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Construction of six non-covalent-bonded supramolecules from reactions of cadmium(II), and zinc(II) with 3,5-dimethylpyrazole and carboxylate ligands

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ABSTRACT

Six new complexes $Cd(Hdmpz)_2(L1)_2$ (**1**) (Hdmpz = 3,5-dimethylpyrazole, L1 = nicotinate), $Zn(Hdmpz)_2(L2)_2$ (**2**) (L2 = N-phenylanthranilate), $Zn(Hdmpz)_2(L3)_2$ (**3**) (L3 = N-phenylmaleamate), $Cd(Hdmpz)_4(L4)_2$ (**4**) (L4 = 5-chlorosalicylate), $Cd_2(Hdmpz)_6(L5)_2Cd(Hdmpz)_4(HL5)_2{\cdot}2H_2O$ (**5**) (HL5 = hydrogen 1,4-cyclohexanedicarboxylate, L5 = 1,4-cyclohexanedicarboxylate), and $Zn(Hdmpz)_2(L6)$ (**6**) (L6 = sebacate) were prepared and 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 trinuclear structures with tetrahedral geometry around each zinc center, and octahedral geometry around each cadmium ion. The Hdmpzs in all compounds are coordinated only in monodentate fashion with its neutral N group. In all of the complexes except **5**, all carboxylate groups behave as monodentate ligands. The uncoordinated O atom of the carboxylate group in **1**, **2**, **4**, **5**, and **6**, forms intramolecular hydrogen bond with the N–H group of the Hdmpz. On the basis of X-ray crystallographic study the rich intra- and intermolecular non-covalent interactions such as classical hydrogen bonds, $Cl{\cdots}O$, $C{-}H{\cdots}O$, $CH_2{\cdots}O$, $CH_3{\cdots}O$, $C{-}H{\cdots}\pi$, $CH_3{-}\pi$, and $\pi{-}\pi$ interactions are analyzed. The extensive nonbonding interactions in these compounds are responsible for different structures such as 3D network, 2D sheet, and 3D layer network structure.

1. Introduction

The design and synthesis of metal–organic framework structures have received enormous attention [1] in recent years due to their potential applications in diverse areas such as magnetism, catalysis, optical, and sorption properties [2,3]. 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, the hydrogen bonding and π–π stacking interactions, the solvent molecules, counterions and the ratio of metal salt to organic ligand also influence the formation of the ultimate architectures.

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

Pyrazole or pyrazole derivative has been widely employed in polypyrazolylborates to stabilize a variety of organometallic and coordination compounds [11,12]. Up to now, a variety of complexes containing 3,5-dimethylpyrazole (Hdmpz) have been synthesized and employed in coordination chemistry or organometallic chemistry [13–15]. Many complexes with simple pyrazole both in terminal as well as in bridging mode are also available [16–18]. But the complexes in the presence of carboxylic acids and pyrazole derivatives are not very common except some recently reported examples in the literatures [19]. We have been working with coordination compounds with mixed ligands of carboxylate and 3,5-dimethylpyrazole [20]. The pyrazole ligand and the carboxylate ligand 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 coordination polymers and the role the weak non-covalent interactions played in forming

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the final supramolecular frameworks, we select the carboxylic acids bearing the NH, CONH, OH and Cl units which are good groups in forming hydrogen bonds [21]. Thus, in the following, we report the synthesis, structural characterization and thermal behaviour of Zn and Cd complexes via combination of 3,5-dimethylpyrazole (Hdmpz) and different carboxylate ligands (Scheme 1), namely Cd(Hdmpz)$_2$(L1)$_2$ (**1**) (Hdmpz = 3,5-dimethylpyrazole, L1 = nicotinate), Zn(Hdmpz)$_2$(L2)$_2$ (**2**) (L2 = N-phenylanthranilate), Zn(Hdmpz)$_2$(L3)$_2$ (**3**) (L3 = N-phenylmaleamate), Cd(Hdmpz)$_4$(L4)$_2$ (**4**) (L4 = 5-chlorosalicylate), Cd$_2$(Hdmpz)$_6$(L5)$_2$Cd(Hdmpz)$_4$(HL5)$_2$·2H$_2$O (**5**) (HL5 = hydrogen 1,4-cyclohexanedicarboxylate), and Zn(Hdmpz)$_2$(L6) (**6**) (L6 = sebacate).

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) 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 N$_2$ atmosphere between room temperature and 800 °C (heating rate 10 °C min^{-1}) using Al crucibles.

2.2. Synthesis of complexes

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

A solution of Cd(CH$_3$COO)$_2$·2H$_2$O (0.027 g, 0.10 mmol) in 6 mL of MeOH was added to a MeOH solution (10 mL) containing Hdmpz (0.019 g, 0.20 mmol) and nicotinic acid (HL1) (0.049 g, 0.40 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 was added till the precipitate dissolved completely. The clear solution was filtered into a test tube, after several days colorless block crystals formed, which was filtered off, washed with MeOH and dried under vacuum to afford 0.082 g of the product. Yield: 75% (Based on Hdmpz). Elemental analysis performed on crystals exposed to the atmosphere: *Anal.* Calc. for C$_{22}$H$_{24}$CdN$_6$O$_4$ (548.87): C, 48.09; H, 4.37; N, 15.30. Found: C, 48.02; H, 4.33; N, 15.22%. Infrared spectrum (KBr disc, cm^{-1}): 3444w(ν_{as}(NH)), 3288w(ν_s(NH)), 3132m, 3035m, 2945m, 2868m, 1614s(ν_{as}(COO)), 1590m, 1565m, 1508m, 1458m, 1419s(ν_s(COO)), 1389m, 1296m, 1228s, 1191m, 1050m, 1016m, 967m, 861m, 804m, 755m, 699m, 645m, 617m.

2.2.2. Synthesis of Zn(Hdmpz)$_2$(L2)$_2$ (**2**)

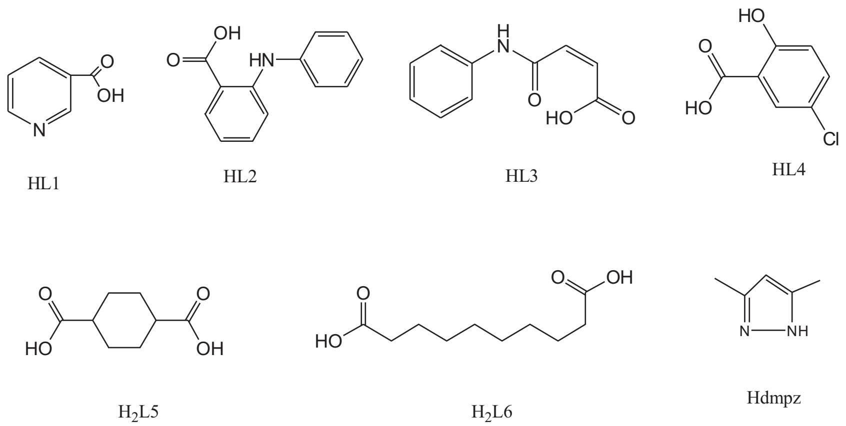
A solution of Zn(CH$_3$COO)$_2$·2H$_2$O (0.022 g, 0.10 mmol) in 5 mL of EtOH was added to a MeOH solution (12 mL) containing Hdmpz (0.019 g, 0.20 mmol) and N-phenylanthranilic acid (HL2) (0.085 g, 0.40 mmol), under continuous stirring. The solution was stirred for about 2 h at room temperature, the solution became turbid, then a few drops of conc. ammonia was added till the solution became clear completely. The clear solution was filtered into the test tube, after several days colorless crystals formed, which was filtered off, washed with EtOH and dried under vacuum to afford 0.10 g of the product. Yield: 76% (Based on Hdmpz). Elemental analysis performed on crystals exposed to the atmosphere: *Anal.* Calc. for C$_{36}$H$_{36}$N$_6$O$_4$Zn (682.08): C, 63.33; H, 5.27; N, 12.31. Found: C, 63.27; H, 5.22; N, 12.23%. Infrared spectrum (KBr disc, cm^{-1}): 3462br, 3333m, 3143m, 3065m, 2990m, 2969w, 2872m, 1627s(ν_{as}(COO)), 1596m, 1525m, 1464m, 1422s(ν_s(COO)), 1381m, 1289m, 1245m, 1169m, 1102m, 1064m, 952m, 887m, 832m, 789m, 744m, 683m, 647m, 609m.

2.2.3. Synthesis of Zn(Hdmpz)$_2$(L3)$_2$ (**3**)

A solution of Zn(CH$_3$COO)$_2$·2H$_2$O (0.022 g, 0.10 mmol) in 5 mL of EtOH was added to an EtOH solution (6 mL) containing Hdmpz (0.019 g, 0.20 mmol) and N-phenylmaleamic acid (HL3) (0.076 g, 0.40 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 was added till the solution became clear completely. The clear solution was filtered into the test tube, after several days colorless crystals formed, which was filtered off, washed with EtOH and dried under vacuum to afford 0.092 g of the product. Yield: 72% (Based on Hdmpz). Elemental analysis performed on crystals exposed to the atmosphere: *Anal.* Calc. for C$_{30}$H$_{32}$N$_6$O$_6$Zn (637.99): C, 56.43; H, 5.01; N, 13.16. Found: C, 56.36; H, 4.92; N, 13.11%. Infrared spectrum (KBr disc, cm^{-1}): 3414w, 3283m, 3072m, 2985m, 2865m, 1660s(C=O), 1623m, 1596s(ν_{as}(COO)), 1497m, 1449m, 1398s(ν_s(COO)), 1326m, 1279m, 1237m, 1176m, 1079m, 1021m, 967m, 882m, 804m, 762m, 721m, 674m, 617m.

