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Syntheses, characterization and crystal structures of eight Cd(II) carboxylates containing 3,5-dimethylpyrazole

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ABSTRACT

Eight new complexes, namely $[Cd(Hdmpz)_2(L1)_20.5H_2O]_2$ (1) (Hdmpz = 3,5-dimethylpyrazole, L1 = trichloroacetate), $[Cd(Hdmpz)_2(L2)_2]$ ·H₂O (2) (L2 = indole-3-acetate), $Cd(Hdmpz)_2(L3)_2$ (3) (L3 = 4-methylbenzoate), $Cd(Hdmpz)_4(L4)_2$ (4) (L4 = 3-methylbenzoate), $Cd(Hdmpz)_4(L5)_2$ (5) (L5 = 4-methoxybenzoate), $Cd(Hdmpz)_2(L6)_2$ (6) (L6 = 2-chloronicotinate), $Cd(Hdmpz)(HL7)_2$ (7) (HL7 = 2-hydroxy-5-(phenyldiazenyl)benzoate) and $[Cd_2(Hdmpz)_6(L8)_2] \cdot (Hdmpz)_2$ (8) (L8 = o-phthalate) have been prepared by the self-assembly of Cd ions, 3,5-dimethylpyrazole and carboxylic acids at room temperature. All the complexes were characterized by elemental analysis. IR spectra, TG and single crystal X-ray diffraction analysis. The X-ray studies revealed that these complexes display mononuclear to dinuclear structures, with an octahedral geometry around each cadmium ion. The 3,5-dimethylpyrazole ligand in all the compounds is coordinated only in a monodentate fashion by its neutral N group. In **2**, **3** and **6**, the carboxylate groups behave as chelating bidentate ligands. In **4** and **5**, the carboxylate groups act as monodentate ligands. The COO⁻ group in **1** is coordinated to the Cd centre in both monodentate and bridging bidentate modes. The carboxylates in 7 coordinate to the Cd centre in tridentate chelating bridging and bidentate bridging fashions, simultaneously, while in 8 there exists a tridentate bridging carboxylate ligand. Based on the X-ray crystallographic study, extensive intra- and intermolecular non-covalent interactions, such as classical hydrogen bonds, CH-Cl, CH₃-Cl, Cl···Cl, Cl···O, CH-N, CH₃-N, C-H···O, CH₃···O, C-H··· π , CH₂··· π , CH₃- π and π - π interactions, are analyzed. These compounds display different structures, such as a OD discrete mononuclear arrangement, sheet, 3D network, and 3D layer network. The thermal stabilities for 1-8 were examined and the results show that the complexes display good thermal stability.

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1. Introduction

Recently, metal coordination complexes have aroused great interest in coordination chemistry because of their intriguing structures and potential as functional materials [1–3]. Research in this field has 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 non-covalent bonds in crystal engineering. The framework structure of coordination complexes is primarily dependent upon the coordination preferences of the central metal ions and the nature of the ligands. Aside from the coordination bonding interactions, noncovalent bonding 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 coordination frameworks.

The study 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, such as architectures of open and porous frameworks [4,5], but also with regard to biological activities [6,7] and physiological effects [8,9]. The carboxylate anions can adopt a wide range of bonding modes, including monodentate, symmetric and asymmetric chelating, and bidentate and monodentate bridging [10]. Cd(II), being a d¹⁰ metal, exhibits a variety of coordination numbers and geometries, depending on the crystal packing and on the ligands [11].







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Pyrazole and its derivatives have been widely employed in polypyrazolylborates to stabilize a variety of organometallic and coordination compounds [12]. Up until now, a large number of complexes containing pyrazole (Hdmpz) ligands have been synthesized and employed in coordination chemistry or organometallic chemistry [13–15]. Many complexes with simple pyrazoles, both in terminal as well as in bridging fashions are also available [16-18]. However, complexes in the presence of carboxylic acids and pyrazole derivatives are not very common, except some recently reported examples in the literature [19]. We have been working on coordination compounds with mixed ligands of carboxylate and 3,5-dimethylpyrazole [20]. The pyrazole and the carboxylate ligands appear to possess similar steric requirements and, to a certain extent, also similar bonding capabilities. In order to know the influence of the carboxylate residue in the formation of new complexes and the role the weak non-covalent interactions played in forming the final supramolecular frameworks, we selected carboxylic acids bearing N/NH, OH, Cl and CH₃ units, which are good groups in forming hydrogen bonds and some other non-bonding interactions [21]. Thus, in the following, we report the synthesis, structural characterization and thermal behaviour of eight Cd complexes with a combination of 3,5-dimethylpyrazole (Hdmpz) and different carboxylates (Scheme 1), namely [Cd(Hdmpz)₂(L1)₂0.5H₂ O_{2} (1) (Hdmpz = 3,5-dimethylpyrazole, L1 = trichloroacetate), $[Cd(Hdmpz)_2(L2)_2] \cdot H_2O$ (2) (L2 = indole-3-acetate), $Cd(Hdmpz)_2$ $(L3)_2$ (3) (L3 = 4-methylbenzoate), Cd(Hdmpz)_4(L4)_2 (4) (L4 = 3methylbenzoate), $Cd(Hdmpz)_4(L5)_2$ (**5**) (L5 = 4-methoxybenzoate), $Cd(Hdmpz)_2(L6)_2$ (6) (L6 = 2-chloronicotinate), $Cd(Hdmpz)(HL7)_2$ (7) (HL7 = 2-hydroxy-5-(phenyldiazenyl)benzoate) and $[Cd_2]$ $(Hdmpz)_6(L8)_2$ · $(Hdmpz)_2$ (8) (L8 = o-phthalate).

2. Experimental

2.1. Materials and physical measurements

The chemicals and solvents used in this work were 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 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 rate 10 °C min⁻¹) using Al crucibles.

