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Structural variations in self-assembled cadmium benzoate complexes

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Abstract

A series of mixed ligand cadmium(II) complexes having 3,5-dimethylpyrazole and aromatic carboxylate are structurally characterized. The effect of substituent on aromatic ring and also the effect of composition on co-ordination behavior of these complexes are ascertained. Hydrogen bonded self-assembled mononuclear complexes are obtained from composition $[Cd(L)_2(L_a)_2]$ where $L_a = $ 3,5-dimethylpyrazole $L = R–C_6H_4COO–$ [R = H (**1**), 2-Cl (**2**), 4-OH (**3**), 2-OH (**4**)]. The cadmium complex (**5**) having composition $[Cd(L)_2(L_a)(H_2O)]$ ($L = 2-NO_2–C_6H_4COO–$) is tetra-nuclear. The complex has eight and six co-ordination around cadmium and self-assembles through hydrogen bonding leading to form extended chain structure. The four complexes (**1**–**4**) have six co-ordinated trigonal prismatic geometry around cadmium ions. Cadmium complexes having composition $[Cd(L)_2(L_a)]$ such as $R = 4-NO_2$ (**6**), 4-Cl (**7**), and 1-naphthoate complex (**8**) are co-ordination polymers with seven co-ordination geometry around cadmium. In these co-ordination polymers different Cd–Cd distances are observed for alternate pair of cadmium ions. For example in the case of the co-ordination polymer of 4-nitro-benzoate complex the Cd–Cd distance between alternate pairs are 4.138 Å, and 3.748 Å. The 1-naphthoate complex having pyridine has composition $[Cd(L)_2(L_b)_2](H_2O)]$ (**9**) where $L_b = $ pyridine and L = 1-naphthoate has seven co-ordination with a distorted pentagonal bipyramid geometry.

Keywords: Cadmium complexes; Self-assembly; Hydrogen-bonding; Co-ordination polymers

1. Introduction

The metal carboxylate chemistry has been of great interest for their co-ordination behavior as well as for making metallo-organic frameworks [1]. Out of different metal carboxylates, cadmium carboxylates are of special interest for their interesting material properties [2] as well as for their versatile co-ordination behavior [3]. Mixed carboxylate complexes of cadmium have interesting polymeric structure [4] and cadmium carboxylates also form double salts having interesting structures [5]. Since there are several possible co-ordination numbers for cadmium complexes [3]; it is important to understand how the co-ordination number as well as preferential co-ordination of a ligand occurs. Multi components reactions under ambient condition may be important to achieve such rationale. Such synthesis would lead to thermodynamically stable complex. It would also throw light on the co-ordination chemistry and nucleation process. One of the criteria to prepare complexes from multiple components, is that the ligands should have comparable reactivity and competitive enough to form complexes containing the components of interest. Since many of the polymeric carboxylate complexes have dinuclear frame in the backbone [1], synthesis of carboxylate complexes under such competitive environment would enable one to establish the limiting condition at which a dinuclear paddle wheel structure would deform and finally lead to a mononuclear structure as shown in Scheme 1. Our recent results suggest that the variation of reaction condition leads to different co-ordination complexes in the case of copper [6a], nickel [6b,6c], cobalt [6d] and zinc [6e].

Among competitive ligands aromatic carboxylic acid along with 3,5-dimethylpyrazole or pyridine with acetate metal salts have been envisaged [6]. With a similar objective

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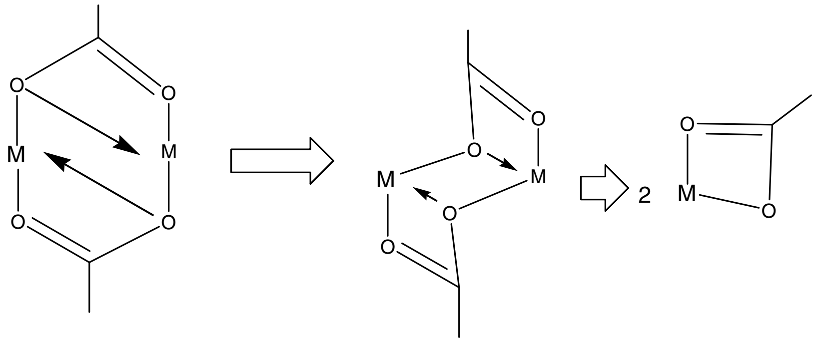

