, which is different from the crystal structure of N-phenylmaleamic acid [29]), but the C(7)=C(8) bond distance is somewhat shortened compared with the corresponding values (1.335 and 1.344 Å) in the neutral molecule [29]. The C–O bond distance for O(1)–C(6) (1.267(3) Å) is somewhat longer than the O(2)–C(6) (1.243(4) Å) bond, and the reason for this may be that O(1) is involved in a stronger H-bond than O(2) (Table 4).

The mononuclear units are linked together in a head to tail fashion via the N-H···O (N(3)-H(3)···O(1)#2, 2.942(3) Å, 161.1°, #2 -x + 1/2, y - 1/2, -z) hydrogen bond and C-H···O associations between the same olefinic CH group of the anion and one coordinated O atom of the carboxylate group and the O atom of the CONH group, with C-O distances of 3.424-3.461 Å, forming a 1D chain running along the diagonal direction of the ab plane. In this regard, the olefinic CH (C(8)H(8)) functions as a bifurcate donor in generating the C-H···O associations. In the chain, the Cd cations are linearly arranged, with a distance of 10.051 Å between two adjacent Cd cations. The 1D chains are further held together by an interchain N-H···O (N(3)-H(3)···O(1)#2, 2.942(3) Å, 161.1°, #2 -x + 1/2, y - 1/2, -z) hydrogen bond and C-H···O associations between the olefinic CH group of the anion and one coordinated O atom of the carboxylate group and the O atom of the CONH group, with C-O distances of 3.424-3.461 Å, forming a 2D square grid sheet extending along the ab plane (Fig. 2). The 2D square grid sheets are further combined together by CH- π interactions between the phenyl CH of the anion and the aromatic ring of the anion, with a C–Cg distance of 3.515 Å, to form a 3D square grid layer structure. Herein the chains from adjacent sheet layers are intersected at an angle of ca. 30° with each other, while the chains in the third sheet layer are parallel to the chains in the first sheet layer, as are the chains in the second sheet layer and the fourth sheet layer.

3.2.2. Crystal and molecular structure of $Cd(Hdmpz)_4(L2)_2$ (2)

Crystals of **2** contain a mononuclear complex of the formulae $Cd(Hdmpz)_4(L2)_2$ (Fig. 3). Compound **2** crystallizes as triclinic colorless block crystals in the space group $P\bar{1}$, and there is one asymmetric structural unit in its cell content. Each Cd ion is octahedrally coordinated by two oxygen atoms of two monodentate L2 ligands and by four nitrogen atoms belonging to four monodentate pyrazole ligands, with a CdN_4O_2 binding set. The Cd ion is located at the inversion center (0, 1, 0.5). The CdN_4O_2 unit possesses coordination distances and angles in the ranges 2.3478(17)-2.3726(19) Å and $87.44(7)-180.0^\circ$, respectively. The Cd–N and Cd–O bond lengths are of comparable values.

In **2**, the non-bonded oxygen atoms, far enough from the Cd ions at a distance of 3.709 Å, are involved in two intramolecular hydrogen bonds (N(4)–H(4)···O(2) and N(2)–H(2)···O(2)#1, #1 -x, -y + 2, -z + 1) with N–O distances ranging from 2.749(3) to 2.751(3) Å, and H–O distances of 1.93–1.95 Å. Herein every non-bonded oxygen atom forms two hydrogen bonds in a bifurcated mode.

The mononuclear units are connected together via $CH_2-\pi$ associations between the CH_2 group from the 1,3-benzodioxole unit of the anion and the aromatic ring of the pyrazole, with a C–Cg distance of 3.672 Å, and CH–O interactions between the phenyl CH of L2 and the O atom of the 1,3-benzodioxole group, with a C–O distance of 3.558 Å, to form a 1D chain. In the chain, the Cd–Cd distance is 12.022 Å. The 1D chains are extended in parallel in the same plane, which has a dihedral angle of ca 60° with the bc plane, to form a 2D sheet (Fig. 4), yet there are no connections between these chains in the same plane. The sheets further stacked along the direction that is perpendicular to its extending direction to form a 3D network structure. There are also no interactions between these sheets.