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

A solution of Cd(CH$_3$COO)$_2$·2H$_2$O (0.027 g, 0.10 mmol) in 6 mL of MeOH was added to an EtOH solution (4 mL) containing Hdmpz (0.019 g, 0.20 mmol) and 5-chlorosalicylic acid (HL4) (0.069 g, 0.40 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 was added till the solution became clear completely. The clear solution was filtered into the test tube, after several days colorless crystals formed, which was



Scheme 1. The ligands used in this paper.

filtered off, washed with EtOH and dried under vacuum to afford 0.062 g of the product. Yield: 74% (Based on $Cd(CH_3COO)_2{\cdot}2H_2O$). Elemental analysis performed on crystals exposed to the atmosphere: *Anal.* Calc. for $C_{34}H_{40}CdCl_2N_8O_6$ (840.04): C, 48.57; H, 4.76; N, 13.33. Found: C, 48.52; H, 4.69; N, 13.26%. Infrared spectrum (KBr disc, cm^{-1}): 3546m, 3425w, 3268m, 3085m, 2928m, 2865m, 1611s(ν_{as}(COO)), 1557m, 1402s(ν_s(COO)), 1337m, 1269m, 1201m, 1176m, 1059m, 986m, 907m, 828m, 768m, 714m, 667m, 605m.

2.2.5. Synthesis of $Cd_2(Hdmpz)_6(L5)_2Cd(Hdmpz)_4(HL5)_2{\cdot}2H_2O$ (**5**)

A solution of $Cd(CH_3COO)_2{\cdot}2H_2O$ (0.027 g, 0.10 mmol) in 6 mL of MeOH was added to a MeOH solution (7 mL) containing Hdmpz (0.019 g, 0.20 mmol) and 1,4-cyclohexanedicarboxylic acid (H_2L5) (0.034 g, 0.20 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 was added till the solution became clear completely. The clear solution was filtered into a test tube, after several days colorless block crystals formed, which was filtered off, washed with MeOH and dried under vacuum to afford 0.044 g of the product. Yield: 44% ($Cd(CH_3COO)_2{\cdot}2H_2O$). Elemental analysis performed on crystals exposed to the atmosphere: *Anal.* Calc. for $C_{82}H_{126}Cd_3N_{20}O_{18}$ (2017.23): C, 48.78; H, 6.24; N, 13.88. Found: C, 48.72; H, 6.16; N, 13.83%. Infrared spectrum (KBr disc, cm^{-1}): 3577s(ν(OH)), 3436m, 3245m, 3119m, 2935s, 2858m, 1664s(ν(C=O)), 1627s, 1609s($\nu_{as}(COO^-)$), 1548m, 1498s, 1421s($\nu_s(COO^-)$), 1365m, 1295s(ν(C–O)), 1267m, 1174m, 1094m, 936m, 894m, 831m, 744m, 681m, 627m.

2.2.6. Synthesis of $Zn(Hdmpz)_2(L6)$ (**6**)

A solution of $Zn(CH_3COO)_2{\cdot}2H_2O$ (0.022 g, 0.10 mmol) in 5 mL of EtOH was added to a MeOH solution (4 mL) containing Hdmpz (0.019 g, 0.20 mmol) and sebacic acid (H_2L6) (0.040 g, 0.20 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 was added till the solution became clear completely. The clear solution was filtered into a test tube, after several days colorless block crystals formed, which was filtered off, washed with MeOH and dried under vacuum to afford 0.026 g of the product. Yield: 57% (Based on Hdmpz). Elemental analysis performed on crystals exposed to the atmosphere: *Anal.* Calc. for $C_{20}H_{32}N_4O_4Zn$ (457.87): C, 52.42; H, 6.98; N, 12.23. Found: C, 52.37; H, 6.91; N, 12.13%. Infrared spectrum (KBr disc, cm^{-1}): 3394m, 3242w, 3116m, 3062m, 2926m, 2851m, 1610s($\nu_{as}(COO^-)$), 1570m, 1509m, 1451m, 1409s($\nu_s(COO^-)$), 1382m, 1305m, 1281m, 1243m, 1184m, 1017m, 935m, 879m, 823m, 742m, 653m, 607m.

2.3. X-ray crystallography

A suitable crystal for single crystal X-ray analysis was mounted on a glass fiber on a Bruker SMART 1000 CCD diffractometer operating at 50 kV and 40 mA using Mo Kα 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 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**–**6** 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**–**6** were prepared in MeOH or EtOH system under room temperature via combination of the metal acetate, Hdmpz group, 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 with yields of 57–76%.

During the process the acetate has been substituted by the corresponding carboxylate ions, and all Hdmpzs retain their NH

Table 1
Summary of X-ray crystallographic data for complexes **1**–**3**.

	1	2	3
Formula	$C_{22}H_{24}CdN_6O_4$	$C_{36}H_{36}N_6O_4Zn$	$C_{30}H_{32}N_6O_6Zn$
Fw	548.87	682.08	637.99
T (K)	298(2)	298(2)	298(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	monoclinic	triclinic	monoclinic
space group	$P2_1/c$	$P\bar{1}$	$P2_1/n$
a (Å)	9.8418(5)	7.8060(6)	11.7551(12)
b (Å)	8.8992(7)	14.5599(13)	14.2725(16)
c (Å)	13.3314(11)	16.0201(15)	18.0856(19)
α (°)	90	109.088(2)	90
β (°)	104.2780(10)	91.9730(10)	94.7860(10)
γ (°)	90	94.4300(10)	90
V (Å^3)	1131.55(14)	1712.1(3)	3023.7(6)
Z	2	2	4
D_{calc} (Mg/m^3)	1.611	1.323	1.401
Absorption coefficient (mm^{-1})	1.007	0.764	0.865
$F(000)$	556	712	1328
Crystal size (mm)	0.32 × 0.19 × 0.12	0.33 × 0.19 × 0.16	0.41 × 0.29 × 0.21
θ Range (°)	2.78–25.02	2.31–25.02	2.25–25.02
Limiting indices	$-8 \leqslant h \leqslant 11$	$-9 \leqslant h \leqslant 9$	$-13 \leqslant h \leqslant 13$
	$-10 \leqslant k \leqslant 10$	$-17 \leqslant k \leqslant 17$	$-16 \leqslant k \leqslant 12$
	$-15 \leqslant l \leqslant 15$	$-11 \leqslant l \leqslant 19$	$-20 \leqslant l \leqslant 21$
Reflections collected	5783	8748	14844
Reflections independent (R_{int})	1992 (0.0864)	5968 (0.0389)	5322 (0.0419)
Goodness-of-fit (GOF) on F^2	0.972	1.040	1.031
R indices [$I > 2\sigma I$]	0.0499, 0.1224	0.0557, 0.1038	0.0350, 0.0773
R indices (all data)	0.0654, 0.1338	0.1252, 0.1318	0.0628, 0.0927
Largest difference peak and hole (e Å^{-3})	1.376, −0.797	0.336, −0.413	0.300, −0.265

Table 2
Summary of X-ray crystallographic data for complexes **4**–**6**.

	4	**5**	**6**
Formula	$C_{34}H_{40}CdCl_2N_8O_6$	$C_{82}H_{126}Cd_3N_{20}O_{18}$	$C_{20}H_{32}N_4O_4Zn$
Fw	840.04	2017.23	457.87
T(K)	298(2)	298(2)	298(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	triclinic,	triclinic,	monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1/c$
a (Å)	9.3950(10)	9.9600(8)	15.6548(12)
b (Å)	9.7139(11)	14.2769(13)	8.8600(6)
c (Å)	11.2071(12)	17.1141(16)	17.7947(14)
α (°)	106.699(2)	93.5620(10)	90
β (°)	90.4330(10)	90.1790(10)	112.7090(10)
γ (°)	105.078(2)	99.931(2)	90
V (Å^3)	942.17(18)	2392.3(4)	2276.8(3)
Z	1	1	4
D_{calc} (Mg/m^3)	1.481	1.400	1.336
Absorption coefficient (mm^{-1})	0.775	0.733	1.110
F(000)	430	1046	968
Crystal size (mm)	0.36 × 0.25 × 0.16	0.46 × 0.35 × 0.32	0.28 × 0.18 × 0.15
θ Range (°)	2.28–25.02	2.38–25.02	2.48–25.01
Limiting indices	$-11 \leqslant h \leqslant 10$ $-9 \leqslant k \leqslant 11$ $-13 \leqslant l \leqslant 13$	$-11 \leqslant h \leqslant 11$ $-16 \leqslant k \leqslant 16$ $-13 \leqslant l \leqslant 20$	$-18 \leqslant h \leqslant 18$ $-10 \leqslant k \leqslant 10$ $-15 \leqslant l \leqslant 21$
Reflections collected	4740	11 876	11 108
Reflections independent (R_{int})	3276 (0.0242)	8275 (0.0495)	4024 (0.0488)
Goodness-of-fit (GOF) on F^2	1.085	1.017	1.043
R indices [$I > 2\sigma I$]	0.0371, 0.0905	0.0677, 0.1650	0.0504, 0.1212
R indices (all data)	0.0419, 0.0954	0.1111, 0.2042	0.0977, 0.1507
Largest difference peak and hole (e Å^{-3})	0.844, −0.626	1.441, −2.010	0.400, −0.429

groups. These compounds are not soluble in almost all common solvents. The infrared spectra of **1**–**6** were fully consistent with their formulations. The IR spectra of **1**–**6** display the characteristic carboxylate bands in the range 1596–1627 cm^{-1} for $v_{as}(CO_2)$ and at 1402–1422 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 of 188–209 cm^{-1} for all of the compounds. This suggests unidentate coordination mode for the carboxylate ligands in all of the compounds. Compound **5** contains additional carboxyl group with the chelating bidentate coordination mode with the $v_{as}(CO_2)$ and $v_s(CO_2)$ bands at 1627, and 1498 cm^{-1} (with the Δ value of 129 cm^{-1}), respectively. Compound **5** also displays strong IR peaks for the COOH groups. There are coordinated neutral Hmdpzs in all of the six compounds which is further confirmed by the presence of the 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 and the olefinic CH group of L3, respectively.