2.2. Synthesis of the complexes

2.2.1. Synthesis of $[Cd(Hdmpz)_2(L1)_20.5H_20]_2$ (1)

A solution of Cd(CH₃COO)₂·2H₂O (0.0270 g, 0.1 mmol) in 8 mL of MeOH was added to a MeOH solution (12 mL) containing Hdmpz (0.0192 g, 0.2 mmol) and trichloroacetic acid (HL1) (0.0654 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 colourless crystals formed, which were filtered off, washed with MeOH and dried under vacuum to afford 0.0450 g of the product. Yield: 70.49% (based on Hdmpz). Elemental analysis performed on crystals exposed to the atmosphere, Anal. Calc. for C₂₈H₃₄Cd₂Cl₁₂N₈O₉ (1276.83): C, 26.32; H, 2.66; N, 8.77. Found: C, 26.25; H, 2.58; N, 8.73%. IR (KBr, cm⁻¹): 3568w, 3322w(v_{as}(NH)), 3294w(v_s(NH)), 3154m, 3035m, 2964m, 2880m, 2782w, 1639m(v_{as}(CO₂)), 1599s(v_{as}(CO₂)), 1560m, 1487m, 1451m(v_s(CO₂)), 1382s(v_s(CO₂)), 1338m, 1287m, 1244m, 1202m, 1154m, 1101m, 1055m, 998m, 949m, 888m, 831m, 784m, 744m, 695m, 643m, 604m.

2.2.2. Synthesis of $[Cd(Hdmpz)_2(L2)_2] \cdot H_2O(2)$

A solution of Cd(CH₃COO)₂·2H₂O (0.0270 g, 0.1 mmol) in 6 mL of MeOH was added to an EtOH solution (15 mL) containing Hdmpz (0.0192 g, 0.2 mmol) and indole-3-acetic acid (HL2) (0.0701 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



Scheme 1. The ligands used in this paper.

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 0.0510 g of the product. Yield 76.00% (based on Hdmpz). Elemental analysis performed on crystals exposed to the atmosphere, *Anal.* Calc for $C_{30}H_{34}CdN_6O_5$ (671.03): C, 53.65; H, 5.07; N, 12.52. Found: C, 53.56; H, 5.01; N, 12.46%. IR (KBr, cm⁻¹): 3606w, 3395w, 3246w, 3172w, 3057w, 2925m, 2847m, 2768w, 1627s($v_{as}(CO_2)$), 1574m, 1521m, 1498s($v_s(CO_2)$), 1457m, 1424s, 1381m, 1287w, 1234m, 1225m, 1116m, 940w, 846m, 805m, 762m, 723, 696m, 645m, 621m.

2.2.3. Synthesis of $Cd(Hdmpz)_2(L3)_2$ (3)

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 4-methylbenzoic acid (HL3) (0.0545 g. 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 0.0472 g of the product. Yield: 82.09% (based on Hdmpz). Elemental analysis performed on crystals exposed to the atmosphere, Anal. Calc. for C₂₆H₃₀CdN₄O₄ (574.94): C, 54.27; H, 5.22; N, 9.74. Found: C, 54.21; H, 5.17; N, 9.69%. IR (KBr, cm⁻¹): 3349w(v_{as}(NH)), 3269w(v_s(NH)), 3177m, 3032m, 2937m, 2870m, 1610s(v_{as}(COO)), 1550m, 1484s(v_s(COO)), 1426m, 1404m 1378m, 1293m, 1245m, 1194m, 1176m, 1060m, 1012m, 852m, 801m, 763m, 698m, 656m, 624m, 602m.

2.2.4. Synthesis of $Cd(Hdmpz)_4(L4)_2$ (4)

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 3-methylbenzoic acid (HL4) (0.0545 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 colourless crystals formed, which were filtered off, washed with EtOH and dried under vacuum to afford 0.0270 g of the product. Yield: 70.38% (based on Hdmpz). Elemental analysis performed on crystals exposed to the atmosphere, Anal. Calc. for C₃₆H₄₆CdN₈O₄ (767.21): C, 56.31; H, 5.99; N, 14.60. Found: C, 56.21; H, 5.87; N, 14.53%. IR (KBr, cm^{-1}): 3367w(v_{as} (NH)), 3261w(v_s(NH)), 3156m, 3082m, 2933m, 2858m, 1614s(v_{as}(COO)), 1555m, 1489m, 1446m, 1398s(v_s(COO)), 1342m, 1298m, 1249m, 1190m, 1136m, 1065m, 1016m, 881m, 834m, 779m, 720m, 679m, 634m, 605m.

2.2.5. Synthesis of Cd(Hdmpz)₄(L5)₂ (**5**)

A solution of Cd(CH₃COO)₂·2H₂O (0.0270 g, 0.1 mmol) in 6 mL of MeOH was added to an EtOH solution (4 mL) containing Hdmpz (0.0192 g, 0.2 mmol) and 4-methoxybenzoic acid (H₂L5) (0.0608 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 colourless crystals formed, which were filtered off, washed with EtOH and dried under vacuum to afford 0.0330 g of the product. Yield: 82.58% (based on Hdmpz). Elemental analysis performed on crystals exposed to the atmosphere, *Anal.* Calc. for C₃₆H₄₆CdN₈O₆ (799.21): C, 54.05; H, 5.76; N, 14.01. Found: C, 53.97; H, 5.69; N, 13.97%. IR (KBr, cm⁻¹): 3374m(v_{as}(NH)), 3258m(v_s(NH)), 3087m, 3082m, 2957m, 2896m, 1610s(v_{as}(COO)), 1558m, 1503m, 1426m, 1405s(v_s(COO)), 1386m, 1335m, 1281m,

1234m, 1170m, 1113m, 1066m, 996m, 951m, 898m, 845m, 785m, 726m, 670m, 639m, 600m.

2.2.6. Synthesis of $Cd(Hdmpz)_2(L6)_2$ (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 (8 mL) containing Hdmpz (0.0192 g, 0.2 mmol) and 2-chloronicotinic acid (HL6) (0.0630 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 0.0541 g of the product. Yield: 87.57% (based on Hdmpz). Elemental analysis performed on crystals exposed to the atmosphere, Anal. Calc. for C₂₂H₂₂CdCl₂N₆O₄ (617.76): C, 42.74; H, 3.56; N, 13.60. Found: C, 42.68; H, 3.49; N, 13.54%. IR (KBr, cm⁻¹): 3346w(v_{as}(NH)), 3245w(v_s(NH)), 2955m, 1613s(v_{as}(COO)), 1583m, 1534m, 1476s(v_s(COO)), 1413m, 1366s, 1306s, 1279w, 1224w, 1170m, 1119m, 1067m, 1012m, 964m, 913m, 865m, 816m, 770m, 723m, 676m, 620m.