3.2.3. Crystal and molecular structure of $Zn_2(\mu-dmpz)_2(Hdmpz)_2(L3)_2$ (3)

The structural determination revealed that compound **3**, of the formula $Zn_2(\mu$ -dmpz)₂(Hdmpz)₂(L3)₂, crystallizes as monoclinic colorless crystals in the centrosymmetric space group P2(1)/n with two formula units in the unit cell. As illustrated in Fig. 5, the asymmetric unit consists of one Zn^{II} cation, one pyrazole molecule, one pyrazolate unit and one carboxylate ligand. The pyrazolate unit acts as an N,N'-exobidentate ligand, keeping the two zinc ions at a non-bonding distance of ca. 3.534 Å. The complex molecule is dinuclear and consists of a Zn^{II} atom positioned at the center of a planar six-membered $[Zn(\mu-dmpz)_2Zn]$ unit; each single unit has a four-coordinate zinc ion with three Zn-N bonds (one Zn-N_{pvrazole} and two Zn-N_{pyrazolato}) and one Zn-O_{carboxylate} bond. The bridging Zn-N distance of 1.96 Å (average) is shorter than the terminal Zn–N distance of 2.010(4) Å, which is similar to the reported values [30]. The carboxylate groups coordinate in a monodentate manner with a Zn(1)-O(1) distance of 1.947(3) Å. The distance (3.364 Å)



Fig. 2. Packing diagram of compound 1 showing the square grid sheet structure extending along the ab plane.



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



Fig. 4. The sheet structure of compound 2 extended in the direction that has a dihedral angle of ca 60° with the bc plane.

between the non-bonded oxygen atom and the zinc ion is too large for the oxygen to coordinate with the metal ion. The coordination arrangement around zinc in complex **3** is a distorted tetrahedron with coordination angles in the range $106.68(13)-112.92(13)^\circ$. The geometrical parameters of this species closely match those recently reported for the analogous [$\{Zn(\mu-C_2H_5COO)(\mu-pz^*)(-Hpz^*)\}_2$] [31] (Hpz^{*} = 4-acetyl-3-amino-5-methylpyrazole) and [$\{Zn(\mu-C_2H_5COO)(\mu-pz)(Hpz)\}_2$] [30] complexes.

In complex **3**, the non-bonded oxygen atom of the carboxylate group forms an intramolecular hydrogen bond, $N(5)-H(5)\cdots O(2)$,



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

with N(5)–O(2) and H(5) \cdots O(2) distances of 2.693(5) and 1.88 Å, respectively. There also exists an intramolecular Cl–O contact between the Cl atom of the anion and the coordinated O atom of the carboxylate group, with a Cl–O distance of 2.905 Å; in this case the Cl–O contact is somewhat stronger than the reported example [32].

The adjacent dinuclear moieties are connected through a C-H...O interaction between the 4-CH group on the pyrazolato ring and the non-bonded O atom (with a C-O distance of 3.516 Å) and a CH₃-Cl association between the 5-CH₃ group of the pyrazole and Cl of the anion, with a C–Cl distance of 3.654 Å, to a form 1D chain. The 1D chains are further joined together by an interchain C–H··· π interaction, existing between 4-CH on the pyrazole ring and the pyrazolato ring in parallel neighboring chains (with a distance of 4-C on the pyrazole ring to the pyrazolato ring of 3.741 Å), and a $CH_3 \cdots \pi$ interaction between 5-CH₃ on the pyrazole ring and the aromatic ring of the anion, with a C–Cg distance of 3.601 Å, to form a 2D sheet extending in the direction that is inclined at an angle of ca. 60° with the ac plane (Fig. 6). The sheets are further stacked along the direction that is perpendicular to its extending direction by intersheet CH-O (between the 4-CH group of the pyrazolato ring and the non-bonded O atom of the carboxylate group of L3, with a C–O distance of 3.516 Å) and CH₃–Cl (between the 5-CH₃ group of the pyrazole ring and the Cl atom of the anion, with a C-Cl distance of 3.654 Å) associations to form a 3D network structure.

3.2.4. Crystal and molecular structure of $Zn(Hdmpz)_2(L4)_2$ (4)

Compound **4** crystallizes in the triclinic system with the space group $P\bar{1}$. An asymmetric unit of $Zn(Hdmpz)_2(L4)_2$ contains one tetrahedrally coordinated Zn(II) ion, two monodentate L4 anions and two Hdmpz groups, which is shown in Fig. 7. The molecular structure of **4** resembles the related $[Zn(CH_3COO)_2(ML)_2]$ monomer (ML = a monodentate nitrogen ligand), like the bisimidazole [33] and bis-pyridine [34] complexes.