Scheme 1. Limiting condition of paddle-wheel structure going to mononuclear structure.

we pursued reactions of cadmium(II)acetate with aromatic carboxylic acids followed by reaction with nitrogen donor ligands such as 3,5-dimethylpyrazoles or pyridine and the results are presented in this article.

2. Experimental

The X-ray diffraction data were collected at room temperature [296(2) K] on a Bruker 3-circle diffractometer (Bruker Nonius SMART APEX 2) equipped with CCD area detectors, and using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) from 60W microfocus Siemens Microsource with glass polycapillary optics. X-ray diffraction data for all the crystals were collected using Bruker SMART software. This software was also used for indexing and determining unit cell parameters. The structures were solved by direct methods and refined by full-matrix least squares against F^2 for all data using SHELXTL software. All non-H atoms were refined by full-matrix least squares in the anisotropic approximation and the hydrogen atoms attached to these atoms the hydrogen atoms have been located on the difference Fourier maps. In all cases the hydrogen atoms attached to polar atoms such as O and N were located on the difference Fourier maps and refined in the final structure in isotropic approximation. Experimental absorption correction method is none in all cases. The crystal data are given in Table 1. The proton NMR spectra were recorded in a Varian 400 MHz spectrophotometer at room temperature while the FT-IR spectra were recorded in NICOLET IMPACT-410 spectrometer using OMNIC software.

3. Experimental procedure for preparation of the complexes 1–9

To a well-stirred solution of benzoic acid/substituted benzoic acid (2 mmol) in methanol (10 ml) a solution of cadmium acetate dihydrate (0.266 g, 1 mmol) in methanol (5 ml) was added. The resulting homogeneous solution was stirred at room temperature for 4 h. To this homogeneous solution 3,5-dimethylpyrazole (2 mmol) or pyridine (2 mmol) was added and the colorless mixture was further stirred for 2 h. The solution was filtered and the filtrate on standing led to crystallization of the product.