2.2.7. Synthesis of $Cd(Hdmpz)(HL7)_2$ (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 2-hydroxy-5-(phenyldiazenyl)benzoic acid (H₂L7) (0.0968 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 red solution was filtered into a test tube and after several days dark red crystals formed, which were filtered off, washed with MeOH and dried under vacuum to afford 0.0540 g of the product. Yield: 78.15% (based on Cd(CH₃COO)₂·2H₂O). Elemental analysis performed on crystals exposed to the atmosphere, Anal. Calc. for C₃₁H₂₆CdN₆O₆ (690.98): C, 53.84; H, 3.76; N, 12.16. Found: C, 53.79; H, 3.65; N, 12.07%. IR (KBr. cm⁻¹): 3647w. 3344w. 3290w. 3138m. 3079m. 2988m, 2866m, $1622s(v_{as}(COO))$, $1596s(v_{as}(COO))$, 1473s (v_{as}(COO)), 1438s(v_{as}(COO)), 1385m, 1331m, 1286m, 1235s, 1178m, 1123m, 1067m, 1014m, 977m, 924m, 862m, 780m, 731m, 684m, 646m, 610m.

2.2.8. Synthesis of $[Cd_2(Hdmpz)_6(L8)_2] \cdot (Hdmpz)_2$ (8)

A solution of Cd(CH₃COO)₂·2H₂O (0.0270 g, 0.1 mmol) in 6 mL of MeOH was added to a MeOH solution (6 mL) containing Hdmpz 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 0.0264 g of the product. Yield: 79.87% (based on Hdmpz). Elemental analysis performed on crystals exposed to the atmosphere, Anal. Calc. for C₅₆H₇₂Cd₂N₁₆O₈ (1322.10): C, 50.83; H, 5.44; N, 16.94. Found: C, 50.75; H, 5.41; N, 16.88%. IR (KBr, cm⁻¹): 3326w, 3237w, 3164m, 3068m, 2992m, 2849m, $1627s(v_{as}(COO^{-}))$, $1591s(v_{as}(CO_{2}))$, 1547m, 1506m, 1439s($v_s(CO_2)$), 1388s($v_s(COO^-)$), 1353s, 1299m, 1247m, 1201m, 1154m, 1100m, 1059m, 1005m, 951m, 892m, 848m, 789m, 735m, 691m, 657m, 622m.

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 the 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 **1–8** are listed in Table S1.

3. Results and discussion

3.1. Preparation and general characterization

Complexes **1–8** were prepared in MeOH or EtOH at room temperature via the combination of the cadmium acetate, Hdmpz and the appropriate carboxylic acid. The corresponding crystals, suitable for X-ray crystallography analysis, were grown upon addition of a few drops of conc. ammonia solution, with yields of 70.38–87.57%.

During the process the acetate ligands were substituted by carboxylate ions and also by the pyrazole group of Hdmpz. The infrared spectra of **1-8** are consistent with their molecular compositions. The IR spectra of **1-8** display characteristic carboxylate bands in the range 1639–1591 cm⁻¹ for $v_{as}(CO_2)$ and 1498– 1382 cm⁻¹ for $v_s(CO_2)$ [24]. Neutral Hmdpz ligands are coordinated in all of the compounds, which is further confirmed by the presence of characteristic NH bands in the region 3500–3200 cm⁻¹ [25]. Weak absorptions observed at 3000–2800 cm⁻¹ can be attributed to the aromatic C–H group in **1-8**.

3.2. Crystal structure description

3.2.1. Crystal and molecular structure of $[Cd(Hdmpz)_2(L1)_2 0.5H_2O]_2$ (1)

Compound **1** was prepared by the reaction of $Cd(CH_3COO)_2 \cdot 2H_2O$, trichloroacetic acid (HL1) and Hdmpz in a ratio of 1:2:4 with MeOH as the solvent, yielding pure $[Cd(Hdmpz)_2(L1)_20.5H_2O]_2$ upon

Table 1	
Summary of X-ray crystallographic data for complexes 1	-4

addition of a few drops of conc. ammonia solution. The structure 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. The Cl22, Cl23 and Cl24 atoms are all disordered over two positions with an occupancy factor of 0.43007. The Cl10, Cl11 and Cl12 atoms are all disordered over two positions with an occupancy factor of 0.62186. Due to the presence of these disorders, the R value for complex **1** is high. Each Cd ion is octahedrally coordinated by four oxygen atoms from three different L1 ligands and one water molecule, and by two nitrogen atoms from two different monodentate pyrazole ligands, generating a distorted trigonal prismatic geometry (Fig. 1). Herein the water molecule acts as a bridging bidentate ligand.

The location of H2, H4, H6 and H8 in **1**, bound to nitrogen and not oxygen atoms, is consistent with the different acidic characters of pyrazole and trichloroacetic acid [26], and is also confirmed by the difference electron density map, used to find the H atoms. The Cd–N distances are 2.21(2)-2.40(2) Å and the Cd–O distances are 2.28(1)-2.46(1) Å. The angles around the Cd atom range from 79.9(5)° to $176.4(6)^{\circ}$.

Moreover **1** is not an ionic species consisting of a monocationic Cd(II) complex and carboxylate counterions. Compound 1 is dinuclear. There are two kinds of L1 in the dinuclear unit, one kind of L1 is coordinated to the Cd in a monodentate mode, and the other kind of L1 is coordinated to two Cd atoms in a bridging bidentate fashion. In the dinuclear aggregate there exist an intramolecular N-H···O hydrogen bond between the NH unit of the pyrazole and the non-bonded O atom of the anion, with an N-O distance of 2.95(2) Å, together with $O-H \cdots O$ hydrogen bonds between the water molecule and the non-bonded O atom with O-O distances of 2.647(19)-2.650(19) Å. The dinuclear aggregates are linked together by a CH–O association between the 4-CH group of the pyrazole and the non-bonded O atom, with a C-O distance of 3.588 Å, and a $CH_3-\pi$ association between the 3- CH_3 group of the pyrazole and the aromatic ring of the pyrazole, with a C-Cg distance of 3.692 Å, to generate a tetranuclear aggregate. The tetranuclear