The ZnN₂O₂ moiety has coordination distances and angles in the ranges 1.951(2)–1.989(2) Å and 95.81(9)–117.00(9)°, respectively; thus the overall coordination arrangement resembles that found in the compounds [Zn(Hpz)₂(Me₃NCH₂CO₂)](ClO₄)₂ [30] and {[Zn(CH₃COO)₂(Hpz)₂]·CH₃COOH} (Hpz = pyrazole) [19]. Although the distortion in the ZnN₂O₂ moiety is somewhat differently oriented in the latter two compounds, the angles around the zinc atoms are in the range 98.94(19)–117.30(18)° and 95.73(7)–118.34(8)°, respectively.

In **4**, the non-bonded oxygen atoms, far enough from the Zn ions with distances of 3.084 and 3.364 Å, are involved in two intramolecular hydrogen bonds $(N(2)-H(2)\cdots O(8) \text{ and } N(4)-H(4)\cdots O(2)$ with the N–O distances ranging from 2.756(3) to 2.838(3) Å and H–O distances of 1.97–2.09 Å).

The mononuclear units are linked together via CH3–O interactions between the 3-CH3 and 5-CH3 groups of the pyrazole and the nitro groups, with C–O distances of 3.546 and 3.378 Å respectively to form a 1D chain running along the *c* axis direction. Such



Fig. 6. The sheet structure of 3 extending in the direction that is inclined at an angle of ca. 60° with the ac plane.



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

chains are joined together by CH3- π interactions between the 5-CH3 group of the pyrazole ring and the aromatic ring of the anion, with a C–Cg distance of 3.484 Å, to form a 2D grid sheet extending parallel to the ac plane (Fig. 8). In the sheet the neighboring Zn–Zn separation along the c axis direction is 12.490 Å and the neighboring Zn–Zn separation along the *a* axis direction is 11.445 Å. The grid sheets are further stacked along the *b* axis direction via an intersheet CH3-O association between the 3-CH3 group of the pyrazole ring and the non-bonded O atom of the anion, with a C-O distance of 3.494 Å, and an $O-\pi$ association between the non-bonded O atom of the carboxylate group of the 3,5-dinitrobenzoate and the phenyl ring of the anion, with an O-Cg distance of 3.112 Å, to form a 3D layer structure. In this regard, adjacent sheets are slipped some distance from each other along the *a* and *c* axis directions, respectively. The corresponding anions and cations in neighboring sheet layers are arranged antiparallel, while the corresponding anions and cations in the third sheet layer are parallel to the corresponding anions and cations in the first sheet layer, as are the corresponding anions and cations in the second sheet layer and the fourth sheet layer.

3.2.5. Crystal and molecular structure of Zn(Hdmpz)₂(HL5)₂ (5)

Compound **5** crystallizes in the triclinic system with the space group *Pbar*1. The asymmetric unit of $Zn(Hdmpz)_2(HL5)_2$ contains one four-coordinated Zn(II) ion, two HL5 anions and two Hdmpz groups, which is shown in Fig. 9. The Zn–O distances are 1.925(2)–1.933(2) Å and the Zn–N distances are 1.977(3) and 2.004(3) Å, which are similar to the corresponding bond distances in **4**.

In **5**, the non-bonded oxygen atoms, far enough from the Zn ions with distances of 3.145 and 3.371 Å, are involved in two intramolecular hydrogen bonds, $N(2)-H(2)\cdots O(2)$ and $N(4)-H(4)\cdots O(5)$, with N–O distances ranging from 2.767(4) to 2.821(4) Å and H–O distances of 1.96–2.07 Å. Because of the presence of an intramolec-



Fig. 8. The grid sheet structure of compound 4 extended parallel to the ac plane.