3.2. Crystal structure description

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

The compound **1** prepared by reaction of $Cd(CH_3COO)_2{\cdot}2H_2O$, nicotinic acid (HL1), and Hdmpz in MeOH solvents with ratios of 1:2:4 yields 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. The complex **1** crystallizes in the monoclinic system with space group $P2_1/c$.

Each Cd ion is octahedrally coordinated by two oxygen atoms of two monodentate L1 ligands, two nitrogen atoms from two L1 ligands, and two nitrogen atoms belonging to two different monodentate pyrazole ligands (Fig. 1). Herein the nicotinate coordinated to two different Cd ions in bismonodentate fashion with its N and one O atom of the carboxylate, respectively. Herein the coordinated N atom and the carboxylate in the same anion are in trans conformation in respect to the C atoms they are attached. The coordination mode of the nicotinate is similar to the reported compound of [Zn(L1)$_2$]$_n$ [26]. The two pyrazole ligands coordinated to the same Cd ion are in trans arrangement, so do the two carboxylate ligands coordinated to the same Cd ion.

The location of the H3 in **1**, binding nitrogen but not oxygen, is consistent with the different acidic characters of pyrazole and nicotinic acid [27], and also confirmed by the difference electron density map which found the H atoms. The Cd–N distances are 2.331(4) Å (Cd–N$_{pyrazole}$) and 2.419(4) Å (Cd–N$_{pyridine}$), respectively, the Cd–O distance is 2.364(3) Å, which are all in the bond length ranges of the reported compounds [28]. Yet the Cd–N$_{pyrazole}$ bond is shorter than the Cd–N$_{pyridine}$ bond. The angles around the Cd atom range from 86.93(13)° to 93.07(13)°.

Moreover **1** is not an ionic species consisting of monocationic Cd(II) complex and carboxylate counterions. In **1**, the non-bonded oxygen atom, far enough from the Cd ion with distance of 3.67 Å, is involved in the intramolecular hydrogen bond (N(3)–H(3)···O(2)#2, #2 $-x, y-1/2, -z-1/2$) with the N–O distance of 2.642(5) Å and H–O distance of 1.81 Å.

The dihedral angle between the pyrazole ring and the pyridine ring of the L1 is 76.3°. The carboxylate O1–C1–O2 rotated about 5.4° from the pyridine ring plane of the anion.

The compound **1** displays 2D sheet structure extending along the *bc* plane, which is shown in Fig. 2. In the sheet there exist CH–O interaction between the 2-CH of one anion and the uncoordinated O atom of the other anion with C–O distance of 3.228 Å, CH_3–O association between the 3-CH_3 group of the pyrazole and the uncoordinated O atom of the carboxylate with C–O distance of 3.397 Å, and π–π association between the aromatic rings of the anions with Cg–Cg distance of 3.393 Å. In the sheet the Cd–Cd separations between the neighboring Cd ions are 8.014 and 8.899 Å, respectively. The 2D sheets were further stacked along the *a* axis direction via the CH_3–π association between 5-CH_3 of the pyrazole and the aromatic ring of the anion with C–Cg distance of 3.500 Å to form 3D network structure.

Table 3
Selected bond lengths (Å) and angles (°) for **1**–**6**.

1			
Cd(1)–N(2)	2.331(4)	Cd(1)–O(1)#2	2.364(3)
Cd(1)–N(1)	2.419(4)	N(1)–C(6)	1.327(6)
N(1)–C(2)	1.337(6)	N(2)–C(8)	1.332(6)
N(2)–N(3)	1.353(6)	N(3)–C(10)	1.346(6)
O(1)–C(1)	1.255(6)	O(2)–C(1)	1.248(5)
N(2)#1–Cd(1)–N(2)	180.0(2)	N(2)#1–Cd(1)–O(1)#2	88.54(13)
N(2)–Cd(1)–O(1)#2	91.46(13)	O(1)#2–Cd(1)–O(1)#3	180.00(15)
N(2)#1–Cd(1)–N(1)	87.52(14)	N(2)–Cd(1)–N(1)	92.48(14)
O(1)#2–Cd(1)–N(1)	93.07(13)	O(1)#3–Cd(1)–N(1)	86.93(13)
N(1)–Cd(1)–N(1)#1	180.00(18)	C(6)–N(1)–C(2)	117.5(4)
O(2)–C(1)–O(1)	125.4(5)		
2			
Zn(1)–O(1)	1.920(3)	Zn(1)–O(3)	1.941(3)
Zn(1)–N(3)	1.994(4)	Zn(1)–N(5)	1.998(4)
N(1)–C(3)	1.384(5)	N(1)–C(8)	1.401(5)
N(2)–C(16)	1.375(5)	N(2)–C(21)	1.388(5)
N(3)–C(28)	1.331(6)	N(3)–N(4)	1.348(4)
N(4)–C(30)	1.324(5)	N(5)–C(33)	1.331(5)
N(5)–N(6)	1.347(4)	N(6)–C(35)	1.334(5)
O(1)–C(1)	1.265(5)	O(2)–C(1)	1.250(5)
O(3)–C(14)	1.267(5)	O(4)–C(14)	1.247(5)
O(1)–Zn(1)–O(3)	104.33(14)	O(1)–Zn(1)–N(3)	114.71(15)
O(3)–Zn(1)–N(3)	105.13(14)	O(1)–Zn(1)–N(5)	103.47(15)
O(3)–Zn(1)–N(5)	114.54(14)	N(3)–Zn(1)–N(5)	114.48(15)
C(3)–N(1)–C(8)	129.9(4)	C(16)–N(2)–C(21)	131.3(4)
O(2)–C(1)–O(1)	123.9(5)	O(4)–C(14)–O(3)	123.0(5)
3			
Zn(1)–O(4)	1.9423(19)	Zn(1)–O(1)	1.9600(18)
Zn(1)–N(5)	1.999(2)	Zn(1)–N(3)	2.034(2)
N(1)–C(4)	1.354(3)	N(1)–C(5)	1.411(3)
N(2)–C(14)	1.347(3)	N(2)–C(15)	1.414(3)
N(3)–C(22)	1.340(3)	N(3)–N(4)	1.357(3)
N(4)–C(24)	1.338(3)	N(5)–C(27)	1.331(3)
N(5)–N(6)	1.364(3)	N(6)–C(29)	1.342(3)
O(1)–C(1)	1.266(3)	O(2)–C(1)	1.218(3)
O(3)–C(4)	1.224(3)	O(4)–C(11)	1.267(3)
O(5)–C(11)	1.230(3)	O(6)–C(14)	1.231(3)
O(4)–Zn(1)–O(1)	112.96(8)	O(4)–Zn(1)–N(5)	108.57(9)
O(1)–Zn(1)–N(5)	109.17(8)	O(4)–Zn(1)–N(3)	125.24(9)
O(1)–Zn(1)–N(3)	94.56(8)	N(5)–Zn(1)–N(3)	105.00(9)
C(4)–N(1)–C(5)	129.1(2)	C(14)–N(2)–C(15)	129.1(2)
O(2)–C(1)–O(1)	126.6(2)	O(5)–C(11)–O(4)	124.1(3)
4			
Cd(1)–O(1)	2.321(2)	Cd(1)–N(3)	2.353(3)
Cd(1)–N(1)	2.383(2)	N(1)–C(9)	1.331(4)
N(1)–N(2)	1.357(3)	N(2)–C(11)	1.341(4)
N(3)–C(14)	1.329(4)	N(3)–N(4)	1.362(3)
N(4)–C(16)	1.334(4)	O(1)–C(1)	1.275(4)
O(2)–C(1)	1.246(4)	O(3)–C(3)	1.344(4)
O(1)#1–Cd(1)–O(1)	180.00(9)	O(1)–Cd(1)–N(3)#1	88.78(9)
O(1)–Cd(1)–N(3)	91.22(9)	N(3)#1–Cd(1)–N(3)	180.0
O(1)–Cd(1)–N(1)#1	88.60(9)	N(3)–Cd(1)–N(1)#1	86.87(9)
O(1)–Cd(1)–N(1)	91.40(9)	N(3)#1–Cd(1)–N(1)	86.87(9)
N(3)–Cd(1)–N(1)	93.13(9)	N(1)#1–Cd(1)–N(1)	180.0
O(2)–C(1)–O(1)	124.3(3)		
5			
Cd(1)–O(4)#1	2.193(5)	Cd(1)–N(3)	2.254(6)
Cd(1)–N(1)	2.333(5)	Cd(1)–O(2)	2.360(4)
Cd(1)–N(5)	2.366(5)	Cd(1)–O(1)	2.513(5)
Cd(2)–N(7)	2.338(6)	Cd(2)–N(9)	2.357(6)
Cd(2)–O(5)	2.387(5)	N(1)–C(18)	1.315(9)
N(1)–N(2)	1.349(8)	N(2)–C(20)	1.339(9)
N(3)–C(23)	1.312(10)	N(3)–N(4)	1.358(8)
N(4)–C(25)	1.342(10)	N(5)–C(28)	1.326(8)
N(5)–N(6)	1.350(7)	N(6)–C(65)	1.338(8)
N(7)–C(31)	1.326(9)	N(7)–N(8)	1.359(7)
N(8)–C(33)	1.322(9)	N(9)–C(36)	1.340(9)
N(9)–N(10)	1.348(8)	N(10)–C(38)	1.330(9)
O(1)–C(1)	1.243(8)	O(2)–C(1)	1.272(8)
O(3)–C(2)	1.239(9)	O(4)–C(2)	1.268(8)
O(5)–C(9)	1.252(8)	O(6)–C(9)	1.265(9)
O(7)–C(10)	1.202(8)	O(8)–C(10)	1.320(8)
O(4)#1–Cd(1)–N(3)	103.4(2)	O(4)#1–Cd(1)–N(1)	102.6(2)
N(3)–Cd(1)–N(1)	93.8(2)	O(4)#1–Cd(1)–O(2)	142.50(18)
N(3)–Cd(1)–O(2)	113.5(2)	N(1)–Cd(1)–O(2)	82.19(18)
O(4)#1–Cd(1)–N(5)	89.1(2)	N(3)–Cd(1)–N(5)	99.2(2)
N(1)–Cd(1)–N(5)	160.1(2)	O(2)–Cd(1)–N(5)	78.78(17)
O(4)#1–Cd(1)–O(1)	89.28(17)	N(3)–Cd(1)–O(1)	166.50(19)
N(1)–Cd(1)–O(1)	87.92(17)	O(2)–Cd(1)–O(1)	53.45(15)
N(5)–Cd(1)–O(1)	76.04(17)	N(7)#2–Cd(2)–N(9)	95.1(2)
N(7)–Cd(2)–N(9)	84.9(2)	N(7)–Cd(2)–O(5)#2	90.98(19)
N(9)–Cd(2)–O(5)#2	87.08(18)	N(7)–Cd(2)–O(5)	89.02(19)
N(9)–Cd(2)–O(5)	92.92(18)	O(1)–C(1)–O(2)	121.6(6)
O(3)–C(2)–O(4)	122.8(8)	O(5)–C(9)–O(6)	123.9(7)
O(7)–C(10)–O(8)	123.8(7)		
6			
Zn(1)–O(1)	1.923(3)	Zn(1)–O(3)	1.927(3)
Zn(1)–N(3)	1.998(4)	Zn(1)–N(1)	2.012(4)
N(1)–C(12)	1.323(6)	N(1)–N(2)	1.357(5)
N(2)–C(14)	1.341(6)	N(3)–C(17)	1.328(6)
N(3)–N(4)	1.364(5)	N(4)–C(19)	1.344(6)
O(1)–C(1)	1.278(5)	O(2)–C(1)	1.218(5)
O(3)–C(10)	1.272(5)	O(4)–C(10)	1.226(5)
O(1)–Zn(1)–O(3)	104.18(14)	O(1)–Zn(1)–N(3)	110.09(15)
O(3)–Zn(1)–N(3)	110.12(16)	O(1)–Zn(1)–N(1)	108.58(16)
O(3)–Zn(1)–N(1)	113.60(15)	N(3)–Zn(1)–N(1)	110.09(16)
O(2)–C(1)–O(1)	124.9(4)	O(4)–C(10)–O(3)	124.8(5)