	1	2	3	4
Formula	C ₂₈ H ₃₄ Cd ₂ Cl ₁₂ N ₈ O ₉	$C_{30}H_{34}CdN_6O_5$	$C_{26}H_{30}CdN_4O_4$	$C_{36}H_{46}CdN_8O_4$
Formula weight	1276.83	671.03	574.94	767.21
T (K)	293(2)	293(2)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Crystal system	triclinic	monoclinic	monoclinic	triclinic
Space group	ΡĪ	P2(1)/c	P2(1)/c	ΡĪ
a (Å)	10.3708(10)	17.6688(18)	10.4478(8)	9.4206(6)
b (Å)	19.6174(12)	8.5825(8)	13.3827(10)	9.4690(5)
c (Å)	24.729(3)	22.297(3)	19.9333(19)	11.1927(7)
α (°)	81.8280(10)	90	90	106.126(5)
β(°)	83.9940(10)	111.745(2)	90.9870(10)	91.460(5)
γ (°)	89.250(2)	90	90	102.179(5)
$V(Å^3)$	4952.7(8)	3140.5(6)	2786.7(4)	933.79(10)
Ζ	4	4	4	1
D_{calcd} (Mg/m ³)	1.712	1.419	1.370	1.364
Absorption coefficient (mm ⁻¹)	1.558	0.742	0.819	0.633
F(000)	2520	1376	1176	398
Crystal size, mm	$0.40 \times 0.27 \times 0.11$	$0.31\times0.26\ \times0.16$	$0.29 \times 0.24 \times 0.18$	$0.30 \times 0.22 \times 0.16$
θ (°)	2.49-25.00	2.57-25.02	2.47-25.02	2.79-25.02
Limiting indices	$-12 \leqslant h \leqslant 12, -23 \leqslant k \leqslant 21,$	$-21\leqslant h\leqslant 17$, $-6\leqslant k\leqslant 10$,	$-12 \leqslant h \leqslant 12$, $-15 \leqslant k \leqslant 15$,	$-11 \leqslant h \leqslant 10, -11 \leqslant k \leqslant 11,$
	$-29 \leqslant l \leqslant 27$	$-26 \leqslant l \leqslant 23$	$-23 \leqslant l \leqslant 23$	$-13 \leq l \leq 13$
Reflections collected	32414	10531	17819	6040
Reflections independent (R_{int})	17465 (0.1310)	5539 (0.0701)	4916 (0.1023)	3290 (0.0316)
Goodness-of-fit (GOF) on F^2	1.077	1.107	1.049	1.046
R indices $[I > 2\sigma I]$	0.1392, 0.3261	0.0887, 0.2109	0.0543, 0.0769	0.0307, 0.0766
R indices (all data)	0.2553, 0.4429	0.1387, 0.2529	0.1311, 0.1131	0.0320, 0.0779
Largest difference in peak and hole ($e \text{ Å}^{-3}$)	5.745 and -1.350	1.783 and -1.304	1.231 and -0.805	0.324 and -0.486

Table 2			
Summary of X-ray	crystallographic data	for complexes 5	5

-8.

	5	6	7	8
Formula	C ₃₆ H ₄₆ CdN ₈ O ₆	$C_{22}H_{22}CdCl_2N_6O_4$	$C_{31}H_{26}CdN_6O_6$	C ₅₆ H ₇₂ Cd ₂ N ₁₆ O ₈
Formula weight	799.21	617.76	690.98	1322.10
T (K)	293(2)	293(2)	298(2)	293(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Crystal system	triclinic,	triclinic	monoclinic	triclinic
Space group	PĪ	ΡĪ	C2/c	ΡĪ
a (Å)	9.0378(7)	10.4146(5)	32.403(3)	11.0827(7)
b (Å)	10.8628(9)	10.8203(8)	8.9030(7)	12.2160(6)
<i>c</i> (Å)	10.8658(10)	11.4181(12)	23.075(2)	13.1214(8)
α (°)	67.047(8)	72.444(6)	90	83.785(5)
β(°)	78.711(7)	88.580(6)	118.020(2)	65.771(6)
γ (°)	84.938(6)	85.092(5)	90	73.324(5)
V (Å ³)	963.21(14)	1222.27(17)	5876.5(9)	1551.75(16)
Z	1	2	8	1
D_{calcd} (Mg/m ³)	1.378	1.679	1.562	1.415
Absorption coefficient (mm ⁻¹)	0.620	1.154	0.798	0.749
F(000)	414	620	2800	680
Crystal size, mm	$0.37 \times 0.28 \times 0.23$	$0.42 \times 0.37 \times 0.31$	$0.34 \times 0.27 \times 0.18$	$0.45 \times 0.31 \times 0.25$
θ (°)	2.81-25.02	2.71-25.02	2.40-25.02	3.06-25.02
Limiting indices	$-10\leqslant h\leqslant 10$, $-12\leqslant k\leqslant 12$,	$-12\leqslant h\leqslant 12$, $-11\leqslant k\leqslant 12$,	$-38\leqslant h\leqslant 34$, $-10\leqslant k\leqslant 10$,	$-12\leqslant h\leqslant 13$, $-14\leqslant k\leqslant 14$,
	$-11 \leqslant l \leqslant 12$	$-7 \leqslant l \leqslant 13$	$-14 \leqslant l \leqslant 27$	$-15 \leqslant l \leqslant 15$
Reflections collected	5753	4317	5179	10752
Reflections independent (R_{int})	3387 (0.0377)	4317 (0.0000)	5179 (0.0000)	5483 (0.0283)
Goodness-of-fit (GOF) on F ²	1.041	1.068	1.049	1.092
R indices $[I > 2\sigma I]$	0.0389, 0.0773	0.0696, 0.1777	0.0631, 0.1631	0.0323, 0.0666
R indices (all data)	0.0444, 0.0811	0.0925, 0.2067	0.0997, 0.1906	0.0414, 0.0736
Largest difference in peak and hole (e $Å^{-3}$)	0.347 and -0.435	3.033 and –1.261	0.794 and -0.851	0.678 and –0.371