Fig. 9. Molecular structure of complex **5** showing the atomic numbering scheme at the 30% ellipsoid probability level.

ular hydrogen bond between the carboxylate groups and the phenol groups $(O(6)-H(6)\cdots O(5), 2.555(3) \text{ Å}; O(3)-H(3)\cdots O(2),$ 2.603(3) Å) in the anion, it is generally expected and found that the carboxylate groups are essentially coplanar with the benzene rings [torsion angles C13-C12-C11-O2, 6.09°, C22-C19-C18-O5, 2.46°]. For the presence of this $O-H \cdots O$ hydrogen bond (Table 4) between the phenol OH groups and the uncoordinated oxygen atoms of the carboxylate group of HL5, there exists a $S_1^{(6)}$ loop motif in the anion. This feature is similar to that found in salicylic acid [33] and in the previously reported structure of a deprotonated compound based on o-hydroxy benzoic acid derivatives [35]. As expected, the O–O separations 2.555(3)–2.603(3) Å (mean: 2.579 Å) are essentially at the upper limit of the documented data [2.531(4)–2.570(4) Å] [36] because of the planarity of the hydrogen bonded carboxylate unit, but they are slightly contracted compared with the non-deprotonated examples (2.547-2.604 Å, mean: 2.588 Å), as a result of the deprotonation.

The mononuclear units are linked together via CH₃–O interactions between the 5-CH₃ group of the pyrazole ring and the phenol group, with a C–O distance of 3.108 Å, to form a 1D chain. Two such chains are joined together by a π – π association between the aromatic ring of the pyrazole and the phenyl ring of the anion, with a Cg–Cg distance of 3.333 Å, to form a double chain structure. The double chains are connected together by a CH–O association between the 4-CH group of the pyrazole ring and the phenol group, with a C–O separation of 3.458 Å, and a CH–Cl association between the 5-CH₃ group of the pyrazole ring and the Cl atom of HL5, with C–Cl a distance of 3.543 Å, to form a 2D sheet extending parallel to the bc plane (Fig. 10). The sheets are further stacked along the *a* axis direction by a Cl–Cl bond, with a Cl–Cl separation of 3.448 Å, to form a 3D network structure. Here the Cl–Cl bond distance is somewhat shorter than our previously reported data [37].

3.2.6. Crystal and molecular structure of Cd(Hdmpz)₂(HL6) (6)

Compound **6**, of the formula Cd(Hdmpz)₂(HL6), crystallizes as orthorhombic crystals in the centrosymmetric space group *Cmc*2(1), and there are four formula units in its cell content. The asymmetric unit contains one Cd, one HL6 and one pyrazole Ligand. The SO₃H and OH groups are both deprotonated, while the COOH group remains protonated. The SO₃⁻ group is coordinated to Cd in a chelating bidentate fashion, whilst all the other groups, namely the COOH, phenolate and pyrazole, coordinated to Cd in monodentate fashion (Fig. 11). The COOH group is coordinated to Cd by its carbonyl unit and the pyrazole by its neutral N moiety. The Cd–N distance is 2.278(3)Å and the Cd–O distances are 2.495(3)–2.500(3)Å. The angles around the Cd atom range from 56.09(11)° to 166.50(10)°.

The Cd atom and the anions are linked together to form a honeycomb structure extending parallel to the bc plane (Fig. 12). The pyrazoles coordinate to the Cd atoms from both faces of the honeycomb, i.e. both pyrazoles are protruded from the honeycomb plane in opposite directions. In the honeycomb intermolecular and intramolecular N–H···O hydrogen bonds exist between the neutral NH unit of the pyrazole ring and the OH of the carboxyl group and the O atom of the SO₃⁻ group, an intramolecular O–H···O hydrogen bond also exists between the COOH group and the phenolate group, with an O–O separation of 2.485(5)Å. The honeycombs are further stacked along the *a* axis direction by an intersheet CH–O association between 4-CH of the pyrazole group and the



Fig. 10. Packing diagram of compound 5 with the sheet structure extended parallel to the bc plane.



Fig. 11. Molecular structure of complex **6** showing the atomic numbering scheme at the 30% ellipsoid probability level.

 SO_3^- unit, with a C–O distance of 3.375 Å, to form a 3D network structure.

