

Solvent induced reactivity of 3,5-dimethylpyrazole towards zinc (II) carboxylates†

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The reactions of 3,5-dimethylpyrazole with zinc(II)acetate dihydrate and varieties of aromatic carboxylic acids led to formation of mono-nuclear zinc complexes of composition $[\text{Zn}(\text{HDMP})_2(\text{RCO}_2)_2]$ ($\text{R} = \text{C}_6\text{H}_5$, $p\text{-CH}_3\text{-C}_6\text{H}_4$, $p\text{-NO}_2\text{-C}_6\text{H}_4$ etc. HDMP = 3,5-dimethylpyrazole) in methanol, whereas the same reactants in dimethylformamide (DMF) gave binuclear 3,5-dimethylpyrazolato bridged zinc carboxylate complexes containing monodentate 3,5-dimethylpyrazole ligands with composition $[\text{Zn}_2(\mu\text{-DMP})_2(\text{HDMP})_2(\text{RCO}_2)_2]$. The mononuclear complexes can be converted to the corresponding binuclear complexes by simply dissolving in DMF. The reaction of zinc(II)acetate dihydrate with p -nitrobenzoic acid and 3,5-dimethylpyrazole in different solvents gave solvated mononuclear complexes of the corresponding solvent. All these solvated complexes having the core $[\text{Zn}(\text{HDMP})_2(p\text{-NO}_2\text{-C}_6\text{H}_4\text{CO}_2)_2]$ contain two structurally independent molecules in the asymmetric unit ($Z' = 2$).

Introduction

Ligands having pyrazole backbone are of interest in the field of biology and co-ordination chemistry.¹ The zinc complexes containing pyrazole ligands are shown to mimic the biological activity of carbonic anhydrase.^{1k,m} The pyrazole as a ligand shows versatility in co-ordination modes towards metals. While, neutral monodentate pyrazole ligands are common,² a number of literatures are available on pyrazole as anionic monodentate and bridging bidentate ligands.³ The bidentate bridging pyrazolato ligand is a precursor for preparation of binuclear or polynuclear metal complexes. Generally, in pyrazolato bridged complexes the metal-metal separations are in the range of 3.0–4.5 Å.⁴ On the other hand binuclear complexes having such a critical metal-metal separation are of interest from their resemblance to the various active sites of zinc containing enzymes.⁵ A good number of literatures are available on pyrazole based ligands that act as monodentate ligands under ambient conditions.^{1,3} Recently we have shown that different types of zinc carboxylate complexes can be prepared by varying either the solvent or substituent on the ligands.⁶ Such structural changes under neutral reaction conditions is of interest to understand the reactivity of ligand and leaves enough scope to understand this simple yet important chemistry in an organized manner to have variation in reactivity. The deprotonation of N-H in amine containing ligands of zinc complexes is of special interest for biological mimics and are studied with great interest.⁷ Herein, we report the formation of a number of mononuclear and binuclear zinc(2+) carboxylate complexes with monodentate 3,5-dimethylpyrazole (HDMP) and

bidentate 3,5-dimethylpyrazolato (DMP) ligand respectively that are prepared just by changing the solvent condition.

Experimental

Synthesis of the complexes

Bis-3,5-dimethylpyrazole bis-benzoato zinc(2+). $[\text{Zn}(\text{C}_6\text{H}_5\text{-COO})_2(\text{HDMP})_2]$ (**1**): To a solution of benzoic acid (2 mmol, 0.244 g) in methanol (15 mL) $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ (1 mmol, 0.219 g) was added. After stirring this reaction mixture for about 30 minutes 3,5-dimethylpyrazole (2 mmol, 0.190 g) was added followed by addition of toluene (5 mL) and stirred for another 30 minutes. The reaction mixture was then kept for crystallization and good quality colorless crystals of **1** were obtained after 3/4 days. Isolated yield 92%. IR (KBr, cm^{-1}): 2927(m), 2850(m), 1614(s), 1553(s), 1481(m), 1448(m), 1385(s), 1295(s), 1191(s), 1049(s), 1017(s), 834(s), 720(s), 679(s), 578(s). ¹H NMR (DMSO- d_6 , ppm): 7.9 (d, 4H, $J = 4$ Hz), 7.5 (m, 6H), 5.7 (s, 2H), 2.1 (b, 12H). Elemental anal calcd for $\text{C}_{24}\text{H}_{26}\text{N}_4\text{O}_4\text{Zn}$; C, 57.66, H, 5.24; found C, 58.08, H, 5.29.

Bis-3,5-dimethylpyrazole di- μ -3,5-dimethylpyrazolato bis-benzoato di-zinc(2+). $[\text{Zn}_2(\text{C}_6\text{H}_5\text{COO})_2(\text{DMP})_2(\text{HDMP})_2]$ (**2**): To a solution of benzoic acid (2 mmol, 0.244 g) in dimethylformamide (15 mL) $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ (1 mmol, 0.219 g) was added. After stirring this reaction mixture for about 30 minutes 3,5-dimethylpyrazole (2 mmol, 0.190 g) was added and stirred for another 30 minutes. The solution was then kept for crystallization. Diffraction quality colorless crystals of **2** were obtained after a week. Isolated yield 78%. IR (KBr, cm^{-1}): 2923(m), 2853(m), 1608(s), 1552(s), 1529(s), 1483(w), 1390(s), 1345(s), 1298(s), 1191(m), 1048(s), 1014(s), 831(m), 721(s), 676(s), 572(s). ¹H NMR (DMSO- d_6 , ppm): 7.9 (d, 4H, $J = 8$ Hz), 7.4 (m, 6H), 5.7 (b, 4H), 2.2 (s, 6H), 2.1 (s, 12H), 1.7 (s, 6H). Elemental anal calcd for $\text{C}_{34}\text{H}_{40}\text{N}_8\text{O}_4\text{Zn}_2$; C, 54.05, H, 5.33; found C, 54.15, H, 5.33.