4. Crystalline yield and spectroscopic data of the compounds

Complex **1**: Crystalline yield 61%, ^{1}H NMR (DMSO-d_6) 7.98–7.96(m, 2H), 7.47–7.39(m, 3H), 5.76(s 1H), 2.13 (s, 6H). IR(KBr, cm^{-1}) 3434(bs), 1596(s), 1538(s), 1404(s), 1279(s), 1166(m), 1147(m), 1040(m), 1024(m), 855(m), 803(m), 723(s). Elemental *Anal.* Calc. for $C_{24}H_{26}CdN_4O_4$: C, 52.66; H, 4.75. Found: C, 52.60; H, 4.74%. Complex **2**: Crystalline yield 30%, ^{1}H NMR (DMSO-d_6) 7.69(md, $J = 8$ Hz, 1H), 7.49–7.30(m, 3H), 5.74(s, 1H), 2.12(s, 6H). IR(KBr, cm^{-1}) 3445(bm), 3199(s), 3146(s), 1577(s), 1550(s), 1396(s), 1299(m), 1169(w), 1149(w), 1050(m), 860(m), 792(m), 755(s). Elemental *Anal.* Calc. for $C_{24}H_{24}CdN_4O_4Cl_2$: C, 46.77; H, 3.90. Found: C, 46.82; H, 3.92%. Complex **3**: Crystalline yield 15%, ^{1}H NMR (DMSO-d_6) 12.00(s, 1H), 7.79–7.78(m, 1H), 7.31–7.27(m, 1H), 6.78–6.71(m, 2H), 5.73(s, 1H), 2.10(s, 6H). IR(KBr, cm^{-1}) 3198(s), 3144(s), 3044(s), 2984(s), 1623(s), 1590(s), 1540(s), 1483(s), 1452(s), 1396(s), 1352(s), 1292(m), 1251(s), 1143(w), 1044(w), 875(w), 760(s). Complex **4**: Crystalline yield 34%, ^{1}H NMR (DMSO-d_6) 9.80(bs, 1H), 7.81(d, 8 Hz, 2H), 6.75(d, 8 Hz, 2H), 5.75(s,1H), 2.12(s, 6H). IR(KBr, cm^{-1}) 3420(bs), 3193(s), 3146(s), 1600(s), 1532(s), 1395(s), 1280(s), 1238(s), 1160(w), 1034(w), 825(m), 780(m). Complex **5**: Crystalline yield 51%, ^{1}H NMR (DMSO-d_6) 7.84(dd, 4, 8 Hz, 2H), 7.75(dd, $J = 4$, 8 Hz, 2H), 7.67–7.56(m, 4H), 5.75(m, 1H), 2.12(s, 6H). IR(KBr, cm^{-1}) 3445(bs), 1592(s), 1573(s), 1393(s),1356(s), 1153(w), 783(w), 741(w). Complex **6**: Crystalline yield 51%, ^{1}H NMR (DMSO-d_6) 8.27–8.25(m, 4H), 8.18–8.16(m, 4H), 5.74(s, 1H), 2.12(s, 6H). IR(KBr, cm^{-1}) 3422(bs), 3199(s), 3136(s), 2931(s), 2875(s), 1572(s), 1388(s), 1339(s), 1031(m), 815(s), 727(m). Elemental *Anal.* Calc. for $C_{19}H_{16}CdN_4O_8$: C, 42.16; H, 2.96. Found: C, 42.20; H, 2.99%. Complex **7**: Crystalline yield 26%, ^{1}H NMR (DMSO-d_6) 7.96–7.93(m, 4H), 7.47–7.45(4H), 5.74(s, 1H), 2.12(s, 6H). IR (KBr, cm^{-1}) 3269(bs), 1590(s), 1500(s), 1411(s), 1284(w), 1096(w), 858(m), 776(m). Complex **8**: Crystalline yield 24%, ^{1}H NMR (DMSO-d_6) 8.58 (s, 2H), 8.04(t, $J = 8$ Hz, 4H), 7.92(t, $J = 8$ Hz , 4H),