3.2.7. Crystal and molecular structure of $Cd_2(Hdmpz)_4(L7)_2$ (7)

Crystals of **7** contain the dinuclear $Cd_2(Hdmpz)_4(L7)_2$ (Fig. 13). Compound **7** crystallizes as triclinic colorless blocks in the space group $P\overline{1}$, and there are two formula units in its cell. Each Cd is octahedrally coordinated by four oxygens of three different L7 anions and by two nitrogens, belonging to two monodentate pyrazoles ligands, with a CdN_2O_4 bonding set. The malonate anion coordinates to one metal ion in a chelating form with two of the four oxygen atoms, and further bridges the neighboring two metal ions with the remaining two oxygen atoms. This coordinating mode is different from the corresponding compound $Zn_2(-Hdmpz)_4(L2)_2$ (H_2L2 = maleic acid) [20a].

The CdN₂O₄ unit possesses coordination distances and angles in the ranges 2.326(10)-2.437(10) Å and $82.0(3)-179.7(4)^{\circ}$, respectively. The C(2)=C(3) and C(6)=C(7) bond distances (1.354(18) and 1.347(19) Å), although longer than the corresponding values of the documented compound [20a], relate to a simple C=C double bond, due to the significant non-coplanarity of the carboxyl and olefinic groups.

The rms deviations of the two pyrazole rings coordinated to Cd1 are 0.0167 (for the ring with N1 and N2) and 0.0188 Å (for the ring bearing N3 and N4). The pair of pyrazoles coordinated to the same Cd centre have dihedral angles of 61° for Cd1 and 54.1° for Cd2. The rms deviations of the two pyrazole rings coordinated to Cd2 are 0.0227 Å for the ring with N5 and N6, and 0.0158 Å for the ring with N7 and N8. The dihedral angles between the pyrazole rings coordinated to different Cd cations are 35.7°, 40.6°, 61.7° and 19.9°.

The carboxylates and the Cd anions form a 1D chain running along the *c* axis direction. In the chain, adjacent Cd–Cd separations are 5.009 and 5.025 Å. The interchain Cd–Cd distance is 8.281 Å. In the chain, the chelated carboxylates and Cd generate a sevenmembered ring, whilst two carboxylates and two Cd centres produce an eight-membered ring, then the seven-membered and eight-membered rings repeat along the chain, and these two kinds of rings are fused together. The pyrazole molecules are attached to the chain via Cd–N bonds. In the chain an N–H···O interaction also exists, arising from the NH moiety of a pyrazole ligand and the O atom of a carboxylate group that did not bond with the same metal ion as the pyrazole donor. The 1D chains are joined together via an interchain CH–O association between the olefinic CH of the anion and a carboxylate group, with a C–O distance of 3.505 Å, to form a sheet structure (Fig. 14).

3.3. Thermogravimetry (TG)

The TGA studies showed that 1 is stable below 160 °C. Its decomposition begins at 165.2 °C. The weight loss of 27.91% in



Fig. 12. The honeycomb structure of compound 6 extending parallel to the bc plane.



Fig. 13. Molecular structure of complex 7 showing the atomic numbering scheme. To prevent crowding, the atomic numbering scheme is not shown.



Fig. 14. The grid sheet structure of compound 7 produced via CH–O associations.

the temperature range 165.2-259.5 °C is caused by the loss of the two pyrazole molecules (Calc. 28.03%). The weight loss of 55.31% from 269.2 to 426.7 °C arises from the loss of two L1 ligands (Calc. 55.47%). Compound 2 is stable below 150 °C. The weight loss of 46.29% in the temperature range 157.7-245.1 °C is caused by the loss of the four pyrazole molecules (Calc. 46.42%). The weight loss of 39.69% from 286.7 to 421.8 °C is due to the loss of the two L2 ligands (Calc. 39.89%). For 3 the first weight loss of 23.03% in the temperature range 152.9–251.4 °C is attributed to the loss of the terminal pyrazole molecules (Calc. 23.23%). The second weight loss of 37.43% from 289.6 to 421.8 °C is due to the loss of the two L3 ligands (Calc. 37.75%) and the third weight loss of 22.64% in the temperature range 443.7-617.9 °C corresponds approximately to the release of the bridging pyrazoles (Calc. 22.99%). For 4, the weight loss of 28.16% (Calc. 28.24%), corresponding to the loss of two Hdmpz molecules, was observed in the temperature range 169.3-282.9 °C, and there is a weight loss of 61.90% between 302.6 and 487.8 °C, which is due to the loss of the two carboxylate ligands (Calc. 62.07%). For 5, the first weight loss stage occurs between 163.1 and 256.0 °C, and corresponds to the removal of 2 mol of Hdmpz ligands (Calc.: 31.96%, Found: 31.87%). The second stage between 268.9 and 434.2 °C is accompanied by a mass loss of 56.71% for two 5-chlorosalicylates (Calc.: 57.09%). Complex **6** experiences a first weight loss of 36.71% in the temperature range 166.2–259.7 °C, which is due to the loss of the pyrazole molecules (Calc. 36.86%). The second weight loss of 41.34% was observed between 297.4 and 439.1 °C, and is attributed to the loss of the bonded carboxylate ligands (Calc. 41.47%). For **7**, the first weight loss of 45.67% (Calc. 45.85%) corresponds to the loss of four Hdmpz molecules in the temperature range 159.7–254.6 °C, and the second weight loss of 27.14% between 283.2 and 421.3 °C arises from the loss of the two L7 ligands (Calc. 27.22%).