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† Electronic supplementary information (ESI) available: The PXRD patterns for the complexes **1** and **2** and the UV-spectra of the complexes **3** and **6** are available. CCDC reference numbers 715018–715024. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b905534g

Aqua and ethanol solvate of bis-3,5-dimethylpyrazole bis-*p*-methylbenzoato zinc(2+). $[\text{Zn}(p\text{-CH}_3\text{-C}_6\text{H}_4\text{COO})_2(\text{HDMP})_2] \cdot \text{H}_2\text{O} \cdot \text{CH}_3\text{CH}_2\text{OH}$ (**3**): The complex **3** was synthesised by the same procedure as complex **1** only difference being it's recrystallization solvent (ethanol). Isolated yield 87%. IR (KBr, cm^{-1}): 3032(m), 2927(m), 2854(m), 1610(s), 1550(s), 1484(m), 1404(m), 1378(s), 1293(s), 1194(s), 1176(s), 1049(s), 1018(s), 847(s), 766(s), 624(s). $^1\text{H NMR}$ (DMSO- d_6 , ppm): 7.8 (d, 4H, $J = 8$ Hz), 7.2 (d, 4H, $J = 8$ Hz), 5.8 (s, 2H), 2.3 (s, 6H), 2.1 (s, 12H). Elemental anal calcd for $\text{C}_{28}\text{H}_{38}\text{N}_4\text{O}_6\text{Zn}$; C, 56.80, H, 6.47; found C, 57.00, H, 6.45.

Bis-3,5-dimethylpyrazole di- μ -3,5-dimethylpyrazolato bis-*p*-methylbenzoato di-zinc(2+). $[\text{Zn}_2(p\text{-CH}_3\text{-C}_6\text{H}_4\text{COO})_2(\text{DMP})_2(\text{HDMP})_2]$ (**4**): The complex **4** was synthesised by the same procedure as complex **2**. Isolated yield 84%. IR (KBr, cm^{-1}): 2925(m), 2853(m), 1608(s), 1583(s), 1548(s), 1527(m), 1483(w), 1394(s), 1342(s), 1303(s), 1193(m), 1048(s), 1012(s), 846(m), 768(s), 694(m), 622(s). $^1\text{H NMR}$ (DMSO- d_6 , ppm): 7.8 (b, 4H), 7.2 (b, 6H), 5.7 (b, 4H), 2.3 (s, 6H), 2.18 (s, 6H), 2.11 (s, 12H), 1.7 (s, 6H). Elemental anal calcd for $\text{C}_{36}\text{H}_{44}\text{N}_8\text{O}_4\text{Zn}_2$; C, 55.18, H, 5.66; found C, 55.32, H, 5.75.

Methanol solvate of bis-3,5-dimethylpyrazole bis-*p*-nitrobenzoato zinc(2+). $[\text{Zn}(p\text{-NO}_2\text{-C}_6\text{H}_4\text{COO})_2(\text{HDMP})_2] \cdot \text{CH}_3\text{OH}$ (**5**): The complex **5** was also synthesised by the same procedure as complex **1**. Isolated yield 82%. IR (KBr, cm^{-1}): 2960(m), 2926(m), 2854(m), 1626(s), 1592(s), 1563(s), 1525(m), 1476(w), 1385(s), 1342(s), 1319(w), 1284(m), 1190(s), 1158(s), 1046(s), 821(s), 726(s), 581(s),

527(s). $^1\text{H NMR}$ (DMSO- d_6 , ppm): 8.1 (b, 8H), 5.8 (s, 2H), 3.2 (s, 3H), 2.1 (b, 12H). Elemental anal calcd for $\text{C}_{25}\text{H}_{26}\text{N}_6\text{O}_9\text{Zn}$; C, 48.44, H, 4.22; found C, 48.65, H, 4.34.

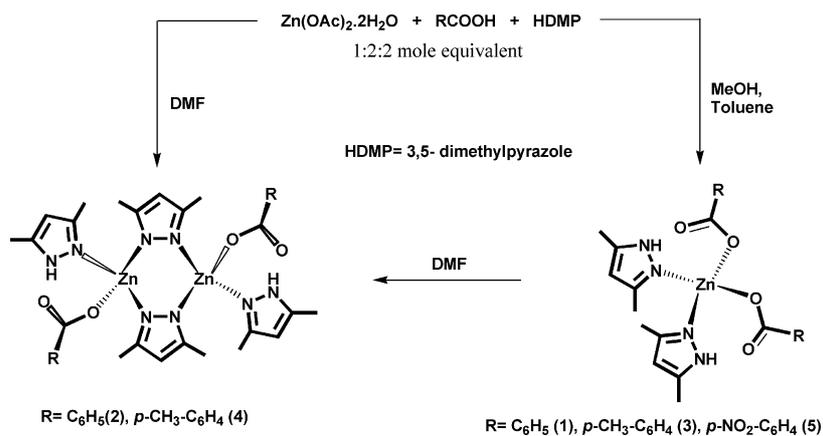
The mononuclear complexes **6** and **7** were synthesised by the same procedure as complex **5** only difference being the solvent. In case of **6** the solvent is acetone whereas in case of **7** the solvent used is dimethylformamide.

X-ray crystallography

The X-ray crystallographic data were collected at 296 K with Mo $\text{K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) using a Bruker Nonius SMART CCD diffractometer equipped with a graphite monochromator. The SMART software was used for data collection and also for indexing the reflections and determining the unit cell parameters; the collected data were integrated using SAINT software.⁸ The structures were solved by direct methods and refined by full-matrix least-squares calculations using SHELXTL software.⁸ All the non-H atoms except C49 and C50 of complex **5** were refined in the anisotropic approximation against F^2 of all reflections. The C49 and C50 of complex **5** are refined isotropically. The H-atoms, except those attached to N and O were placed at their calculated positions and refined in the isotropic approximation; those attached to hetero-atoms (N, O) were located in the difference Fourier maps, and refined with isotropic displacement coefficients. However, some of the hydrogen atoms attached to solvent molecule could not be located for the structures **5** and **7**. The crystallographic parameters are given in Table 1.