Fig. 1. Molecular structure of complex 1 at the 30% ellipsoid probability level. Due to the crowded nature of the structure, the atomic numbering is not shown.

aggregates are held together via a CH–Cl association between 4-CH of the pyrazole and the Cl of CCl₃, with a C–Cl distance of 3.716 Å, to form a chain. The chains are combined together by interchain Cl–Cl bonds with Cl–Cl separations of 3.399–3.457 Å to form a sheet extending in a direction that makes a dihedral angle of ca. 60° with the bc plane (Fig. 2). The sheets are further stacked along the direction that is perpendicular to its extending direction via a CH–O association between 4-CH of the pyrazole and the nonbonded O atom of the carboxylate, with a C–O separation of 3.303 Å, CH₃–Cl associations between 3-CH₃ of the pyrazole and the Cl of CCl₃ with C–Cl distances of 3.579–3.621 Å and a CH₃– π association between 3-CH₃ of the pyrazole ring, with a C–Cg distance of 3.561 Å, to form a 3D layer network

structure. Herein the neighboring sheets are slipped some distance from each other along the extending directions.

3.2.2. Crystal and molecular structure of $[Cd(Hdmpz)_2(L2)_2] \cdot H_2O(2)$

Crystals of **2** contain a mononuclear complex of the formulation $[Cd(Hdmpz)_2(L2)_2]\cdot H_2O$ (Fig. 3). Each Cd ion is octahedrally coordinated by four oxygen atoms of two chelating bidentate L2 ligands and by two nitrogen atoms, belonging to two monodentate pyrazole ligands, creating a CdN_2O_4 binding set. The coordination mode of the Cd centre is similar to the reported compounds $[Cd(La)_2 (Hdmpz)_2]$ where La = R-C₆H₄COO- (R = H, 2-Cl, 4-OH and 2-OH) [27]. The CdN₄O₂ unit possesses coordination distances and angles in the ranges 2.254(6)–2.463(7) Å and 54.3(2)–149.8(2)°,



Fig. 2. Packing diagram of compound 1 showing the sheet extending in the direction that makes a dihedral angle of ca. 60° with the bc plane.



Fig. 3. Molecular structure of complex 2 at the 30% ellipsoid probability level. Due to the crowded nature of the structure, the atomic numbering is not shown.

respectively. The two pyrazole ligands and the two carboxylates coordinated to the same Cd centre are in a cis arrangement.

The rms deviations of the pyrazole rings containing N1 and N2, and N3 and N4 atoms are 0.0051 and 0.0063 Å, respectively, and both rings are inclined at an angle of 102.3° to each other. The rms deviation of the indole ring containing the N5–C(13)–C(20) atoms is 0.0112 Å, and this ring forms dihedral angles of 10.8° and 96.4° with the above two pyrazole rings, respectively. The plane defined by the indole ring is almost perpendicular to the pyrazole ring containing the N3 and N4 atoms. The rms deviation of the indole ring the N6–C(23)–C(30) atoms is 0.0076 Å,

and this ring forms dihedral angles of 90.8° and 15.4° with the above two pyrazole rings, respectively. The two indole rings are inclined at an angle of 86.6° with each other. Due to the flexible bridge between the carboxylate and the pyrrole ring, the plane defined by the carboxylate is perpendicular to the aromatic ring to which it is attached.

At every mononuclear unit there is a water molecule attached through an N–H \cdots O_w hydrogen bond arising from the NH unit of the pyrazole, with an N–O distance of 2.801(9) Å, and an O–H_w \cdots O hydrogen bond between the water molecule (donor) and the carboxylate, with an O–O separation of 2.716(8) Å. The mononuclear

units are linked together by an N–H···O hydrogen bond between the pyrrole NH and the carboxylate, with an N–O distance of 2.938(9) Å, an N–H···O hydrogen bond between the NH of the pyrazole and the water molecule, with an N–O distance of 2.807(9) Å, and an O–Hw···O hydrogen bond between the water molecule and the carboxylate, with an O–O distance of 2.744(8) Å, to form a chain running along the b axis direction. In the chain the Cd–Cd separation of neighboring Cd centres in the same chain is 8.582 Å, which is equal to the length of the b axis. The Cd–Cd distance between two adjacent chains is 11.215 Å, while the Cd–Cd separation between the third chain and the first chain is 22.297 Å, which is equal to the length of the *c* axis.

The chains are combined together by an interchain $CH-\pi$ association between the phenyl CH of the anion and the aromatic ring of the indole-3-acetate, with a C-Cg distance of 3.512 Å, to form a sheet extending parallel to the bc plane (Fig. 4). Two sheets are joined together by an intersheet $CH-\pi$ association between 4-CH of the pyrazole and the pyrazole ring, with a C-Cg distance of 3.741 Å, to form a double sheet structure. The double sheets are further stacked along the a axis direction via a $CH_2-\pi$ association between the CH_2 spacer of the anion and the aromatic ring of the indole moiety, with a C-Cg distance of 3.647 Å, to form a 3D layer network structure. Herein the adjacent sheets are slipped some distance from each other along the *b* and *c* axis directions.

3.2.3. Crystal and molecular structure of $Cd(Hdmpz)_2(L3)_2$ (3)

The structural determination revealed that compound **3**, of the formula Cd(Hdmpz)₂(L3)₂, has 4 formula units in the unit cell. As illustrated in Fig. 5, the asymmetric unit consists of one Cd^{II} cation, two pyrazole molecules and two 4-methylbenzoate ligands. The pyrazolate unit acts as a monodentate terminal ligand. The carboxylates are coordinated to the Cd^{II} cation in a bischelating bidentate fashion. Similar to compound **2**, the Cd centre has a hexa-coordinate geometry with two Cd–N bonds and four Cd–O_{carboxylate} bonds. The Cd–N distances are in the range 2.281(6)–2.304(5) Å. The Cd–O_{carboxylate} distances are in the range 2.282(4)–2.449(5) Å.

The coordination arrangement around the Cd centre in complex **3** is a distorted octahedron, with coordination angles in the range $54.7(2)-132.6(2)^{\circ}$. The geometrical parameters of this species closely match those of compound **2**.