Table 1
Crystal data and refinement parameters for **1**–**9**

	1	**2**	**3**	**4**	**5**
Formulae	$C_{24}H_{26}CdN_4O_4$	$C_{24}H_{24}CdN_4O_4Cl_2$	$C_{24}H_{26}CdN_4O_6$	$C_{24}H_{26}CdN_4O_6$	$C_{76}H_{72}CdN_{16}O_{36}$
Molecular weight	546.89	615.77	578.89	578.89	2235.10
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	triclinic
Space group	$P2_1/n$	$C2/c$	$P2_1/n$	$P2_1/c$	$P\bar{1}$
a (Å)	12.6043(5)	23.7361(15)	13.1139(3)	10.0548(5)	14.0437(8)
b (Å)	13.9558(6)	11.2097(6)	13.0501(3)	21.1953(12)	14.1965(9)
c (Å)	14.2804(6)	10.6339(12)	14.7963(4)	12.0152(7)	14.6448(10)
α (°)	90.00	90.00	90.00	90.00	63.324(4)
β (°)	93.250(2)	115.578(5)	94.2690(10)	109.5650(10)	62.683(3)
γ (°)	90.00	90.00	90.00	90.00	64.211(3)
V (Å^3)	2507.03(18)	2552.1(4)	2525.18(11)	2412.8(11)	2219.5(2)
Z	4	4	4	4	1
Density (g cm^{-3})	1.448	1.603	1.523	1.594	1.672
Absorption coefficient (mm^{-1})	0.906	1.103	0.910	0.953	1.042
$F(000)$	1112	1240	1176	1176	1120
Total number of reflections	9137	16001	25494	12211	24479
Reflections $I > 2\sigma(I)$	5097	2703	4609	4351	9028
Maximum 2θ (°)	28.40	28.21	28.37	28.38	28.38
Ranges (h,k,l)	$-16 \leqslant h \leqslant 16$, $-18 \leqslant k \leqslant 18$, $-19 \leqslant 1 \leqslant 19$	$-29 \leqslant h \leqslant 31$, $-14 \leqslant k \leqslant 14$, $-14 \leqslant 1 \leqslant 13$	$-17 \leqslant h \leqslant 17$, $-17 \leqslant k \leqslant 17$, $-19 \leqslant 1 \leqslant 19$	$-13 \leqslant h \leqslant 13$, $-25 \leqslant k \leqslant 15$, $-16 \leqslant 1 \leqslant 13$	$-18 \leqslant h \leqslant 18$, $-18 \leqslant k \leqslant 18$, $-19 \leqslant 1 \leqslant 18$
Complete to 2θ (%)	99.1	96.4	99.2	89.1	97.8
Data/restraints/parameters	6235/0/310	3044/0/161	6270/0/336	5394/0/336	10849/0/623
Goodness of fit (F^2)	1.019	1.050	1.012	0.995	1.017
R indices [$I > 2\sigma(I)$]	0.0252	0.0292	0.0289	0.0260	0.0243
R indices (all data)	0.0689	0.0785	0.0683	0.0628	0.0615

	6	**7**	**8**	**9**
Formulae	$C_{19}H_{16}CdN_4O_8$	$C_{19}H_{16}CdN_2O_4Cl_2$	$C_{27}H_{22}CdN_2O_4$	$C_{32}H_{26}CdN_2O_5$
Molecular weight	540.76	519.64	550.87	630.95
Crystal system	triclinic	triclinic	monoclinic	monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1/c$	$P2_1/n$
a (Å)	7.8825(6)	7.8546(4)	7.9424(9)	15.7113(15)
b (Å)	11.4426(10)	10.8632(7)	29.076(4)	6.0304(5)
c (Å)	12.2286(10)	13.3295(8)	10.5680(12)	29.197(3)
α (°)	85.004(5)	111.717(3)	90.00	90.00
β (°)	72.214(5)	91.225(3)	97.118(7)	92.195(6)
γ (°)	82.499(5)	97.744(2)	90.00	90.00
V (Å^3)	1039.97(15)	1043.85(11)	2421.3(5)	2764.3(4)
Z	2	2	4	4
Density (g cm^{-3})	1.727	1.653	1.511	1.516
Absorption coefficient (mm^{-1})	1.105	1.328	0.973	0.834
$F(000)$	540	516	1112	1280
Total number of reflections	8297	13329	30720	23494
Reflections ($I > 2\sigma(I)$)	3342	4609	3591	5021
Maximum 2θ (°)	26.00	28.33	28.33	28.34
Ranges (h,k,l)	$-9 \leqslant h \leqslant 9$, $-13 \leqslant k \leqslant 13$, $-15 \leqslant 1 \leqslant 15$	$-10 \leqslant h \leqslant 10$, $-14 \leqslant k \leqslant 14$, $-17 \leqslant 1 \leqslant 17$	$-10 \leqslant h \leqslant 10$, $-38 \leqslant k \leqslant 38$, $-13 \leqslant 1 \leqslant 14$	$-20 \leqslant h \leqslant 20$, $-7 \leqslant k \leqslant 8$, $-37 \leqslant 1 \leqslant 39$
Complete to 2θ (%)	88.3	97.5	99.3	98.3
Data/restraints/parameters	3609/0/195	5087/0/260	5994/0/313	6766/0/369
Goodness-of-fit (F^2)	1.077	1.031	1.041	1.012
R indices [$I > 2\sigma(I)$]	0.0202	0.0243	0.0531	0.0325
R indices (all data)	0.0527	0.0643	0.1410	0.0675