Table 1 The crystallographic parameters of complexes 1–7†

Compound No.	1	2	3	4	5	6	7
CCDC No.	715018	715019	715020	715021	715022	715023	715024
Formulae	$\text{C}_{24}\text{H}_{26}\text{N}_4\text{O}_4\text{Zn}$	$\text{C}_{34}\text{H}_{40}\text{N}_8\text{O}_4\text{Zn}_2$	$\text{C}_{28}\text{H}_{38}\text{N}_4\text{O}_6\text{Zn}$	$\text{C}_{36}\text{H}_{44}\text{N}_8\text{O}_4\text{Zn}_2$	$\text{C}_{25}\text{H}_{28}\text{N}_6\text{O}_9\text{Zn}$	$\text{C}_{24}\text{H}_{24}\text{N}_6\text{O}_9\text{Zn}$	$\text{C}_{51}\text{H}_{56}\text{N}_{13}\text{O}_{18}\text{Zn}_2$
Formula. wt.	499.86	755.48	591.99	783.53	621.90	605.86	1269.83
Temperature	296 K	296 K	296 K	296 K	296 K	296 K	296 K
Crystal system	Triclinic	Monoclinic	Monoclinic	Orthorhombic	Triclinic	Monoclinic	Triclinic
Space group	P-1	P2(1)/c	P2(1)	Fdd2	P-1	P2(1)/c	P-1
$a/\text{\AA}$	8.7460(3)	8.2047(11)	8.1158(3)	16.8246(8)	12.5156(11)	12.1934(6)	12.7147(12)
$b/\text{\AA}$	12.0489(4)	16.175(2)	8.3981(3)	33.419(2)	13.3426(13)	19.9578(14)	14.2450(14)
$c/\text{\AA}$	13.0519(4)	14.222(2)	22.7637(8)	14.0874(8)	19.6335(19)	23.6281(16)	17.2331(14)
$\alpha/^\circ$	96.598(2)	90.00	90.00	90.00	102.918(4)	90.00	76.935(4)
$\beta/^\circ$	103.186(2)	105.266(7)	95.686(2)	90.00	90.692(4)	93.779(2)	82.892(6)
$\gamma/^\circ$	108.004(2)	90.00	90.00	90.00	113.340(3)	90.00	84.316(6)
$V/\text{\AA}^3$	1247.78(7)	1820.9(4)	1543.88(10)	7920.7(8)	2915.5(5)	5737.5(6)	3008.9(5)
Z	2	2	2	8	4	8	2
Density/ mg m^{-3}	1.330	1.378	1.273	1.314	1.417	1.403	1.402
Abs. Coeff./ mm^{-1}	1.020	1.364	0.839	1.257	0.902	0.915	0.876
F(000)	520	784	624	3264	1288	2496	1314
Total no. of reflections	6812	21213	16951	15854	27296	57413	11927
Reflections, $I > 2\sigma(I)$	4202	4513	5176	4836	12913	14065	3797
Max. $\theta/^\circ$	24.99	28.34	25.50	28.43	27.38	28.27	17.52
Ranges (h, k, l)	$-10 \leq h \leq 10$ $-14 \leq k \leq 6$ $-14 \leq l \leq 15$	$-9 \leq h \leq 10$ $-20 \leq k \leq 21$ $-18 \leq l \leq 17$	$-9 \leq h \leq 9$ $-9 \leq k \leq 10$ $-27 \leq l \leq 27$	$-22 \leq h \leq 21$ $-28 \leq k \leq 44$ $-18 \leq l \leq 18$	$-16 \leq h \leq 6$ $-16 \leq k \leq 17$ $-25 \leq l \leq 25$	$-6 \leq h \leq 16$ $-26 \leq k \leq 26$ $-31 \leq l \leq 31$	$-10 \leq h \leq 10$ $-12 \leq k \leq 12$ $-14 \leq l \leq 14$
Complete to 2θ (%)	95.4	99.4	98.7	99.1	97.6	98.8	99.3
Flack parameter	—	—	-0.002(12)	0.00	—	—	—
Data/Restraints/Parameters	4202/0/300	4513/0/221	5176/1/367	4836/0/233	12913/0/729	14065/0/729	3797/18/767
Goof (F^2)	1.000	1.017	1.051	1.023	1.242	0.955	1.081
R indices [$I > 2\sigma(I)$]	0.0330	0.0337	0.0355	0.0328	0.0785	0.0515	0.0872
R indices (all data)	0.0428	0.0661	0.0469	0.0475	0.1502	0.1514	0.1025
wR2 (for all data)	0.0835	0.0960	0.0957	0.0873	0.2505	0.1607	0.2604
R(int)	0.0150	0.0345	0.0300	0.0278	0.0475	0.0495	0.0446



Scheme 1 Formation of mono and dinuclear complexes from two different solvents.

Results and discussion

A series of zinc(2+) carboxylate complexes with 3,5-dimethylpyrazole are prepared in one pot reactions using different solvents (Scheme 1). Either dinuclear or mononuclear complexes are formed depending on the solvent used. The reaction between zinc (2+) acetate dihydrate, aromatic carboxylic acid and 3,5-dimethylpyrazole in a mixed solvent of methanol : toluene (3 : 1) leads to the formation of mononuclear complexes having composition $[\text{Zn}(\text{RCOO})_2(\text{HDMP})_2]$ ($\text{R} = \text{C}_6\text{H}_5, p\text{-NO}_2\text{-C}_6\text{H}_4, p\text{-CH}_3\text{-C}_6\text{H}_4$ etc. HDMP = 3,5-dimethylpyrazole). The same reaction when carried out in dimethylformamide solvent leads to the formation of binuclear complexes having composition $[\text{Zn}_2(\text{RCOO})_2(\text{DMP})_2(\text{HDMP})_2]$ (where DMP = 3,5-dimethylpyrazolato anion). On the other hand, the mononuclear complexes get transformed to the binuclear complexes on dissolution in dimethylformamide. The reactions are illustrated in Scheme 1. All the complexes are characterized by various spectroscopic techniques and with single crystal X-ray crystallography.

The zinc complex prepared from benzoic acid in presence of 3,5-dimethylpyrazole from a mixed solvent of methanol : toluene (3 : 1) is a mononuclear complex having composition $[\text{Zn}(\text{C}_6\text{H}_5\text{COO})_2(\text{HDMP})_2]$ **1**. The complex **1** has a near tetrahedral geometry around the metal centre with both the HDMP unit in *cis*-orientation to each other. It crystallizes in the triclinic P-1 space group. The crystal structure of **1** is shown in Fig. 1a. The H-atom of the HDMP remains involved in an intra-molecular H-bonding with the carboxylato-O of the nearest carboxylate group. Apart from this interaction, there exist an intermolecular C-H...O interaction between the H12 of phenyl group and the O2 carboxylato oxygen ($d_{\text{D-H}\cdots\text{A}}$ (Å), C12-H12...O2, 2.59 and $\angle\text{D-H}\cdots\text{A}$ (°), $\angle\text{C12-H12}\cdots\text{O2}$, 129) thereby leading to a one dimensional H-bonded chain structure. This is shown in Fig. 1b.