The root mean square (rms) deviations of the pyrazole rings containing the N1 and N2 atoms, and the N3 and N4 atoms are 0.0046 and 0.0036 Å, respectively, and the dihedral angle between the two pyrazole rings is 76.5°. The rms deviations of the phenyl rings of the anions are 0.0030 Å for the group C12–C17, and 0.0104 Å for the group C20–C25, and the two phenyl rings have a dihedral angle of 116.9° to each other.

The adjacent mononuclear moieties are connected together through N–H···O hydrogen bonds between the NH unit at the pyrazole and the carboxylate, with N-O distances of 2.878(7)-2.904(7) Å. CH₃...O interactions between the 5-CH₃ of the pyrazole and the O atom of the anion, with C-O separations of 3.404-3.461 Å, to form a chain running along the *b* axis direction. In the chain the neighboring Cd-Cd distance is 6.746 Å, the distance between the first Cd and the third Cd centres is 13.383 Å, which is equal to the length of the b axis. The interchain Cd-Cd distance is 10.448 Å. The chains are held together by an interchain CH…O interaction between the phenyl CH of the anion and the carboxylate, with a C–O distance of 3.422 Å, and a CH₃…O association between the CH₃ of the anion and the carboxylate, with a C-O distance of 3.483 Å, to form a sheet extending along the ab plane (Fig. 6). The sheets are further stacked along the c axis direction via an intersheet $CH_3-\pi$ association between the CH_3 group at the anion and the phenyl ring of the anion, with a C-Cg distance of 3.508 Å to form a 3D layer network structure. Herein the neighboring sheets are slipped some distance from each other along the a and b axis directions.

3.2.4. Crystal and molecular structure of $Cd(Hdmpz)_4(L4)_2$ (4)

The asymmetric unit of **4**, $(Cd(Hdmpz)_4(L4)_2)$, contains one octahedrally coordinated Cd(II) ion, two monodentate L4 anions and four Hdmpz groups, as shown in Fig. 7. The Cd ion is located



Fig. 4. The sheet structure of compound 2 extending parallel to the bc plane.



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



Fig. 6. The sheet structure of 3 extending along the ab plane.

at (0.5, 0.5, 0). The molecular structure of **4** resembles complexes **2** and **3**.

The CdN₄O₂ moiety has coordination distances and angles in the ranges 2.289(2)–2.402(2) Å and 87.24(7)–180.0°, respectively. The root mean square (rms) deviations of the pyrazole ring containing the N1 and N2 atoms, and N3 and N4 atoms are 0.0013 and 0.0020 Å, respectively, and the dihedral angle between the two pyrazole rings is 73.2°. The rms deviation of the phenyl ring of the anion with C12–C17 is 0.0016 Å, and the phenyl ring intersects the above two pyrazole rings with angles of 127.0° and 54.0° respectively. In **4**, the non-bonded oxygen atoms, far enough from the Cd ions with distances of 3.742 Å, are involved in two intramolecular hydrogen bonds, (N(2)–H(2)···O(2) and N(4)–H(4)···O(2),

with N–O distances ranging from 2.807(3) to 2.832(3) Å and H–O distances of 1.98–2.00 Å.

Compound **4** is mononuclear. The mononuclear units are arranged linearly in the ab plane with a Cd–Cd distance of 11.865 Å. There are, however no bonding interactions between these mononuclear units (Fig. 8).

3.2.5. Crystal and molecular structure of $Cd(Hdmpz)_4(L5)_2$ (5)

For compound **5**, the asymmetric unit of Cd(Hdmpz)₄(L5)₂ contains one six-coordinated Cd(II) ion, two L5 anions and four Hdmpz groups, as is shown in Fig. 9. The Cd ion is located at the inversion center (0.5, 0.5, 0.5). The Cd–O distance are 2.365(2) Å, the Cd–N distances are 2.362(2) and 2.389(2) Å, which are similar to the corresponding bond distances in **4**. In this case, the Cd(1)–O(1), and Cd(1)–N(1) bond lengths are of comparable values.

The root mean square (rms) deviations of the pyrazole ring containing the N1 and N2 atoms, and the N3 and N4 atoms are 0.0021 and 0.0018 Å, respectively, and the dihedral angle between the two pyrazole rings is 109.1°. The rms deviation of the benzene ring, C12–C17, of the anion is 0.0027 Å, and this forms dihedral angles of 65.0° and 48.5° with the above two pyrazole rings, respectively.

In **5**, the non-bonded oxygen atoms, far enough from the Cd ions with distances of 3.688 Å, are involved in two intramolecular hydrogen bonds, $(N(2)-H(2)\cdots O(2) \text{ and } N(4)-H(4)\cdots O(2)$, with N–O distances ranging from 2.706(3) to 2.737(3) Å and H–O distances of 1.91 Å.

The mononuclear moieties are linked together via CH– π interactions between the phenyl CH of the anion and the phenyl ring of the anion, with a C–Cg distance of 3.581 Å, to form chain. The chains are arranged in parallel in the same plane, that is parallel to the ab plane, to form a sheet (Fig. 10), yet there are no bonding interactions between these chains.

3.2.6. Crystal and molecular structure of $Cd(Hdmpz)_2(L6)_2$ (6)

The structural determination reveals that compound **6**, of the formula $Cd(Hdmpz)_2(L6)_2$, crystallizes with 2 formula units in the unit cell. As illustrated in Fig. 11, the asymmetric unit consists of one Cd^{II} cation, two pyrazole molecules and two carboxylate ligands. The pyrazole unit acts as a monodentate terminal ligand, with Cd–N distances of 2.260(7)–2.275(6) Å. The complex is mononuclear and the pair of pyrazoles and the anions are in cis positions. The carboxylate groups coordinate in a chelating bidentate manner with Cd–O distances of 2.343(5)–2.398(6) Å. The



Fig. 7. Molecular structure of complex 4 at the 30% ellipsoid probability level. Due to the crowded nature of the structure, the atomic numbering is not shown.