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

Table 4
Hydrogen bond distances and angles in studied structures of **1**–**6**.

D–H···A	d(D–H) (Å)	d(H···A) (Å)	d(D···A) (Å)	<(DHA)(°)
1				
N(3)–H(3)···O(2)#2	0.86	1.81	2.642(5)	162.9
2				
N(6)–H(6)···O(4)	0.86	1.87	2.655(5)	150.8
N(4)–H(4)···O(2)	0.86	1.88	2.678(5)	152.9
N(2)–H(2)···O(4)	0.86	1.87	2.594(5)	141.5
N(1)–H(1)···O(2)	0.86	1.93	2.636(5)	138.1
3				
N(6)–H(6)···O(6)	0.86	2.06	2.900(3)	167.0
N(4)–H(4)···O(3)	0.86	1.92	2.774(3)	171.9
N(2)–H(2)···O(2)#1	0.86	2.12	2.934(3)	158.4
N(1)–H(1)···O(5)#2	0.86	1.99	2.831(3)	164.1
4				
O(3)–H(3)···O(1)	0.82	1.85	2.564(4)	145.3
N(4)–H(4)···O(2)	0.86	2.01	2.835(4)	159.6
N(2)–H(2)···O(2)	0.86	1.98	2.804(4)	159.0
5				
O(9)–H(9D)···O(3)#3	0.85	2.05	2.877(10)	164.9
O(9)–H(9C)···O(6)	0.85	2.03	2.858(9)	164.9
O(8)–H(8A)···O(2)#4	0.82	1.72	2.530(7)	172.4
N(10)–H(10)···O(6)#2	0.86	1.92	2.756(8)	163.8
N(8)–H(8)···O(6)	0.86	1.90	2.747(8)	166.7
N(6)–H(6)···O(1)#1	0.86	2.23	2.983(7)	146.1
N(4)–H(4)···O(3)#1	0.86	1.87	2.713(9)	167.1
N(2)–H(2)···O(2)	0.86	2.45	2.988(7)	121.5
N(2)–H(2)···O(7)#5	0.86	2.20	2.991(8)	153.2
6				
N(4)–H(4)···O(2)	0.86	1.88	2.704(5)	158.7
N(2)–H(2)···O(4)	0.86	1.92	2.692(5)	149.3

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

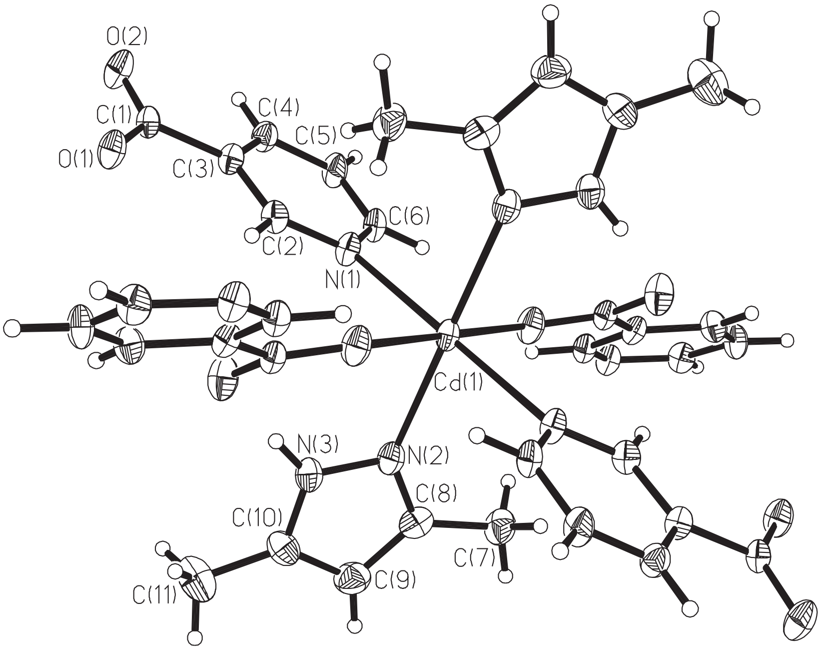


Fig. 1. Molecular structure of complex **1** showing the atomic numbering scheme at 30% ellipsoid probability level.

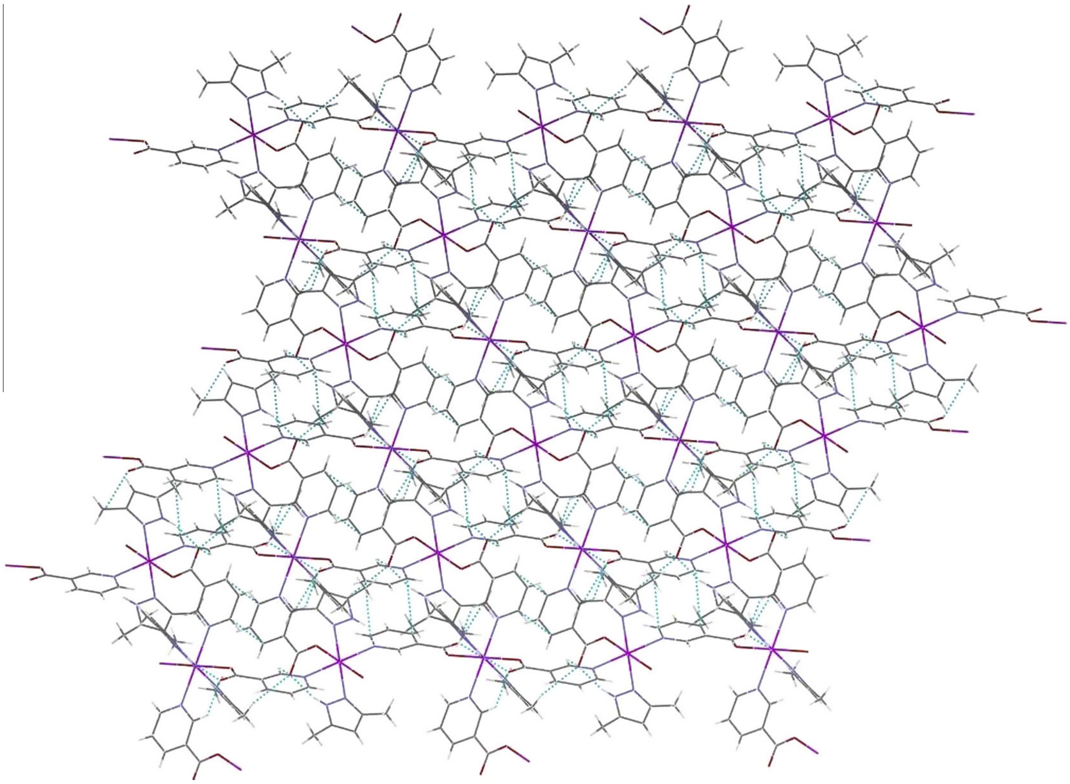


Fig. 2. Packing diagram of compound **1** showing the 2D sheet structure extending along the *bc* plane.