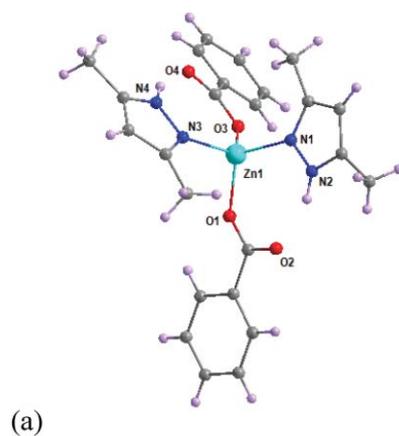
The same reaction in dimethylformamide results in the formation of the binuclear species **2** having composition $[\text{Zn}_2(\text{C}_6\text{H}_5\text{COO})_2(\text{DMP})_2(\text{HDMP})_2]$. In this case also the two zinc centers adopt a near tetrahedral geometry. The pair of HDMP as well as the pair of benzoato ligands across the metal centers is in *trans* geometry to each other. The bridging dimethylpyrazolate anions and the two-zinc centers adopt a planar arrangement, which generates a hexagonal geometry at the core. The complex **2** crystallizes in the monoclinic space group P2(1)/c. It exhibits the

Table 2 Selected bond lengths (Å) and angles (°) in **1** and **2**

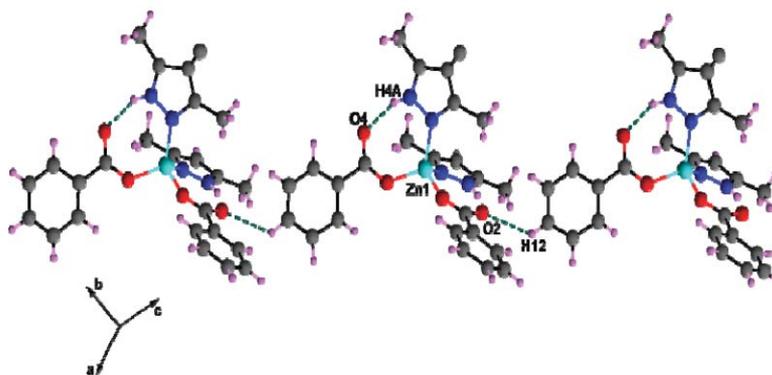
Complex 1		Complex 2	
Zn1-O3	1.9325(17)	O1-Zn1	1.9474(15)
Zn1-O1	1.9380(17)	N1-Zn1	2.0205(18)
Zn1-N1	2.003(2)	N3-Zn1	1.9837(17)
Zn1-N3	2.011(2)	N4-Zn1	1.9768(18)
O3-Zn1-O1	102.45(8)	O1-Zn1-N4	107.81(8)
O3-Zn1-N1	111.36(8)	O1-Zn1-N3	107.98(7)
O1-Zn1-N1	114.59(8)	O1-Zn1-N1	109.60(7)
O3-Zn1-N3	113.87(8)	N3-Zn1-N1	108.20(7)
O1-Zn1-N3	106.87(8)	N4-Zn1-N1	111.00(8)
N1-Zn1-N3	107.72(8)	N4-Zn1-N3	112.18(7)

intra-molecular H-bonding (as in **1**) between the N-H atom and carboxylato-O. The structure of **2** is shown in Fig. 2. Some of the selected bond lengths and bond angles are tabulated in Table 2. To check the phase purity of the complexes **1** and **2** we have also recorded the PXRD patterns which are found to be matched to a good extent with the simulated patterns (please refer to the supplementary materials†).

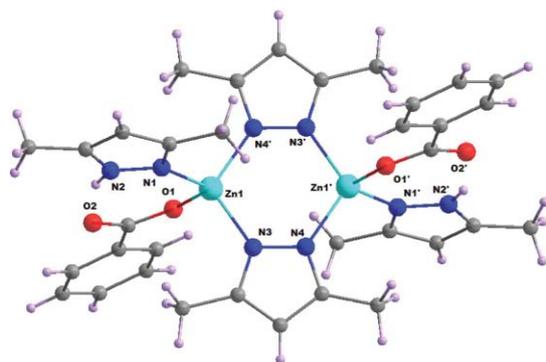
The complex obtained from the reaction of zinc (II) acetate dihydrate with *p*-methylbenzoic acid and 3,5-dimethylpyrazole in methanol : toluene (3 : 1) on crystallization from ethanol gives a solvated mononuclear complex **3** having the composition $[\text{Zn}(p\text{-CH}_3\text{-C}_6\text{H}_4\text{COO})_2(\text{HDMP})_2] \cdot \text{H}_2\text{O} \cdot \text{CH}_3\text{CH}_2\text{OH}$. The complex crystallizes in the monoclinic space group P2₁. The solvent water molecule remains hydrogen bonded to one of the carboxylato-O atoms of the complex as well as to the ethanol molecule through O5-H...O4, O5-H...O6 and O6-H...O5 interactions. Similar to the molecule **1**, here also the HDMP molecules are arranged in a *cis* orientation relative to each other and the H-atom of the HDMP remains involved in an intra-molecular H-bonding with the carboxylato-O of the nearest carboxylate group. Thus the O4 remains H-bonded through two different interactions, one intramolecular N4-H...O4 and the other an intermolecular O5-H...O4 interaction. This intermolecular interaction along with the other O-H...O interactions ($d_{\text{D-H}\cdots\text{A}}$ (Å), O6-H6...O5, 1.92; O5-H5...O6, 2.05; O5-H5...O4, 1.98 and $\angle\text{D-H}\cdots\text{A}$ (°), $\angle\text{O6-H6}\cdots\text{O5}$, 167; $\angle\text{O5-H5}\cdots\text{O6}$, 176; $\angle\text{O5-H5}\cdots\text{O4}$, 154) imparts the molecule a one dimensional H-bonded structure with a solvent channel in between two layers of the assembled mononuclear



(a)



(b)

Fig. 1 (a) The mononuclear complex $[\text{Zn}(\text{C}_6\text{H}_5\text{COO})_2(\text{HDMP})_2]$ (**1**), (b) the 1-D H-bonded chain of **1**.**Fig. 2** The binuclear complex $[\text{Zn}_2(\text{C}_6\text{H}_5\text{COO})_2(\text{DMP})_2(\text{HDMP})_2]$ (**2**).

moiety. The crystal structure of **3** is shown in Fig. 3a along with its one-dimensional structure in Fig. 3b.