Fig. 8. The packing diagram showing the linearly arranged mononuclear units in the ab plane.

coordination arrangement around the Cd centre in complex 6 is a distorted octahedron with coordination angles in the range $54.9(2)-175.4(2)^{\circ}$. The mononuclear units are linked together through N-H-O hydrogen bonds between the NH unit of the pyrazole and the carboxylate, with N-O distances of 2.779(9)-2.782(9) Å, and a $CH_3 \cdots O$ interaction between the 5- CH_3 group of the pyrazole and the O atom of the carboxylate, with a C-O separation of 3.575 Å, to form a chain running along the a axis direction. In complex 6, there also exist intramolecular Cl-O contacts between the Cl atom of the anion and the coordinated O atoms of the carboxylate, with Cl-O distances of 2.995-3.057 Å. In this case, the Cl-O contact is somewhat stronger than a reported example [28]. In the chain, the neighboring Cd–Cd distances are 5.419 and 5.514 Å. The distance between the first Cd and the third Cd centres are 10.415 Å, which is equal to the length of the a axis, while the interchain Cd-Cd distances are 12.671 and 15.221 Å. The chains are held together by interchain π - π interactions between the pyridinic rings of the anion, with a Cg-Cg distance of 3.249 Å, to form a sheet extending along the direction that makes an angle of ca. 60° with the ab plane (Fig. 12). The sheets are further stacked along the direction that is perpendicular with its

extending direction via intersheet π - π stacking interactions between the pyridinic rings, with a Cg–Cg distance of 3.31 Å, to form a 3D layer network structure. In this regard, neighboring sheets are also slipped by some distance from each other along the extending direction.

3.2.7. Crystal and molecular structure of Cd(Hdmpz)(HL7)₂ (7)

In compound **7**, there are 8 formula units in the unit cell. Each Cd ion is octahedrally coordinated by five oxygen atoms of four HL7 ligands and by one nitrogen atom, belonging to the monodentate pyrazole ligand (Fig. 13). The N6, C28, C29, C30 and C31 atoms are all disordered over two positions with equal occupancy. The carboxylate of one anion is coordinated to two Cd centres in a tridentate chelating bridging fashion, while the other anion is coordinated to two Cd centres in a bidentate bridging mode. The CdNO₅ moiety possesses coordination distances and angles in the ranges 2.177(7)-2.532(6) Å and $55.2(2)-170.1(2)^{\circ}$, respectively; thus, the overall coordination geometry of the Cd centre is distorted octahedral. The two pairs of C–N bond distances related with the azo groups in the two anions are almost equal to each other, to within the experimental error [N(1)–C(6),



Fig. 9. Molecular structure of complex 5, at the 30% ellipsoid probability level. Due to the crowded nature of the structure, the atomic numbering is not shown.



Fig. 10. Packing diagram of compound 5 with the sheet structure extending parallel to the ab plane.

1.422(10) Å; N(2)–C(8), 1.427(11) Å; N(3)–C(19), 1.431(9) Å; N(4)–C(21), 1.434(10) Å], indicating equal orbital overlap between the N and C atoms. In compound **7** the ligand HL7, (2-hydroxy-5-(phenyldiazenyl)benzoate), adopts an E conformation about the N=N bond.

There exists an intramolecular hydrogen bond $(N(6)-H(6)\cdots O(5))$ in **7** with an N–O distance of 2.934(11) Å and an H–O distance of 2.15 Å. In addition to the intramolecular N–H···O hydrogen bond, there also exists intramolecular O–H···O hydrogen bonds between the phenol OH group and the oxygen atoms of the carboxylate to produce an S¹₁(6) loop motif. This feature is similar

to that found in salicylic acid [29], and in the previously reported structure of a deprotonated compound based on o-hydroxy benzoic acid derivatives [30]. As expected, the O–O separations, 2.556(8)–2.563(10) Å (mean: 2.559 Å), are essentially in the upper limit of the documented data [2.531(4)–2.570(4) Å] [31] 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, mean: 2.588 Å), as a result of the deprotonation.

The carboxylate of one anion coordinates to two Cd centres in a tridentate chelating bridging fashion, while the other anion coordi-



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

nates to two Cd centres in a bidentate bridging mode. The anions and the Cd centres form a chain running along the b axis direction. In this regard the corresponding pyrazole and anions are arranged antiparallel on both sides of the chain. The Cd-Cd distances along the chain are 4.027 and 4.895 Å. The pyrazole ligands are attached to the chain via the Cd-N bonds. There exist an intrachain CH-N association between the CH group of the benzene ring in the anion and the azo group, with a C-N separation of 3.630 Å, and a CH₃-O interaction between the 5-CH₃ group of the pyrazole and the phenol unit, with a C–O distance of 3.195 Å. The chains are joined together by a CH-O interaction between the 4-CH group of the pyrazole and the phenol unit, with a C-O distance of 3.402 Å, and a CH₃-N association between the 5-CH₃ group of the pyrazole and the azo group, with a C-N separation of 3.651 Å, to form a sheet extending parallel to the bc plane (Fig. 14).

3.2.8. Crystal and molecular structure of [Cd₂(Hdmpz)₆(L8)₂]·(Hdmpz)₂ (**8**)

Crystals of **8** contain a dinuclear $[Cd_2(Hdmpz)_6(L8)_2]$ moiety (Fig. 15), and there is 1 formula unit in the unit cell. Each Cd centre is octahedrally coordinated by three oxygen atoms of two different L8 anions and by three nitrogen atoms belonging to three monodentate pyrazoles, with a CdN_3O_3 bonding set. The phthalate anion coordinates to one metal ion in a chelating form with two of the four oxygen atoms, and further bridges a neighboring metal ion with one O of the remaining two oxygen atoms. This coordinating mode is different from the corresponding compound $Zn_3(\mu-dmpz)_4(Hdmpz)_2(L8)$ [20b]. The CdN₃O₃ unit possesses coordination distances and angles in the ranges 2.271(2)–2.463(2) Å and 78.48(6)–175.77(7)°, respectively.