3.2.2. *Crystal and molecular structure of Zn(Hdmpz)$_2$(L2)$_2$ (**2**)*

Crystals of **2** contain mononuclear complex of Zn(Hdmpz)$_2$(L2)$_2$ formulation (Fig. 3). Compound **2** crystallizes in the triclinic space group $P\bar{1}$, and there are 2 formula units in its cell content. Each zinc ion is tetrahedrally coordinated by two oxygen atoms of two monodentate L2 ligands and by two nitrogen atoms, belonging to two monodentate pyrazole ligands with ZnN_2O_2 binding set. The molecular structure of **2** resembles the related [Zn(CH$_3$COO)$_2$(ML)$_2$] monomers, in which ML is a monodentate nitrogen ligand, such as imidazole [29] and pyridine [30].

The ZnN_2O_2 unit possesses coordination distances and angles in the ranges of 1.920(3)–1.998(4) Å and 104.33(14)–114.71(15)°, respectively; thus, the overall coordination geometry resembles that found in the compounds {[Zn(CH$_3$COO)$_2$(Hpz)$_2$]·CH$_3$COOH} (Hpz = pyrazole) [19a], and [Zn(Hpz)$_2$(Me$_3$NCH$_2$CO$_2$)](ClO$_4$)$_2$ [19d]. Although the distortion in the ZnN_2O_2 moiety is differently

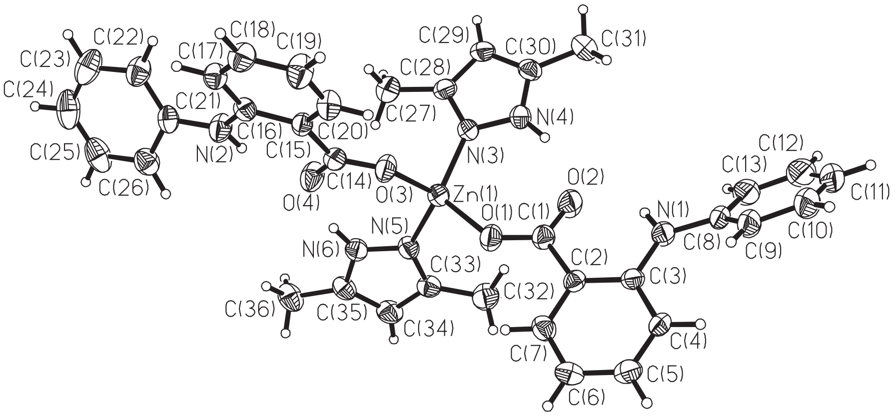


Fig. 3. Molecular structure of complex **2** showing the atomic numbering scheme at 30% ellipsoid probability level.

oriented in the later two compounds, the angles around zinc atoms are 98.94(19)–117.30(18)° and 95.73(7)–118.34(8)°, respectively.

In **2**, the non-bonded oxygen atoms, far enough from the zinc with distances of 3.138 and 3.238 Å, respectively, are involved in two intramolecular hydrogen bonds (N(6)–H(6)···O(4), and N(4)–H(4)···O(2)) with the N–O distances ranging from 2.655(5) to 2.678(5) Å and H–O distances of 1.87–1.88 Å. In addition to the intramolecular N–H···O hydrogen bonds produced by the N–H moieties of the pyrazole, there also exists intramolecular N–H···O hydrogen bond (Table 4) in the anion between the NH group and the non-bonded oxygen atom of the same L2 to produce a $S_1^1(6)$ loop motif according to Bernstein [31]. Thus the non-bonded oxygen atom forms two hydrogen bonds in bifurcate mode.

The dihedral angle between the two pyrazole rings with N3 and N4, and N5 and N6 atoms was 120.5°. The phenyl ring bearing C2–C7 atoms made dihedral angles of 7.7° and 113.6° with the above two pyrazole rings, respectively. The phenyl ring bearing C8–C13 made dihedral angles of 50.5° and 72.8° with the two pyrazole rings bearing N3 and N4, and N5 and N6, respectively. The phenyl ring bearing C15–C20 atoms made dihedral angles of 96.7° and 26.9° with the pyrazole rings bearing N3 and N4, and N5 and N6 atoms, respectively. The phenyl ring bearing C21–C26 atoms intersected at angles of 133° and 18.5° with the above two pyrazole rings, respectively.

Two mononuclear units are combined together via the CH–π association between the phenyl CH of the anion and the phenyl ring of adjacent mononuclear moiety with C–Cg distance of 3.732 Å to form a dinuclear aggregate. In the dinuclear aggregate the Zn–Zn distance is 8.982 Å, and there existed an inversion centre at the middle point of the two Zn ions. The dinuclear aggregates were linked together via the CH–π association between the phenyl CH of the anion and the phenyl ring of the adjacent mononuclear moiety with C–Cg distance of 3.732 Å to form a 1D chain running along the *b* axis direction (Fig. 4). The chains were arranged parallel to each other on the *ab* plane forming 2D sheet structure, yet there were no connections between these chains in the 2D sheet.

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

Compound **3** of the formula $Zn(Hdmpz)_2(L3)_2$ crystallizes in the monoclinic space group $P2_1/n$ with the 4 formula units in the unit cell. Each zinc ion is tetrahedrally coordinated by two oxygen atoms of two monodentate L3 ligands and by two nitrogen atoms of two different monodentate pyrazole ligands (Fig. 5).

The molecular structure of **3** resembles compound **2**, and the related $[Zn(CH_3COO)_2(ML)_2]$ monomers (ML = a monodentate nitrogen ligand) also, like the bisimidazole [29] and bis-pyridine [30] complexes.

The C(2)=C(3) and C(12)=C(13) bond distances (1.323(3) and 1.322(4) Å) are apparently for a simple C=C double bond, due to the significant non-coplanarity of the carboxyl and the olefinic groups (herein the carboxyl group is almost perpendicular with the plane defined by the amide and the olefinic groups which is different from the crystal of N-phenylmaleamic acid [32]). But the C(2)=C(3) and C(12)=C(13) bond distances are somewhat shortened compared with the corresponding values (1.335 and 1.344 Å) in the neutral molecule of N-phenylmaleamic acid [32]. The C–O bond distances (O(1)–C(1),1.266(3) Å; O(4)–C(11), 1.267(3) Å) involving the O atoms that coordinated to the Zn are longer than the C–O bond distances (O(2)–C(1), 1.218(3) Å; O(5)–C(11), 1.230(3) Å) that did not coordinate with the Zn, although they form some nonbonding interactions. The reason may be that the coordinate bonds are stronger than the weak nonbonding interactions.

The phenyl rings composed of C5–C10 and C15–C20 in the two anions intersected at an angle of 78° with each other. The pyrazole ring with N3 and N4 atoms made dihedral angles of 55.1° and 124.2° with the phenyl rings of the above two anions, respectively. The pyrazole ring with N5 and N6 atoms made dihedral angles of 71.5° and 38.1° with the phenyl rings of the two anions, respectively. The pair of pyrazoles coordinated to the same Zn has dihedral angle of 126.2°. The dihedral angles between the phenyl rings and the amide groups (–NHCO–) in the same anion are 3.7° (for the amide group H1—N1—C4=O3) and 4.4° (for the amide group H2—N2—C14=O6), respectively. The conformation of the N–H and C=O bonds in the amide segment of the structure is *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. 5).

The ZnN_2O_2 moiety possesses coordination distances and angles in the ranges of 1.9423(19)–2.034(2) Å and 94.56(8)–125.24(9)°, respectively; thus, the overall coordination geometry resembles that found in the compounds **2**, $\{[Zn(CH_3COO)_2(Hpz)_2]\cdot CH_3COOH\}$ (Hpz = pyrazole) [19a], and $[Zn(Hpz)_2(Me_3NCH_2CO_2)](ClO_4)_2$ [19d]. Although the distortion in the ZnN_2O_2 moiety is differently oriented in the later two compounds, the angles around the zinc atoms are in the range of 98.94(19)–117.30(18)° and 95.73(7)–118.34(8)°, respectively. Compound **3** is not an ionic species consisting of monocationic zinc(II) complex and carboxylate counterions, either. In **3**, the non-bonded oxygen atoms, far enough from the zinc ions with distances of 2.868 and 3.162 Å, respectively, are not involved in the intramolecular hydrogen bonds. But the carbonyl units in the amide groups are involved in the intramolecular N–H···O hydrogen bonds (N(4)–H(4)···O(3), 1.92 Å, 2.774(3) Å; and N(6)–H(6)···O(6), 2.06 Å, 2.900(3) Å).

The mononuclear units were linked together in head to tail fashion via the C–H···O associations between the phenyl CH

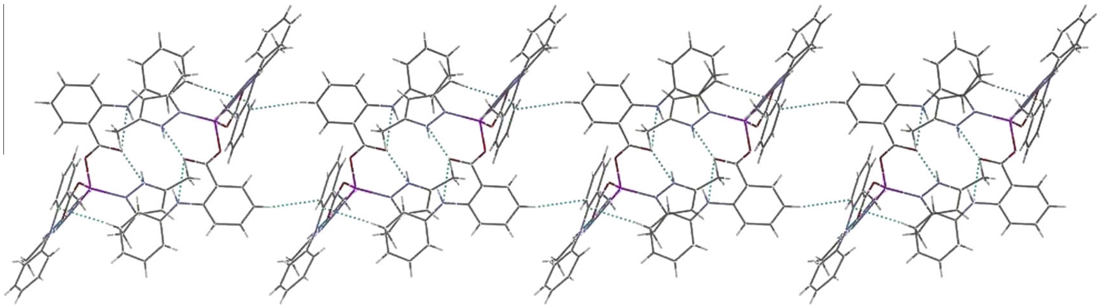


Fig. 4. The 1D chain structure of **2** running along the *b* axis direction which is formed through the CH–π associations between the dinuclear aggregates.