The reaction of zinc (II) acetate dihydrate with *p*-methylbenzoic acid in presence of 3,5-dimethylpyrazole in dimethylformamide leads to the binuclear species **4** having composition $[\text{Zn}_2(p\text{-CH}_3\text{-C}_6\text{H}_4\text{COO})_2(\text{DMP})_2(\text{HDMP})_2]$. The complex **4** crystallizes in the orthorhombic space group *Fdd2*. Like the structure **2**, in this complex (**4**) also each of the metal centers have tetrahedral coordination environment. However, unlike in **2**, in the complex **4** the 3,5-dimethylpyrazolato bridged core does not adopt a planar hexagonal geometry because of the steric congestion between the methyl groups of the pyrazolato anions and that of the *p*-toluic acid of an adjacent binuclear unit. This is shown in Fig. 4b. Some

Table 3 Selected bond lengths (Å) and angles (°) in **3** and **4**

Complex 3		Complex 4	
O1-Zn1	1.949(3)	O1-Zn1	1.9463(17)
O3-Zn1	1.940(2)	N1-Zn1	2.013(2)
N1-Zn1	2.005(3)	N3-Zn1	1.981(2)
N3-Zn1	2.015(3)	N4-Zn1	1.986(2)
O3-Zn1-O1	105.97(12)	O1-Zn1-N3	107.64(13)
O3-Zn1-N1	107.51(12)	O1-Zn1-N4	107.62(14)
O1-Zn1-N1	113.10(11)	O1-Zn1-N1	110.46(8)
O3-Zn1-N3	117.06(11)	N3-Zn1-N1	107.45(11)
O1-Zn1-N3	104.79(13)	N4-Zn1-N1	111.20(11)
N1-Zn1-N3	108.55(12)	N3-Zn1-N4	112.43(7)

of the selected bond lengths and bond angles are tabulated in Table 3.

The formation of the two different types of products viz. mononuclear and binuclear is confirmed by recording their $^1\text{H-NMR}$ spectra. As a representative case the $^1\text{H-NMR}$ spectra of the complexes **3** and **4** are shown in Fig. 5. From the figure it is amply clear that the mononuclear complex **3** has only two peaks in the aliphatic region of proton NMR. The signals for one set of methyl groups from 3,5-dimethylpyrazole and as well as from methyl groups of *p*-methyl benzoate groups appears together at 2.14 ppm, while the peak at 2.34 ppm appears due to the other set of methyl protons of 3,5-dimethylpyrazole ligands. The proton NMR spectrum for the binuclear complex **4** has a total of four peaks in the aliphatic region; of which, three different peaks at 1.76,

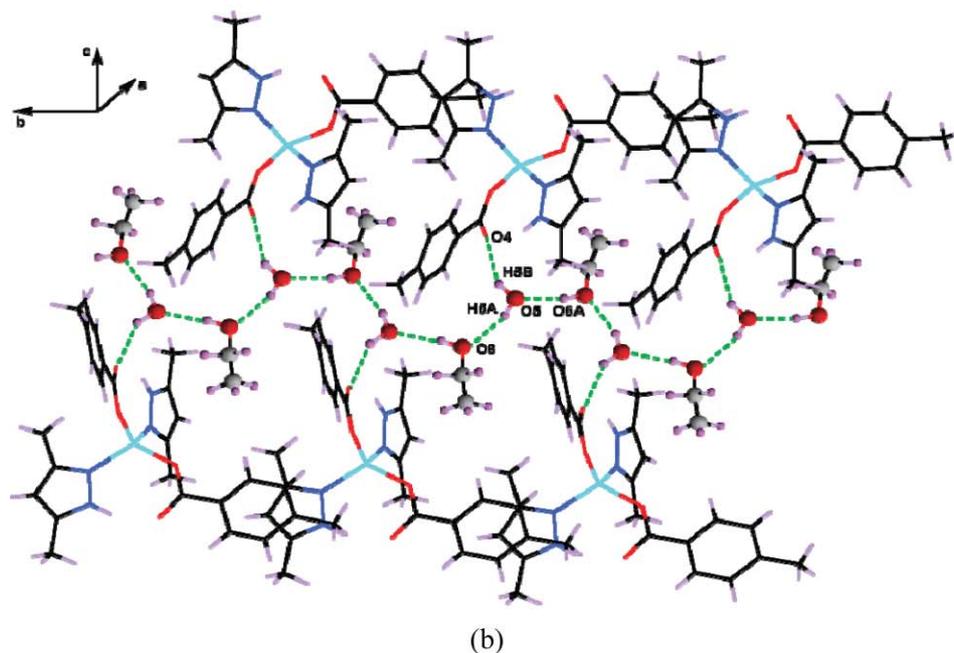
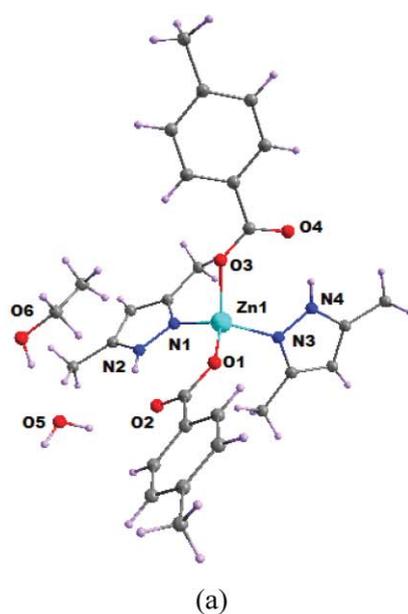


Fig. 3 (a) The solvated mononuclear complex $[\text{Zn}(p\text{-CH}_3\text{-C}_6\text{H}_4\text{COO})_2(\text{HDMP})_2] \cdot \text{H}_2\text{O} \cdot \text{CH}_3\text{CH}_2\text{OH}$ (**3**), (b) the 1-D H-bonded chain of **3** showing the solvent channel.

2.11 and 2.33 ppm are due to the three sets of methyl protons of 3,5-dimethylpyrazole and 3,5-dimethylpyrazolate ligands. Another peak at 2.18 ppm is due to the methyl groups of the *p*-methyl benzoate groups. Moreover, the integration and nature of the independent peaks of two complexes in $^1\text{H-NMR}$ spectra reflects the purity of both the complexes.