The Cd–Cd separation in 8 is 5.333 Å. In the dinuclear units there are two pyrazole molecules bonded through an N-H...N hydrogen bond between the NH group of the coordinated pyrazole and the ring N of the non-coordinated pyrazole, with an N-N distance of 2.943(4) Å, and an N-H···O hydrogen bond between the NH group of the non-coordinated pyrazole and the O of the carboxylate, with an N–O distance of 2.810(3) Å. The dinuclear moieties, with the pyrazole ligands, were linked together by a $CH_3-\pi$ association between the 3-CH₃ group of the coordinated pyrazole and the aromatic ring of a non-coordinated pyrazole, with a C-Cg distance of 3.741 Å, to form a chain. In the chain the Cd–Cd separation between adjacent dinuclear moieties is 9.768 Å. The chains running parallel in the same plane form a sheet extending along the direction that makes an angle of ca. 60° with the bc plane (Fig. 16). However, no associations were found between these chains. The sheets are further stacked along the direction that is perpendicular with the extending direction by an intersheet CH₃-O association between the CH₃ group of the coordinated pyrazole and the nonbonded O atom of the carboxylate, with a C-O distance of 3.485 Å, to form a 3D network structure.

3.3. Thermogravimetry (TG)

For **1**, the water molecule was released between 94.8 and 115.7 °C (Found 1.32%, Calcd. 1.41%). The weight loss of 29.98% (Calcd. 30.07%) corresponds to the loss of four Hdmpz molecules in the temperature range 173.6–269.2 °C, and the weight loss of 50.84% between 292.2 and 457.3 °C arises from the loss of the four trichloroacetates (Calcd. 50.91%). For **2** the water molecule was liberated between 91.5 and 102.6 °C (Found 2.61%, Calcd. 2.68%). The



Fig. 12. The sheet structure of compound 6 extending along the direction that makes an angle of ca. 60° with the ab plane.



Fig. 13. Molecular structure of complex 7, at the 30% ellipsoid probability level. Due to the crowded nature of the structure, the atomic numbering is not shown.



Fig. 14. The sheet structure of compound 7 extending parallel to the *bc* plane.

two Hdmpz molecules were removed in the temperature range 167.4-258.9 °C (Found 28.55%, Calcd. 28.61%) and the carboxylates were decomposed at 315.7-421.2 °C (Found 51.87%, Calcd. 51.94%). The TGA studies showed that **3** is stable below 160 °C. Its decomposition begins at 165.2 °C. The weight loss of 33.33% in the temperature range 165.2-255.8 °C is caused by the loss of the two pyrazole molecules (Calcd. 33.39%). The weight loss of 46.94% from 320.2 to 427.7 °C arises from the loss of two L3 ligands (Calcd. 47.05%). For **4**, the first weight loss of 49.96% in the temperature range 152.9-249.8 °C is attributed to the loss of four pyrazole molecules (Calcd. 50.05%). The second weight loss of 35.18% from 289.6 to 409.8 °C is due to the loss of the two L4 ligands

(Calcd. 35.26%). For **5**, the first weight loss stage occurs between 163.1 and 256.0 °C and corresponds to the removal of four Hdmpz ligands (calcd.: 48.05%, found: 47.97%). The second stage between 296.8 and 414.6 °C is accompanied by a mass loss of 37.71% for two 4-methoxybenzoates (calcd.: 37.79%). Complex **6** experiences a first weight loss of 31.02% in the temperature range 167.6-260.5 °C, which is due to the loss of two pyrazole molecules (Calcd. 31.08%). The second weight loss of 50.61% was observed between 301.0 and 443.9 °C, which is attributed to the loss of the bonded carboxylates (Calcd. 50.67%). For **7**, the first weight loss between 161.5 and 225.6 °C corresponds to the release of two neutral pyrazoles (found: 13.82%, calcd. 13.89%). The carboxylate ligands are



Fig. 15. Molecular structure of complex 8, at the 30% ellipsoid probability level. Due to the crowded nature of the structure, the atomic numbering is not shown.



Fig. 16. The sheet structure of compound 8 extending along the direction that makes an angle of ca. 60° with the *bc* plane.

lost in the second stage in the temperature range 312.8-431.7.0 °C (found: 69.67%, calcd. 69.76%). For **8**, the first weight loss of 58.02% (Calcd. 58.09%) corresponds to the loss of 8 Hdmpz molecules in the temperature range 142.7–264.5 °C, and the second weight loss of 24.73% between 293.3 and 452.1 °C arises from the loss of the two L8 ligands (Calcd. 24.81%).

4. Summary

In summary, the use of 3,5-dimethylpyrazole and different carboxylate ligands afforded a series of mononuclear to dinuclear Cd complexes. Although synthesized by the same method, they showed different structures ranging from a 0D discrete mononuclear arrangement, sheet, 3D network to a 3D layer network. The octahedral geometry for Cd was observed in the X-ray studies, with N_4O_2 , N_3O_3 , N_2O_4 and NO_5 bonding sets around the Cd centres. In these complexes, the metal centers are coordinated by 3,5-dimethylpyrazole, and there are no deprotonated 3,5-dimethylpyrazole anions. The carboxylate groups behave as monodentate, chelating bidentate, bidentate bridging and tridentate bridging ligands.

Complexes **1–8** have a great deal of intra- and intermolecular non-bonding interactions (including classical hydrogen bonds, CH–Cl, CH₃–Cl, Cl···Cl, Cl···O, CH–N, CH₃–N, C–H···O, CH₃···O, C–H··· π , CH₂··· π , CH₃– π and π – π interactions) in their crystals, which contribute to the formation and stabilization of the final structures.

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Appendix A. Supplementary data

CCDC 927746, 927736, 927738, 927739, 930290, 930292, 937416 and 926288 contains the supplementary crystallographic data for **1–8**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK: fax: (+44) 1223-336-033: or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/ 10.1016/j.poly.2014.02.041.

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, J. Chem. Soc., 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] D.G. Tuck, Rev. Inorg. Chem. 1 (1979) 209.
- [12] (a) 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;
- 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, T. Friscić, N. Blagden, 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] 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.
- [27] K. Bania, N. Barooah, J.B. Baruah, Polyhedron 26 (2007) 2612.
- [28] S.W. Jin, D.Q. Wang, Y.C. Xu, J. Coord. Chem. 65 (2012) 1953.
- [29] X.M. Chen, Z.T. Xu, X.C. Huang, J. Chem. Soc., Dalton Trans. (1994) 2331.
 [30] M. Sundaralingam, L.H. Jensen, Acta Crystallogr. 18 (1965) 1053.
- [31] G. Simith, A.W. Hartono, U.D. Wermuth, P.C. Healy, J.M. White, A.D. Rae, Aust. J. Chem. 58 (2005) 47.