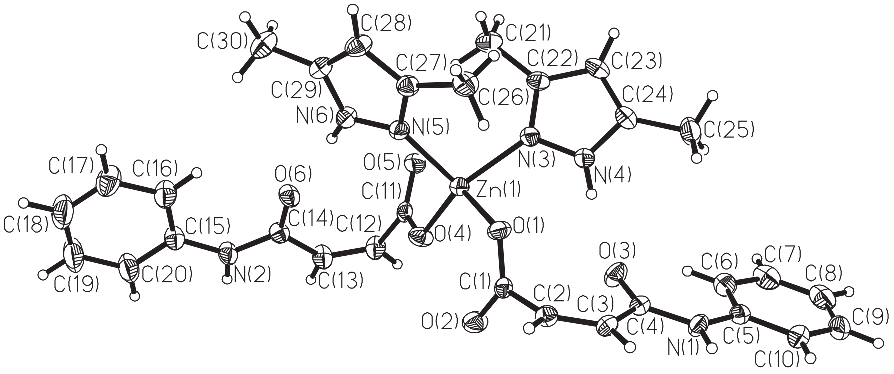


Fig. 5. Molecular structure of complex **3** showing the atomic numbering scheme at 30% ellipsoid probability level.

group of the anion and the noncoordinated O atom of the carboxylate and the O atom at the CONH with C–O distances of 3.439–3.549 Å to form 1D chain running along the *a* axis direction. Two neighboring chains were linked together by the C–H···O association between the phenyl CH of the anion and the non-coordinated O atom of the carboxylate with C–O distance of 3.430 Å, N–H···O hydrogen bond between the amide NH and the non-bonded O atom of the carboxylate with N–O distance of 2.934(3) Å, and C–H···π association between the olefinic CH of the anion and the aromatic ring of the anion with C–Cg distance of 3.486 Å to form 1D flat pipe structure running along the *a* axis direction. The 1D flat pipes were joined together by the CH_3···π interaction between the 3-CH_3 of the pyrazole and the aromatic ring of the anion with C–Cg distance of 3.544 Å to form 2D sheet extending parallel to the *ab* plane (Fig. 6). The 2D sheets were further stacked along the *c* axis direction via the C–H···O association between the olefinic CH of the anion and the C═O of the amide with C–O distance of 3.391 Å, N–H···O hydrogen bond between the amide group and the uncoordinated O atom of the carboxylate with N–O distance of 2.831(3) Å, and CH_3···O association between the 5-CH_3 of the pyrazole and the uncoordinated O atom of the carboxylate with C–O distance of 3.376 Å to form 3D layer network structure.

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

Compound **4** crystallizes in the triclinic system with space group $P\bar{1}$. An asymmetric unit of $Cd(Hdmpz)_4(L4)_2$ contains one six-coordinated Cd(II) ion, a L4 anion, and two Hdmpz groups, which is shown in Fig. 7. The Cd atom is at (0.5, 0.5, 0). The Cd–O distance is 2.321(2) Å, the Cd–N distances are 2.353(3) and 2.383(2) Å, respectively, which are similar to the corresponding bond distances in **1**.

The pyrazole rings containing the N1 and N2, and N3 and N4 atoms inclined at an angle of 69.2° with each other. The phenyl ring of the anion made dihedral angles of 58.3° and 127.4° with the above two pyrazole rings, respectively.

In **4**, the non-bonded oxygen atom, far enough from the Cd ion with distance of 3.699 Å, is involved in two intramolecular hydrogen bonds (N(2)–H(2)···O(2), and N(4)–H(4)···O(2) with the N–O distances ranging from 2.804(4) to 2.835(4) Å and H–O distances of 1.98–2.01 Å. Because of the presence of the intramolecular hydrogen bond between the carboxylate group and the phenol group (O(3)–H(3)···O(1), 2.564(4) Å) in the anion, it is generally expected and found that the carboxylate group is essentially coplanar with the benzene ring [torsion angle C3–C2–C1–O2, 179.34°]. For the presence of this O–H···O hydrogen bond (Table 4) between the phenol group and the coordinated oxygen atom of L4, there exists a $S_1^1(6)$ loop motif in the anion. This feature is similar to that found in the salicylic acid [33], and in the previously reported structure of deprotonated compound based on o-hydroxy benzoic acid derivatives [34]. As expected the O–O separation (2.564(4) Å) is essentially in the range of the documented data [2.531(4)–2.570(4) Å] [35] because of the planarity of the hydrogen bonded carboxylate unit, but it is slightly contracted compared with the nondeprotonated examples (2.547–2.604, mean: 2.588 Å), as a result of deprotonation.

The mononuclear units were linked together via the CH_3–O interactions between the 5-CH_3 group of the pyrazole and the phenol group with C–O distance of 3.114 Å to form a 1D chain running along the *b* axis direction. Such kind of chains were joined together by the Cl–O contact between the Cl atom and the uncoordinated O atom of the carboxylate with Cl–O distance of 3.240 Å to form 2D corrugated sheet extending in the direction that formed a dihedral angle of ca. 45° with the *ab* plane (Fig. 8). Herein the Cl–O contact is weaker than that found in 5-chloro-1,2-dimethyl-4-nitro-1H-imidazole [36]. Thus the non-bonded oxygen atom forms two hydrogen bonds in bifurcate mode. The sheets were further stacked along the direction that is perpendicular with its extending direction to form 3D network structure. However there are no associations between the neighboring sheets.

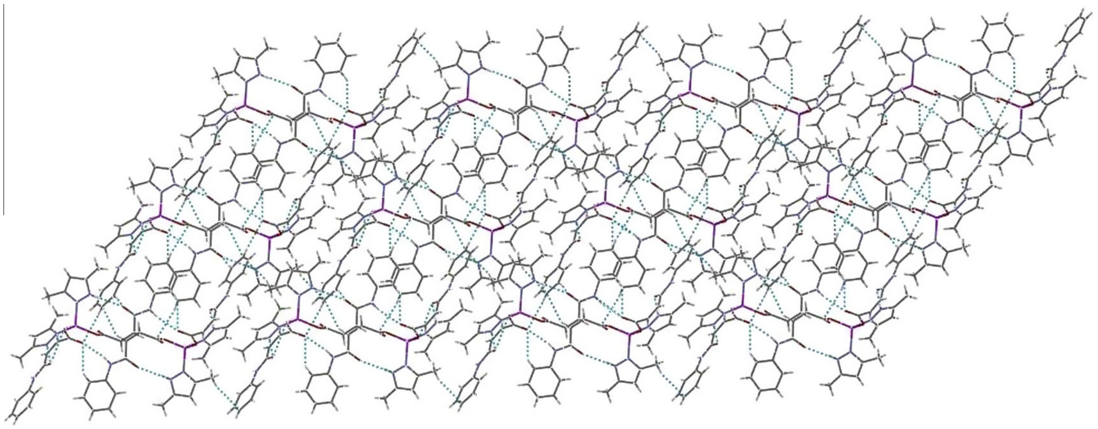


Fig. 6. 2D sheet structure of **3** extending parallel to the *ab* plane.

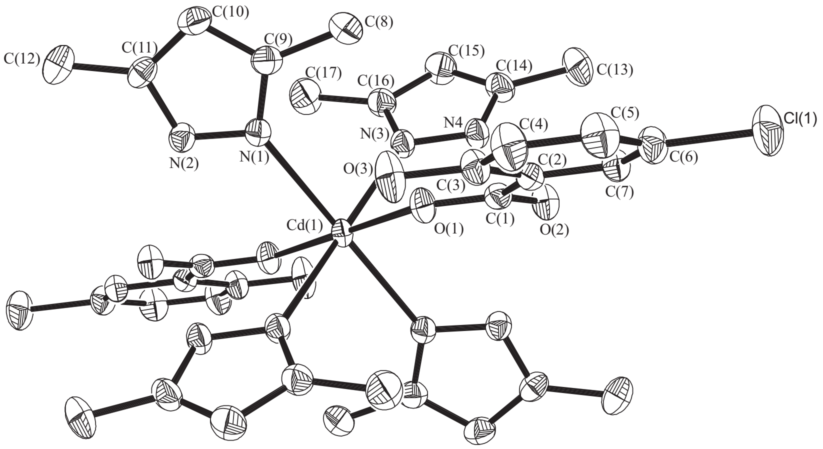


Fig. 7. Molecular structure of complex **4** showing the atomic numbering scheme at 30% ellipsoid probability level, the H atoms were omitted for clarity.

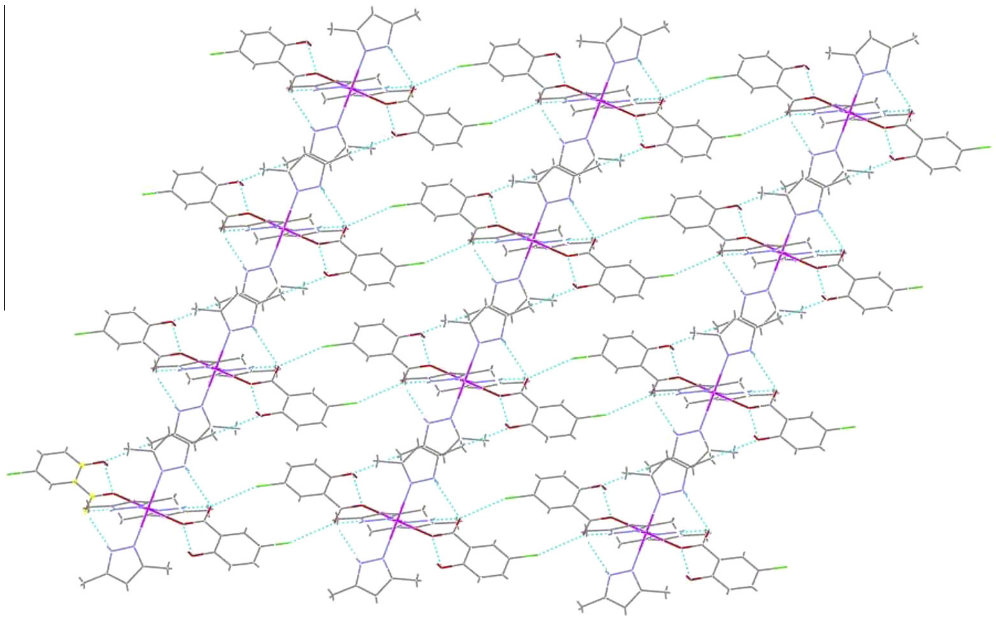


Fig. 8. 2D corrugated sheet structure of compound **4**.