The formation of mononuclear and binuclear complexes from different solvents clearly indicates a role of solvent in their formation. Based on the observation of conversion of mononuclear complexes to dinuclear complexes in dimethylformamide it may be suggested that during the transformation of the mononuclear

complexes to the binuclear one, the solvent molecule gets coordinated to the metal center, thereby leading to a five coordinated species. We have recently shown that such a penta-coordinated complex of zinc(II) carboxylate complex can be prepared with appropriate ancillary ligands.⁹ Since, the 3,5-dimethylpyrazole N-H in the mononuclear complexes are intra-molecularly H-bonded in the mononuclear complexes, the acidity of the N-H is enhanced and this also facilitates the deprotonation process during formation of the bridged structures. The formation of such five coordinated species helps the mononuclear complex to lose one molecule of carboxylic acid resulting in the formation

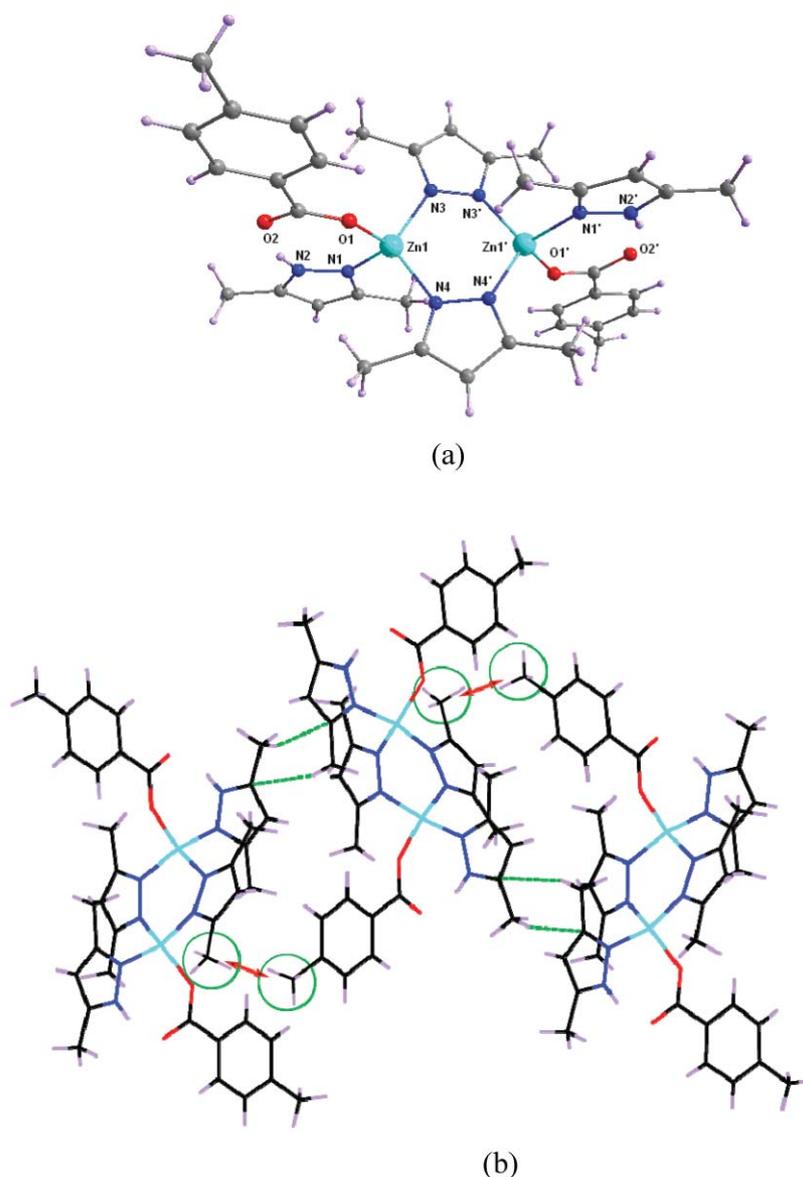


Fig. 4 (a) The binuclear complex $[\text{Zn}_2(p\text{-CH}_3\text{-C}_6\text{H}_4\text{COO})_2(\text{DMP})_2(\text{HDMP})_2]$ (**4**), (b) the steric congestion between methyl group (demarcated by circles) leading to the loss of planarity of the hexagonal core.

of the binuclear complex. Further support to this result comes from the fact that the molar conductance of the mononuclear and the binuclear complex in two different solvents viz. methanol and dimethylformamide are found to be different. The molar conductance of complex **1** is $229 \text{ S cm}^2 \text{ mol}^{-1}$ in methanol and $107 \text{ S cm}^2 \text{ mol}^{-1}$ in dimethylformamide. For complex **2**, the molar conductance in dimethylformamide is found to be $104 \text{ S cm}^2 \text{ mol}^{-1}$. This suggests that on dissolution of complex **1** in dimethylformamide it readily transforms to the binuclear complex. On the basis of these observations a probable pathway for the transformation is proposed as shown in Scheme 2.

The role of solvent in the transformation of complex **1** to **2** has been followed spectrophotometrically by observing the spectral changes that take place upon incremental addition of dimethylformamide to a methanolic solution (10^{-3} M) of complex **1** (Fig. 6). It has been observed that the complex **1** has absorption

at around 270 nm with a shoulder at 277 nm due to the 3,5-dimethylpyrazole group. On addition of dimethylformamide this absorption peak undergoes a hypsochromic shift and the successive absorption curves pass through an isosbestic point at 264 nm . The presence of this isosbestic point clearly supports the presence of the two forms **1** and **2** in equilibrium. A similar observation is found in the case of the transformation of complex **3** to **4** (please refer to the supplementary materials†).

Interestingly the binuclear complex is not formed in the case of *p*-nitrobenzoic acid. When zinc (II) acetate is reacted with *p*-nitrobenzoic acid and 3,5-dimethylpyrazole in methanol : toluene (3 : 1) solvent mixture, it leads to the formation of mononuclear complex **5** co-crystallizing with methanol. The complex crystallizes in a triclinic P-1 space group and it contains two structurally independent molecules in the asymmetric unit ($Z' = 2$). Each of the metal centers in **5** is tetrahedrally coordinated