7.60–7.55(m, 4H), 5.73(s, 1H), 2.12(s,6H). IR(KBr, cm^{-1}) 3392(bs), 3056(w), 2923(w), 1547(s), 1396(s), 792(s). Complex **9**: Crystalline yield 23%, ^{1}H NMR (DMSO-d_6) 8.59(s, 1H), 8.09–8.04(m, 2H), 7.94(t, $J = 8$ Hz , 2H), 7.78(mt, $J = 8$ Hz, 2H), 7.61–7.54(m,2H), 7.41–7.38(m, 3H). IR(KBr, cm^{-1}) 3444(bs), 2925(m), 1631(s), 1602(s), 1537(s), 1504(m), 1046(m), 1400(s), 1281(w), 1035(m), 790(s).

5. Results and discussion

The reaction of cadmium acetate with aromatic carboxylic acid followed by treatment with 3,5-dimethylpyrazole (L_a) led to mixed ligand cadmium complexes. The number of (L_a) ligand/s in cadmium carboxylate complexes varies with the aromatic carboxylic acid from which it is prepared. Either two nitrogen donor ligands or one nitrogen donor ligand per cadmium ion are observed depending on the substituents present in the aromatic carboxylate. For example, the reaction of cadmium acetate dihydrate with aromatic carboxylic acids such as benzoic acid, 2-chlorobenzoic acid, 2-hydroxybenzoic acid or 4-hydroxybenzoic acid in the presence of (L_a) led to the formation of corresponding benzoate complexes having two benzoate groups and two (L_a) ligands. The 2-nitro-, 4-nitro-, 4-chloro-benzoic acids and 1-naphthoic acid led to complex having one (L_a) and two carboxylate ligands per cadmium. However, the 2-nitrobenzoate complex of cadmium contains an additional aqua ligand; which is absent in the case of 4-nitrobenzoate complex. The results are depicted Scheme 2.

The crystal structure of each of these complexes is determined and the structures of the complexes **1**–**4** are shown in Fig. 1. Trigonal prismatic geometry with six co-ordination around cadmium ions are observed in the cases of the complexes **1**–**4**. The bond angles and bond distances of the complexes are listed in Table 2 and structures of the complexes are shown in Fig. 1. It may be mentioned that in the case of **1** two types of cadmium ligand bonds in terms of bond length are observed. There are four cadmium–ligand bonds of similar length and two other are slightly longer. It has been already reported [3a] that in cadmium complexes outer and inner co-ordination spheres are possible and the outer Cd–N bond lengths are in the range of 2.5–2.7 Å whereas inner ones are less by about 0.3 Å from the outer ones. In our system also the bond distances of the four Cd–N and Cd–O bonds are comparable and makes a pseudo tetrahedral inner structure comprising of Cd–O3, Cd–O4, Cd–N1 and Cd–N4 bonds. The other two Cd–O1 and

$Cd(OAc)_2\,2H_2O + RC_6H_4COOH + La \longrightarrow [Cd(RC_6H_4COO)_2(La)_2]$

When R = H (**1**), 2-Cl (**2**) 4-OH (**3**), 2-OH (**4**)

$\downarrow$ L_a = 3,5-dimethylpyrazole

$[Cd\,(RC_6H_4COO)_2(L_a)(H_2O)_n]$

When R = 2-NO_2, n = 1 (**5**); when R = 4-NO_2, n = 0 (**6**) when R= 4-Cl, n =0 (**7**)
when RC_6H_4 = 1-naphthyl, n= 0 (**8**)

Scheme 2.