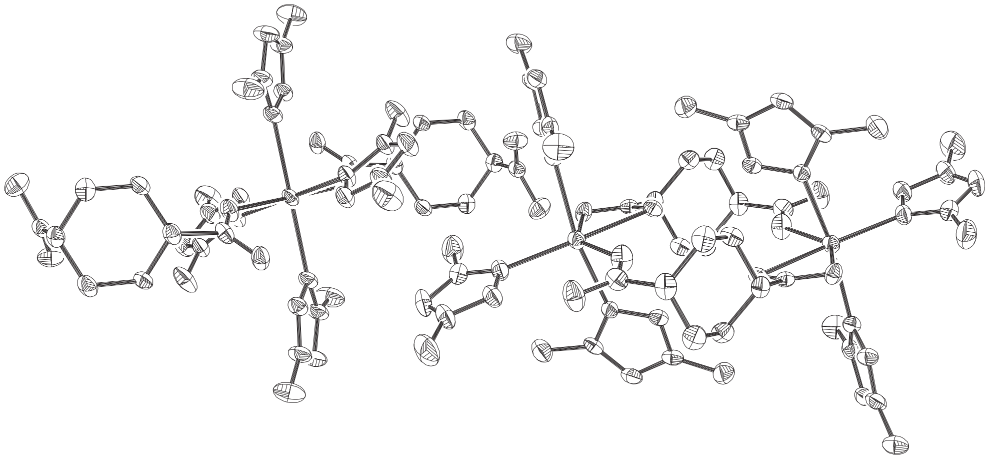


Fig. 9. Molecular structure of complex **5** showing the atomic numbering scheme at 30% ellipsoid probability level. Atom-numbering and H atoms were omitted for clarity.

3.2.5. Crystal and molecular structure of $Cd_2(Hdmpz)_6(L5)_2Cd(Hdmpz)_4(HL5)_2{\cdot}2H_2O$ (5)

The asymmetric unit of **5** consists of half of dinuclear unit with the formula of $Cd_2(Hdmpz)_6(L5)_2$, half of mononuclear unit of $Cd(Hdmpz)_4(HL5)_2$, and one water molecule (Fig. 9). In the dinuclear unit the Cd atom is coordinated with three N atoms from three pyrazole molecules and three O atoms of the carboxylate to form a CdN_3O_3 bonding set. The carboxylate groups in the L5 coordinated to the Cd in two modes, one carboxylate coordinated to the metal centre in unidentate fashion, while the other carboxylate coordinated to the Cd in bidentate chelating fashion. In the asymmetry moiety of the mononuclear unit $Cd(Hdmpz)_4(HL5)_2$, there existed two neutral Hdmpz molecules, and one hydrogen 1,4-cyclohexanedicarboxylate. In the hydrogen 1,4-cyclohexanedicarboxylate the deprotonated carboxyl coordinated to the Cd in unidentate mode, the pyrazole coordinated to the Cd in monodentate fashion.

The C–O bond lengths of the COOH (O(8)–C(10)–O(7)) group of the hydrogen 1,4-cyclohexanedicarboxylate ranged from 1.202(8) to 1.320(8) Å with the Δ value of 0.118 Å. The C–O bond lengths of the monodentate coordinated COO^- group of the anion ranged from 1.239(9) (O(3)–C(2)) to 1.268(8) Å (O(4)–C(2)) with the Δ value of 0.029 Å. The C–O bond lengths of the bischelating coordinated COO^- group of the anion ranged from 1.243(8) (O(1)–C(1)) to 1.272(8) Å (O(2)–C(1)) with the average value of 1.257 Å. The difference in bond lengths between the pair of C–O bonds in the carboxyl group is expected for unionized COOH group. And the differences in bond lengths between the two pairs of C–O bonds in the COO^- groups agree well with the Δ values in the deprotonated COOH groups, which further confirms our correct assignment of the H atom that is attached to the carboxyl group. Herein the cyclohexane rings of the anions adopt chair conformation with the two carboxyl units in e, a positions, respectively.

The mononuclear units and the dinuclear units were linked together to form 1D chain. The mononuclear units and the dinuclear units alternate at the chain. In the chain there exist CH–π interaction between the 4-CH of the pyrazole in the dinuclear unit and the aromatic ring of the pyrazole in the mononuclear unit with C–Cg distance of 3.611 Å, CH_3–π interaction between the 3-CH_3 of the pyrazole in the dinuclear unit and the aromatic ring of the pyrazole in the mononuclear unit with C–Cg distance of 3.671 Å, CH–O interaction between the CH of the 1,4-cyclohexane moiety and the OH group of the COOH moiety with C–O distance of 3.431 Å, CH_3–O interaction between the 5-CH_3 of the pyrazole in the dinuclear unit and the C=O of the hydrogen 1,4-cyclohexanedicarboxylate with C–O distance of 3.492 Å, N–H···O hydrogen bond between the NH group of the pyrazole and the C=O group that is involved in CH_3–O interaction with N–O distance of 2.991(8) Å, and O–H···O hydrogen bond between the OH unit of the COOH group and one coordinated O atom of the carboxylate with O–O distance of 2.530(7) Å. The 1D chains were joined together by the water molecules to form 2D sheet extending at the direction that made an angle of 45° with the *ac* plane (Fig. 10). Herein the water molecules act as bisunidentate donor forming O–H···O hydrogen bonds with the unbonded O atom of the mononuclear units and the unbonded O atom in the dinuclear unit with O–O separations of 2.858(9)–2.877(10) Å. The 2D sheets were further stacked along

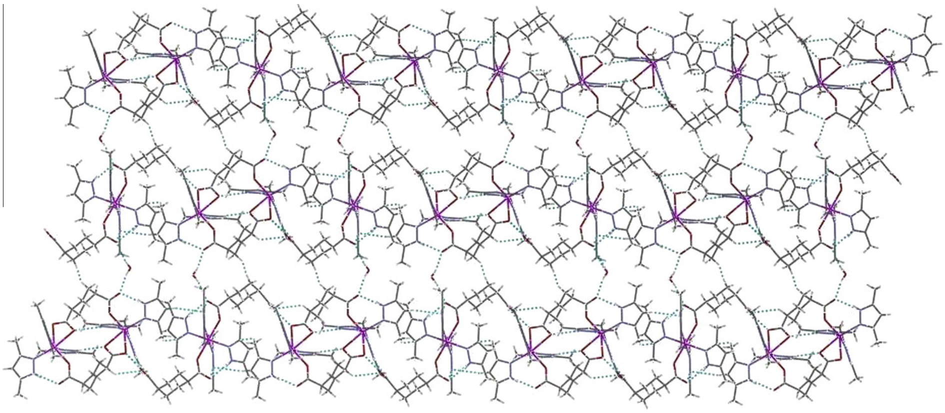


Fig. 10. Packing diagram of compound **5** with 2D sheet structure extending at the direction that made an angle of 45° with the *ac* plane.

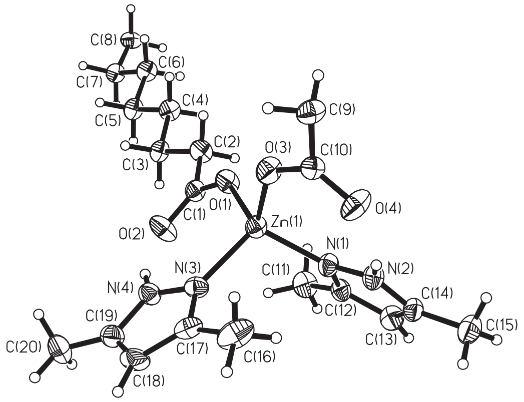


Fig. 11. Molecular structure of complex **6** showing the atomic numbering scheme at 30% ellipsoid probability level.

the direction that is perpendicular with its extending direction via the CH_3–π interaction between the 5-CH_3 of the pyrazole in the mononuclear unit and the aromatic ring of the pyrazole in the dinuclear unit with C–Cg distance of 3.349 Å, CH_3–O contact between the 5-CH_3 of the pyrazole in the dinuclear unit and the carbonyl group of the mononuclear unit with C–O distance of 3.498 Å to form 3D network structure.

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

Compound **6** of the formula Zn(Hdmpz)$_2$(L6) crystallizes in the monoclinic space group $P2_1/c$, and there are 4 formula units in its cell content. Each zinc ion is tetrahedrally coordinated by two oxygen atoms of two monodentate L6 ligands, and two nitrogen atoms, belonging to two different monodentate pyrazole ligands (Fig. 11). Here the L6 acts as a bismonodentate ligand. The molecular structure of **6** resembles the compounds **2** and **3**, except that here the dicarboxylate substituted the monocarboxylates in **2** and **3**.