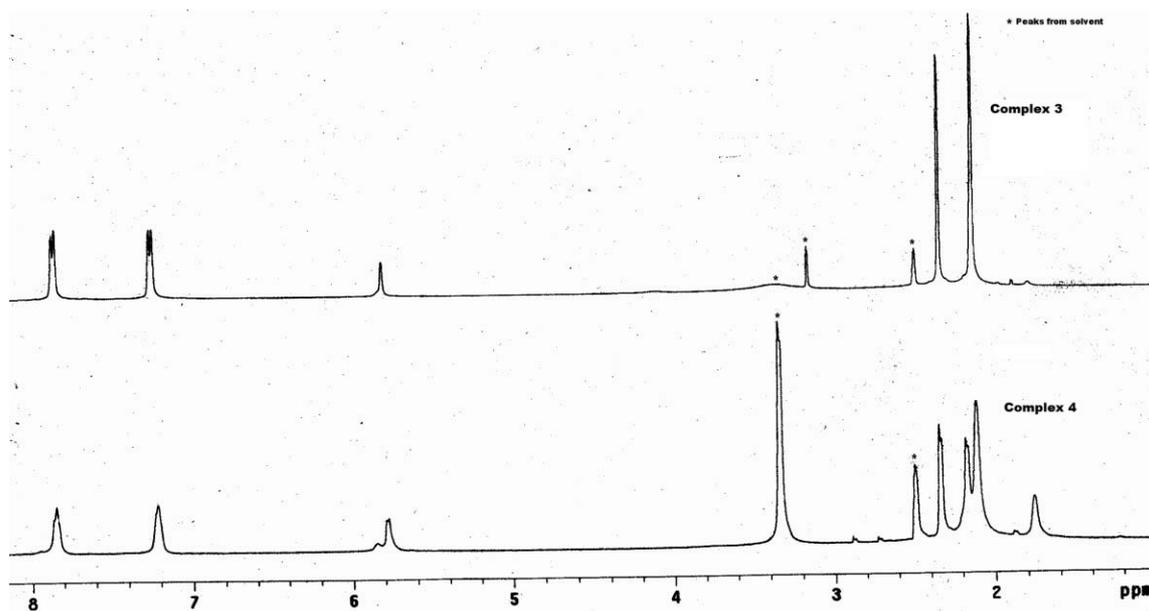
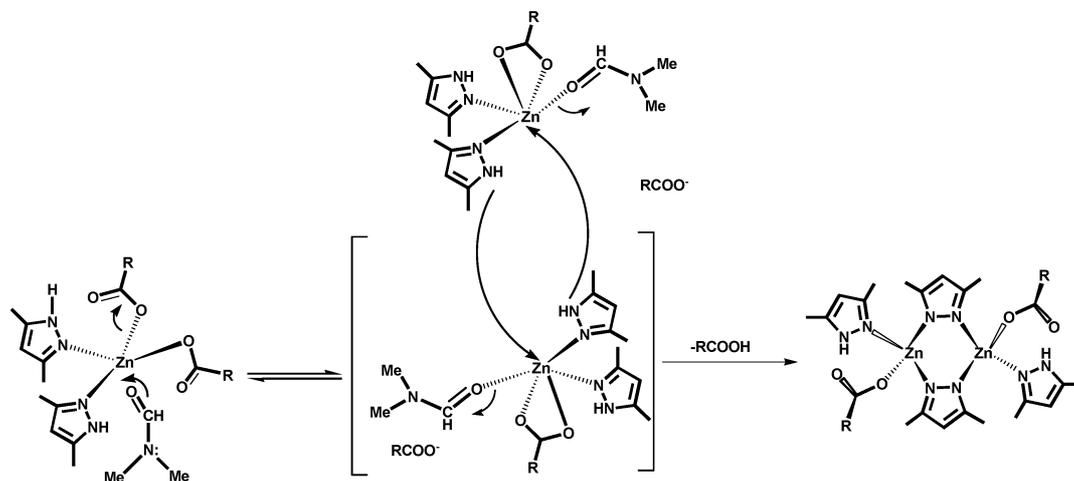


Fig. 5 $^1\text{H-NMR}$ spectra (DMSO-d_6) of the complexes 3 and 4 (signals from solvent are marked with *).



Scheme 2 A possible path for transformation of mono-nuclear zinc complex to di-nuclear zinc complex through ligand dissociation.

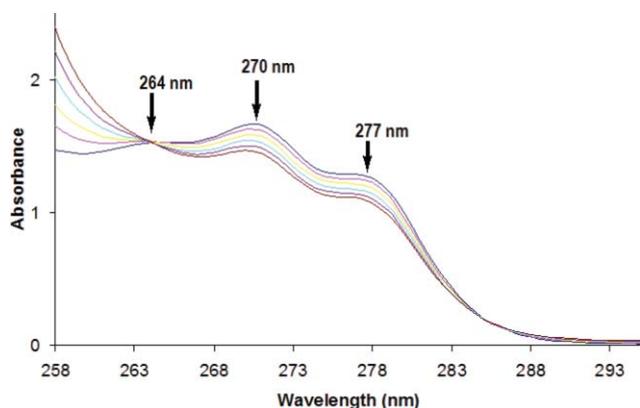


Fig. 6 Ultraviolet absorption spectra of complex 1 in methanol (10^{-3} M) upon addition of dimethylformamide (100 μl per aliquot).

to two *p*-nitrobenzoate and two 3,5-dimethylpyrazole ligands. Like the structures 1 and 3 here also the HDMP ligands are in *cis*-orientation to each other and the H-atom of the HDMP remains involved in an intra-molecular H-bonding with the carboxylato-O of the nearest carboxylate group. The C-H \cdots O interactions stabilize the assemblies of the symmetry non-equivalent molecules in the lattice as illustrated in Fig. 7. These short range interactions results in a chain like self assembly of the molecule growing along the 'a' crystallographic axis. The structure of 5 is shown in Fig. 7a below along with the self assembly formation in Fig. 7b.

It is interesting to note here that the symmetry non-equivalence is independent of the solvent, as in other solvents also the cocrystals have similar structure with $Z' = 2$. The same reaction independently carried out in acetone or dimethylformamide gives the pseudo-polymorphs with inclusion of water $[\text{Zn}(p\text{-NO}_2\text{-C}_6\text{H}_4\text{COO})_2(\text{HDMP})_2]\cdot\text{H}_2\text{O}$ (6) or dimethylformamide $[\text{Zn}(p\text{-NO}_2\text{-C}_6\text{H}_4\text{COO})_2(\text{HDMP})_2]\cdot 3\text{H}_2\text{O}\cdot\text{DMF}$ (7) respectively (Fig. 8). We have recorded the UV- spectrum of the complex 6 in