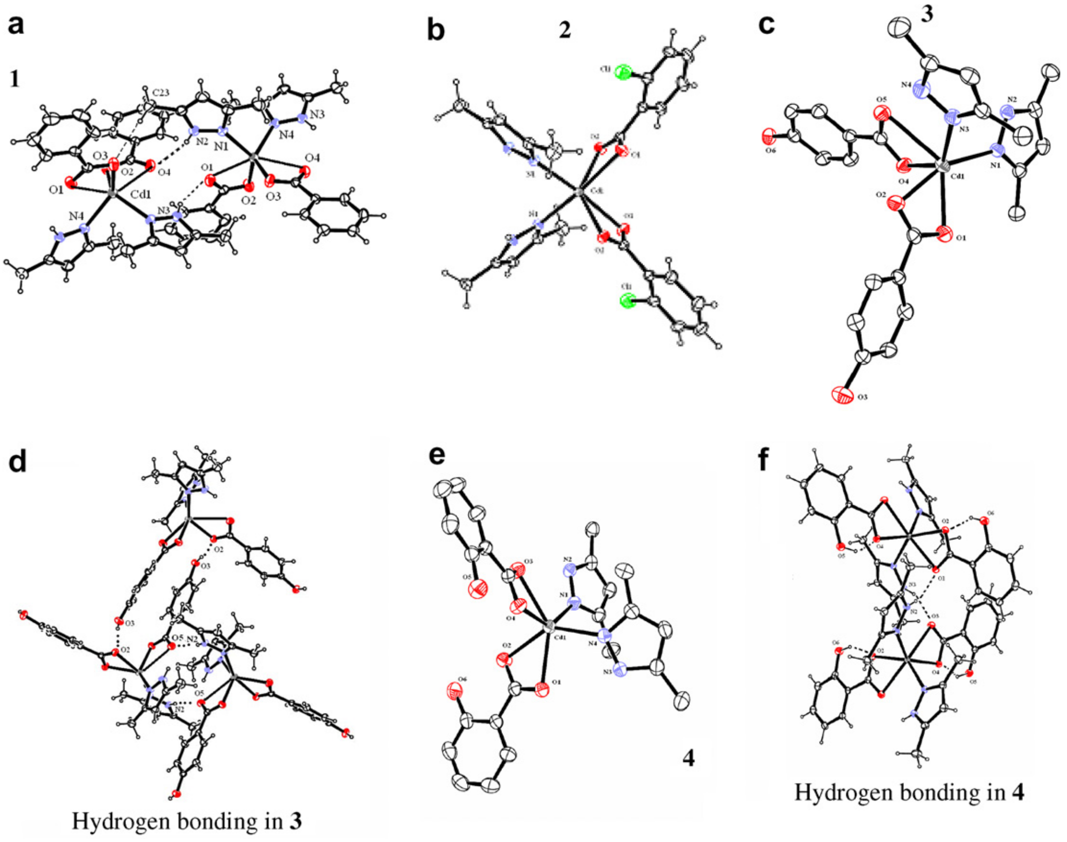

Fig. 1. Structures of cadmium benzoate complexes **1**–**4** and their hydrogen bonded assembly [ORTEP are drawn with 20% thermal ellipsoid, in cases of (c) and (e) hydrogen atoms are omitted for clarity].