The Zn and the dicarboxylate were linked alternatively to form a 1D chain running along the *a* axis direction. Herein one carboxylate (C10–O3–O4) of the anion was rotated out of the plane defined by the remaining part (O1, O2, C1, C2, C3, C4, C5, C6, C7, and C8) of the dicarboxylate. The pyrazoles were attached to the chain via the Zn–N coordination bonds. The pair of pyrazoles coordinated to the same Zn is almost perpendicular to each other. There are also intramolecular N–H···O hydrogen bonds produced between the NH group of the pyrazole and the non-bonded O atom of the carboxylate with N–O distances of 2.692(5)–2.704(5) Å. In the anion there are found intramolecular CH_2–O associations between the CH_2 spacers of the anion and the uncoordinated O atom of the anion with C–O distances of 2.815–3.248 Å. Thus one of the unbonded O atoms of the anion acted as a triple acceptor, while the other uncoordinated O atom in the same anion only functioned as a single acceptor. Neighboring chains were joined together via the interchain CH_3–O association between the 5-CH_3 of the pyrazole and the coordinated O atom with C–O distance of 3.289 Å to form 2D grid sheet extending along the *ab* plane (Fig. 12). Herein one pyrazole is at the plane defined by the sheet, while another pyrazole is protruded from the sheet plane. Two adjacent sheets were held together by the CH_3–O association between the 3-CH_3 of the pyrazole and the uncoordinated O atom of the anion with C–O distance of 3.476 Å to form 2D double sheet structure. The chains of the second sheet were located at the center of the grid at the first sheet. In this regard the pyrazoles at the double sheets that are protruded from the sheet plane are oppositely arranged, i.e. one kind of pyrazole is protruded above the sheet plane that it is attached, while another kind of pyrazole is protruded below the sheet plane that it is attached. The double sheets were further stacked along the *c* axis direction to form 3D layer network structure. It is worth pointing out that neighboring double sheets appear to have sled away from each other along the *a* and *b* axis direction.

3.3. Thermogravimetry (TG)

For **1**, the first weight loss of 34.67% (Calcd. 34.98%) corresponds to the loss of both Hdmpz molecules in the temperature range of 174.6–266.6 °C, and the second weight loss of 44.32% between

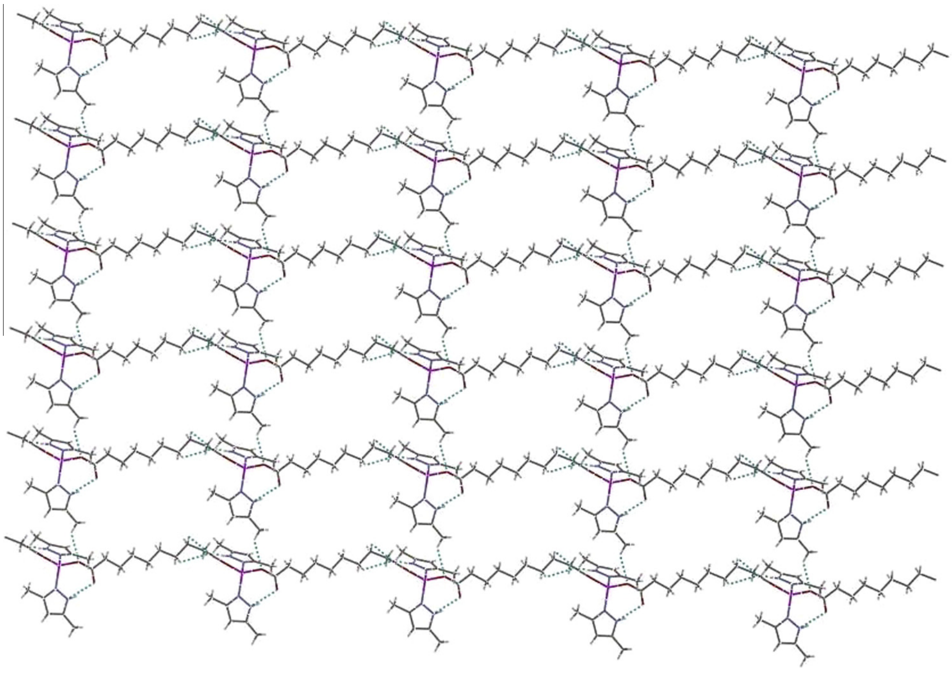


Fig. 12. 2D grid sheet structure of compound **6** produced via CH_3–O associations.

274.2 and 321.4 °C arises from the loss of the two L1 ligands (Calcd. 44.45%). For **2**, the weight loss of 28.06% (Calcd. 28.15%) corresponding to the loss of two Hdmpz molecules was observed in the temperature range of 171.3–283.5 °C, and there was a weight loss of 62.16% between 297.6 and 476.8 °C which is due to the loss of the two carboxylate ligands (Calcd. 62.23%). The TGA studies showed that **3** is stable below 150 °C. Its decomposition begins at 159.6 °C. The weight loss of 29.89% in the temperature range of 159.6–251.3 °C is caused by the loss of the two pyrazole molecules (Calcd. 30.09%). The weight loss of 59.42% from 258.5 to 416.7 °C is due to the loss of two L3 ligands (Calcd. 59.56%). For **4**, the first weight loss stage occurs between 161.0 and 250.0 °C and corresponds to the removal of 4 mol of Hdmpz ligands (calcd.: 45.71%, found: 45.63%). The second stage between 267.0 and 423.0 °C is accompanied by a mass loss of 40.78% for two 5-chlorosalicylates (calcd.: 40.83%). For **5**, the weight loss of 1.69% in the temperature range of 78.5–83.6 °C was attributed to the liberation of both lattice water molecules (calcd.: 1.78%), the weight loss of 47.51% in the temperature of 186.1–276.5 °C is caused by the loss of the ten Hdmpz ligands (calcd.: 47.59%), all of the HL5 and L5 were removed at the temperature range of 283.0–478.0 °C (Calcd. 33.84%, found 33.77%). Complex **6** experiences the first weight loss of 41.85% in the temperature range of 166.6–255.9 °C which is due to the loss of the pyrazole molecules (Calcd. 41.93%). The second weight loss of 43.74% was observed between 279.4 and 431.8 °C which was attributed to the loss of the bonded carboxylate ligands (Calcd. 43.90%).

4. Summary

In summary, use of 3,5-dimethylpyrazole and different carboxylate ligands afforded a series of mononuclear to trinuclear divalent metal complexes. Although synthesized by the same method, they showed different structures ranging from 2D sheet, 3D network, to 3D layer network structure. The central metal ions are coordinated in N_4O_2, N_2O_2, and N_3O_3 fashions. A distorted octahedral geometry in the case of Cd, and tetrahedral geometry for Zn were observed in the X-ray studies. It indicated that the geometry of the coordination metal complexes is determined not only by the coordination environment but also by the metal entity itself.

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. In addition, every carboxylate group acts as monodentate ligand toward the metal ion except the carboxylate in **5**. In **5**, there existed COOH and COO^- groups simultaneously, and the COO^- coordinated to the metal in both monodentate and chelating bidentate fashion. The strong structural propensity toward tetracoordination in Zn compounds seems to disfavour the formation of 'paddlewheel' dimeric complexes [30,37]. The nonbonded O atoms of the carboxylates in all compounds except **3** are involved in the formation of the intramolecular hydrogen bonds with the N–H group of the 3,5-dimethylpyrazole.

Complexes **1**–**6** have abundant intra- and intermolecular weak non-covalent interactions (including classical hydrogen bonds, Cl···O, C–H···O, CH_2···O, CH_3···O, C–H···π, CH_3–π, and π–π interactions) in their crystals, which lead to the formation and stabilization of the final structures.

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Appendix A. Supplementary material

CCDC 867488 for **1**, 866455 for **2**, 866456 for **3**, 841385 for **4**, 866462 for **5**, and 852746 for **6** contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.ica.2014.02.027.

References

[1] J.M. Lehn, Supramolecular Chemistry: Concepts and Perspectives, VCH, Weinheim, 1995.

[2] See, for example: (a) 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;
(d) J. Li, J.H. Zhou, Y.Z. Li, L.H. Weng, X.T. Chen, Z. Yu, Z. Xue, Inorg. Chem. Commun. 7 (2004) 538.

[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. Friščić, 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.Y. Lu, E.E. Kohler, Inorg. Chem. Commun. 5 (2002) 600.
[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] K. Bania, N. Barooah, J.B. Baruah, Polyhedron 26 (2007) 2612.
[29] X.M. Chen, Z.T. Xu, X.C. Huang, J. Chem. Soc., Dalton Trans. (1994) 2331.
[30] B. Singh, J.R. Long, F. Fabrizi de Biani, D. Gatteschi, P. Stavropoulos, J. Am. Chem. Soc. 119 (1997) 7030.
[31] J. Bernstein, R.E. Davis, L. Shimoni, N.L. Chang, Angew. Chem., Int. Ed. 34 (1995) 1555.
[32] K.M. Lo, S.W. Ng, Acta Crystallogr., Sect. E 65 (2009) o1101.
[33] M. Sundaralingam, L.H. Jensen, Acta Crystallogr. 18 (1965) 1053.
[34] G. Simith, A.W. Hartono, U.D. Wermuth, P.C. Healy, J.M. White, A.D. Rae, Aust. J. Chem. 58 (2005) 47.
[35] Y. Yang, P. Du, J.F. Ma, W.Q. Kan, B. Liu, J. Yang, Cryst. Growth Des. 11 (2011) 5540.
[36] M. Kubicki, P. Wagner, Acta Crystallogr., Sect. C 63 (2007) o454.
[37] H.L. Chun, D.N. Dybtsev, H. Kin, K. Kim, Chem. Eur. J. 11 (2005) 3521. and references cited therein.