4. Summary

In summary, a series of mononuclear to dinuclear divalent Zn/ Cd complexes with 3,5-dimethylpyrazole and different carboxylate ligands were synthesized and structurally characterized. These complexes exhibit 2D sheet, 3D network to 3D layer structures. The central metal ions are coordinated in N₂O₄, N₄O₂, N₃O and N₂O₂ fashions. A distorted octahedral geometry in the case of Cd and a tetrahedral geometry for Zn were observed in the X-ray studies.

The crystallographic studies demonstrated that in these complexes, the metal centers are coordinated by 3,5-dimethylpyrazole and there are no deprotonated 3,5-dimethylpyrazole anions except for compound **3**. In addition, the carboxylate groups act as monodentate ligands toward the metal ion in 2, 3, 4, 5 and 6. The COOgroup in **1** and SO_3^{-} in **6** both coordinate to the metals in a chelating bidentate fashion. The carboxylate group in 7 functions as a tetradentate bridging ligand. The strong structural propensity toward tetracoordination in the Zn compounds seems to disfavor the formation of 'paddlewheel' dimeric complexes [34,38]. The nonbonded O atoms of the carboxylate ligands in all the compounds are involved in the formation of intramolecular hydrogen bonds with the N-H group of 3,5-dimethylpyrazole. It is worth noting that the H-bonds in complexes 2-5 are intracomplex and do not contribute to the formation of an extended architecture, while in complexes 6 and 7 H-bonds are located in the polymeric groups and do not extend their dimensionality.

Complexes 1–7 have abundant intra- and intermolecular weak interactions (including classical hydrogen bonds, CH-Cl, CH₃-Cl, Cl···Cl, Cl···O, C–H···O, CH₃···O, C–H··· π , CH₂··· π , CH₃– π , O– π and π - π interactions) in their crystals, which lead to the formation and stabilization of the final structures.

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References

- [1] J.M. Lehn, Supramolecular Chemistry: Concepts and Perspectives, VCH, Weinheim, 1995.
- [2] (a) See, for example: A.M. Kutasi, D.R. Turner, P. Jensen, B. Moubaraki, S.R. Batten, K.S. Murray, CrystEngComm 11 (2009) 2089;
 - (b) J.A. Hoshiko, G.B. Wang, J.W. Ziller, G.T. Yee, A.F. Heyduk, Dalton Trans. (2008) 5712:
 - (c) J.Y. Zhang, Y. Ma, A.L. Cheng, Q. Yue, Q. Sun, E.Q. Gao, Dalton Trans. (2008) 2061:
 - (d) C. Janiak, J.K. Vieth, New J. Chem. 34 (2010) 2366;
 - (e) J.P. Zou, G.W. Zhou, X. Zhang, M.S. Wang, Y.B. Lu, W.W. Zhou, Z.J. Zhang, G.C. Guo, J.S. Huang, CrystEngComm 11 (2009) 972;
 - (f) O.M. Yaghi, M. O'Keeffe, N.W. Ockwig, H.K. Chae, M. Eddaoudi, J. Kim, Nature 423 (2003) 705;
 - (g) G. Férey, Chem. Soc. Rev. 37 (2008) 191:
- (h) X.Q. Zhao, P. Cui, B. Zhao, W. Shi, P. Cheng, Dalton Trans. 40 (2011) 805. [3] C. Janiak, J. Chem. Soc., Dalton Trans. (2001) 2781.
- [4] R.L. Rardin, W.B. Tolman, S.J. Lippard, New J. Chem. 15 (1991) 417.
- [5] H. Adams, S. Clunas, D.E. Fenton, S.E. Spey, Dalton Trans. (2002) 441.
- [6] J. Kuzelka, J.R. Farrell, S.J. Lippard, Inorg. Chem. 42 (2003) 8652.
- [7] Y. Tshuva, S.J. Lippard, Chem. Rev. 104 (2004) 987.
- [8] A. Salifoglou, Coord. Chem. Rev. 228 (2002) 297.
- [9] P. Lemoine, B. Viossat, G. Morgant, F.T. Greenaway, A. Tomas, N.H. Dung, R.J. Sorenson, J. Inorg. Biochem. 89 (2002) 18.