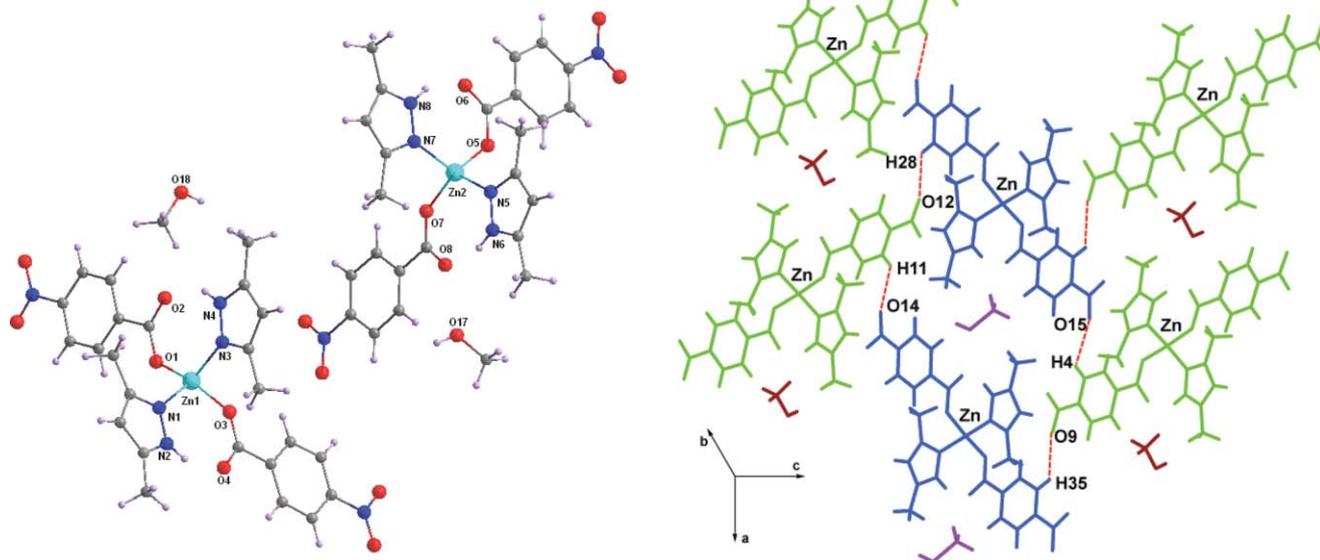


Fig. 7 (a) The asymmetric unit of mononuclear complex **5**, (b) crystal packing in **5** showing the symmetry non-equivalence. Some important weak interactions are ($d_{D-H \cdots A}$ (Å), $\angle C13-H13 \cdots O14$, 2.65; $\angle C28-H28 \cdots O12$, 2.56; $\angle C35-H35 \cdots O10$, 2.46; $\angle C6-H6 \cdots O16$, 2.60 and with angle $\angle D-H \cdots A$ ($^\circ$), $\angle C13-H13 \cdots O14$, 127; $\angle C28-H28 \cdots O12$, 130.2; $\angle C35-H35 \cdots O10$, 132; $\angle C6-H6 \cdots O16$, 132).

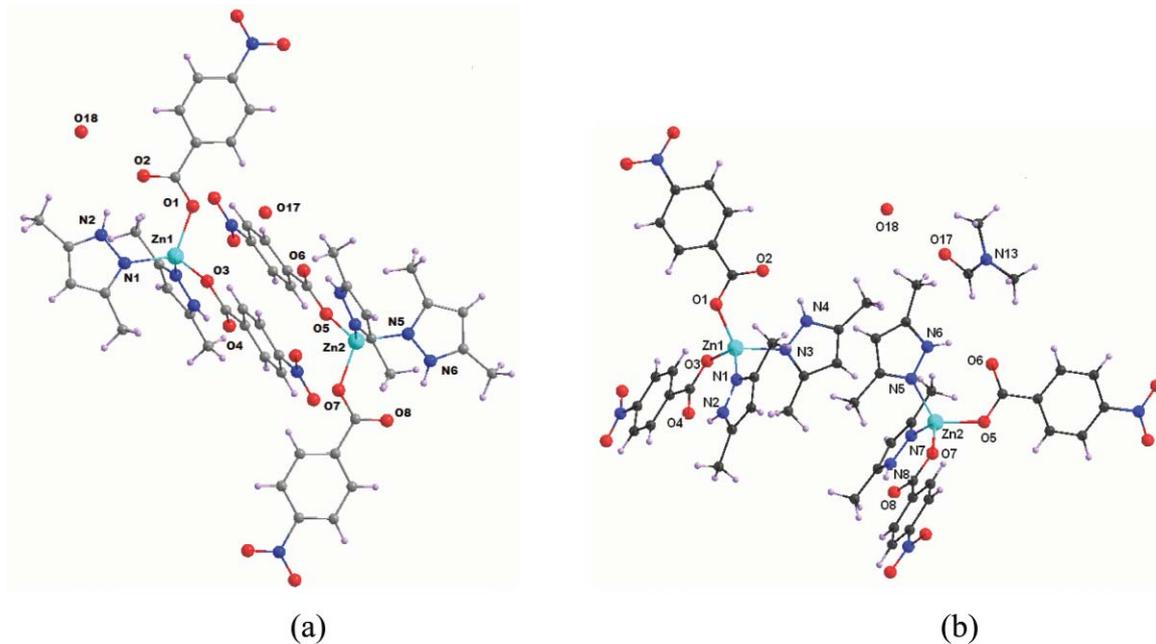


Fig. 8 The asymmetric unit of mononuclear complex (a) **6**, (b) **7**.

methanol (10^{-3} M) and followed the change in the spectrum on addition of dimethylformamide. In the case of **6** a distinct isosbestic point is not found, and in the case of **7** also the changes are not distinct which can be attributed to the formation of a solvate in solution. Based on the above observations it can be inferred that in the case of *p*-nitrobenzoic acid, it is the solvent inclusion mononuclear complexes that are favored probably due to supramolecular interactions that are implicated in solid state solvated species; which prevents isolation of a dinuclear complex.

Conclusions

In literature it is reported that the 3,5-dimethylpyrazolato bridged zinc (2+) complexes can be prepared from metallic zinc using acetone as solvent;^{10a} however the difference of these complexes from our system is that those complexes are devoid of carboxylate ligands. It is worthwhile to note that the carboxylato bridged zinc (2+) complexes having monodentate 3,5-dimethylpyrazole are also known.^{10b} In contrast, we have shown examples of 3,5-dimethylpyrazolato bridged carboxylate complexes. Our

results add an extra dimension to the existing compounds by understanding them structurally. Understanding the transformation of mononuclear to dinuclear complexes through loss of carboxylate groups provides avenues for exploring them under neutral conditions. In conclusion a number of mononuclear and binuclear complexes 1–7 are prepared under similar reaction condition by varying the solvents. Conversion of mononuclear to binuclear complexes by solvent is established in zinc(2+) 3,5-dimethylpyrazole complexes.

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