- [10] (a) C. Policar, F. Lambert, M. Cesario, I. Morgenstern-Badarau, Eur. J. Inorg. Chem. (1999) 2201:
 - (b) P.R. Levstein, R. Calvo, Inorg. Chem. 29 (1990) 1581;
 - (c) E. Colacio, J.M. Dominguez-Vera, R. Kivekäs, J.M. Moreno, A. Romerosa, J. Ruiz, Inorg. Chim. Acta 212 (1993) 115;
 - (d) J.M. Rueff, N. Masciocchi, P. Rabu, A. Sironi, A. Skoulios, Eur. J. Inorg. Chem. (2001) 2843;
 - (e) R.L. Rardin, A. Bino, P. Poganiuch, W.B. Tolman, S. Liu, S.J. Lippard, Angew. Chem., Int. Ed. Engl. 129 (1990) 812.
- [11] Y.H. Xing, Y.H. Zhang, Z. Sun, L. Ye, Y.T. Xu, M.F. Ge, B.L. Zhang, S.Y. Niu, J. Inorg. Biochem. 101 (2007) 36.
- [12] L.M.R. Hill, M.K. Taylor, V.W. Lin Ng, C.G. Young, Inorg. Chem. 47 (2008) 1044.
- [13] K. Umakoshi, T. Kojima, K. Saito, S. Akatsu, M. Onishi, S. Ishizaka, N. Kitamura, Y. Nakao, S. Sakaki, Y. Ozawa, Inorg. Chem. 47 (2008) 5033.
- [14] B. Machura, M. Jaworska, R. Kruszynski, Polyhedron 23 (2004) 2523.
- [15] Y.J. Sun, B. Zhao, P. Cheng, Inorg. Chem. Commun. 10 (2007) 583.
- [16] (a) A.A. Mohamed, S. Ricci, A. Burini, R. Galassi, C. Santini, G.M. Chiarella, D.Y. Melgarejo, J.P. Fackler Jr., Inorg. Chem. 50 (2011) 1014; (b) R. Mukheerjee, Coord. Chem. Rev. 203 (2000) 151; (c) K. Umakoshi, Y. Yamauchi, K. Nakamiya, T. Kojima, M. Yamasaki, H. Kawano, M. Onishi, Inorg. Chem. 42 (2003) 3907.
- [17] (a) J.E. Cosgriff, G.B. Deacon, Angew. Chem., Int. Ed. Engl. 37 (1998) 286; (b) G.B. Deacon, E.E. Delbridge, B.W. Skelton, A.H. White, Angew. Chem., Int. Ed. Engl. 37 (1998) 2251: (c) G.B. Deacon, C.M. Forsyth, A. Gitlits, R. Harika, P.C. Junk, B.W. Skelton, A.H.
 - White, Angew. Chem., Int. Ed. Engl. 41 (2002) 3249;
 - (d) I.A. Guzei, A.G. Baboul, G.P.A. Yap, A.L. Rheingold, H.B. Schlegel, C.H. Winter, J. Am. Chem. Soc. 119 (1997) 3387;
 - (e) D. Pfeiffer, M.J. Heeg, C.H. Winter, Inorg. Chem. 39 (2000) 2377.
- [18] J.R. Perera, M.J. Heeg, H.B. Schlegel, C.H. Winter, J. Am. Chem. Soc. 121 (1999) 4536.
- [19] (a) A. Cingolani, S. Galli, N. Masciocchi, L. Pandolf, C. Pettinari, A. Sironi, Dalton Trans. (2006) 2479;
 - (b) R. Sarma, D. Kalita, J.B. Baruah, Dalton Trans. (2009) 7428;
 - (c) U.P. Singh, P. Tyagi, S. Pal, Inorg. Chim. Acta 362 (2009) 4403.
- [20] (a) S.W. Jin, D.Q. Wang, Z. Anorg. Allg. Chem. 637 (2011) 618;
- (b) S.W. Jin, D.Q. Wang, J. Coord. Chem. 64 (2011) 1940.
- [21] (a) P. Metrangolo, H. Neukirch, T. Pilati, G. Resnati, Acc. Chem. Res. 47 (2005) 386:

(b) T.R. Shattock, K.K. Arora, P. Vishweshwar, M.J. Zaworotko, Cryst. Growth Des. 8 (2008) 4533;

- (c) K. Biradha, G. Mahata, Cryst. Growth Des. 5 (2005) 61;
- (d) B.Q. Ma, P. Coppens, Chem. Commun. (2003) 504;
- (e) D.J. Berry, C.C. Seaton, W. Clegg, R.W. Harrington, S.J. Coles, P.N. Horton, M.B. Hursthouse, R. Storey, W. Jones, Cryst. Growth Des. 8 (2008) 1697;
- (f) L. Fábián, N. Hamill, K.S. Eccles, H.A. Moynihan, A.R. Maguire, L.
- McCausland, S.E. Lawrence, Cryst. Growth Des. 11 (2011) 3522.
- [22] Bruker, SMART and SAINT, Bruker AXS Inc., Madison, WI, USA, 2004.
- [23] SHELXTL-PC, version 5.03, Siemens Analytical Instruments, Madison, WI, 1994.
- [24] Y.P. Wu, D.S. Li, F. Fu, W.W. Dong, L. Tang, Y.Y. Wang, Inorg. Chem. Commun. 13 (2010) 1005.
- [25] Y.J. Sun, P. Chen, S.P. Yan, D.Z. Liao, Z.H. Jiang, P.W. Shen, J. Coord. Chem. 55 (2002) 363.
- [26] K. Bania, N. Barooah, J.B. Baruah, Polyhedron 26 (2007) 2612.
- [27] J. Li, Y.H. Xing, H.Y. Zhao, Z.P. Li, C. Guang Wang, X.Q. Zeng, M.F. Ge, S.Y. Niu, Inorg. Chim. Acta 362 (2009) 2788.
- [28] A. Michaelides, C.D. Papadimitriou, J.C. Plakatouras, S. Skoulika, P.G. Veltsistas, Polyhedron 23 (2004) 25873.
- [29] K.M. Lo, S.W. Ng, Acta Crystallogr., Sect. E 65 (2009) o1101.
- [30] J. Li, J.H. Zhou, Y.Z. Li, L.H. Weng, X.T. Chen, Z. Yu, Z. Xue, Inorg. Chem. Commun. 7 (2004) 538.
- [31] Z.D. Tomic, Z.K. Jacimovic, V.M. Leovac, V.I. Cesljevi, Acta Crystallogr., Sect. C 56 (2000) 777
- [32] S.W. Jin, D.O. Wang, Y.C. Xu, J. Coord. Chem. 65 (2012) 1953.
 [33] X.M. Chen, Z.T. Xu, X.C. Huang, J. Chem. Soc., Dalton Trans. (1994) 2331.
- [34] B. Singh, J.R. Long, F. De Biani, D. Gatteschi, P. Stavropoulos, J. Am. Chem. Soc. 119 (1997) 7030
- [35] M. Sundaralingam, L.H. Jensen, Acta Crystallogr. 18 (1965) 1053.
- [36] G. Simith, A.W. Hartono, U.D. Wermuth, P.C. Healy, J.M. White, A.D. Rae, Aust. J. Chem. 58 (2005) 47.
- [37] S.W. Jin, D.Q. Wang, X.L. Wang, M. Guo, Q.J. Zhao, J. Inorg. Organomet. Polym. 18 (2008) 300.
- [38] H.L. Chun, D.N. Dybtsev, H. Kin, K. Kim, Chem. Eur. J. 11 (2005) 3521. and references cited therein.