Table 2
Cadmium–ligand bond geometry (distances and angles) in complexes **1**–**4**

Cd–L	Co–L (Å)	L–Cd···L	∠L–Cd···L (°)	Cd–L	Co–L (Å)	L–Cd···L	∠L–Cd···L (°)
*For **1***				*For **2***			
Cd–O1	2.561	O4–Cd–N4	80.96	Cd–O1	2.371	O1–Cd–N1	114.56
Cd–O2	2.234	O4–Cd–N1	125.52	Cd–O2	2.358	N1–Cd–N2	87.34
Cd–O3	2.276	O3–Cd–O1	95.16	Cd–O1	2.371	O2–Cd–N1	92.27
Cd–O4	2.480	O4–Cd–O2	107.04	Cd–O2	2.358	O1–Cd–O2	92.77
Cd–N4	2.254	O3–Cd–N1	93.87	Cd–N1	2.272	O2–Cd–O2	89.89
Cd–N1	2.278	O3–Cd–N4	132.13	Cd–N1	2.272	O1–Cd–O1	136.88
*For **3***				*For **4***			
Cd–O1	2.288	N1–Cd–O4	95.64	Cd–O1	2.365	O1–Cd–N4	85.03
Cd–O2	2.400	O2–Cd–O5	90.98	Cd–O2	2.379	O3–Cd–O2	97.98
Cd–O5	2.779	O1–Cd–O4	96.84	Cd–O3	2.422	O1–Cd–O4	100.11
Cd–O4	2.222	O1–Cd–N1	105.56	Cd–O4	2.302	O3–Cd–N1	85.20
Cd–N1	2.259	O2–Cd–N3	90.74	Cd–N1	2.251	O2–Cd–N4	139.05
Cd–N3	2.779	N3–Cd–N1	94.27	Cd–N4	2.276	O2–Cd–N1	100.64

Cd–O4 bonds have bond length 2.561 and 2.480 Å and with bond angles O1–Cd–O4 137.62°, respectively. This suggests that under suitable condition these two atoms would serve as bridging group if another metal atom can approach. However, in this case presence of two 3,5-dimethylpyrazole ligands prevents further approach oxygen to the cadmium ion to form co-ordination polymer. The 2-chlorobenzoate complex **2** has a more symmetric trigonal prismatic structure. Both the compounds **1** and **2** have similar hydrogen bonding interactions and they remain as hydrogen bonded self-assemblies. In these two complexes the N–H bond of 3,5-dimethylpyrazole interacts with the carbonyl group of co-ordinated carboxylate ligand of another molecule to form self-assemblies. Such assemblies are further held by C23–H···O2 interaction between C–H of a methyl group with an oxygen atom of carboxylate group of another molecule (Fig. 1a). The important bond angles and distances for compound **1** are listed in Table 2. Cadmium complex of 4-amino-carboxylic acid adopts two dimensional polymeric hydrogen bonded structure [7]. The structure of the complexes **3** and **4** are shown in Fig. 1c and e respectively. Both these complexes have six co-ordinations with distorted trigonal prismatic geometry and in the solid state they form H-bonded self-assembly. The complex **3** has a one dimensional layer structure held by N–H···O interactions between the N–H of 3,5-dimethylpyrazole un-coordinated nitrogen atoms with carbonyl oxygen of 2-hydroxybenzoate. There is also intra-molecular hydrogen bonding (O6–H···O2) between the hydroxy groups with the carbonyl oxygen of the benzoate (Table 3). In the 4-hydroxybenzoate complex **4**, hydrogen bonding between hydroxy groups and the carbonyl oxygen of another molecule adjacent to it takes place. In addition to this, the opposite side of the molecule is associated with N–H···O interactions with another neighboring molecule as illustrated in Fig. 3f. These interactions result in the formation of three-dimensional hydrogen bonded network. It is already reported that the picolinic acid forms six-coordinated polymeric network. Our results also support that N1O5 environment around cadmium [1n,2] can lead to co-ordination polymer in one-dimension.

The nitro-substituent on the aromatic carboxylic acid affects the structure as well as the co-ordination environment of cadmium complexes. The complex **5** has an aqua-ligand and it is a tetra nuclear complex as shown in Fig. 2a. The formation of such tetra nuclear complex is attributed to the variation in composition due to the steric effect of nitro-group at *ortho*-position leading to a thermodynamically stable product. The complex **5** has eight co-ordination around two central cadmium ion and the other two cadmium ions at both the ends of the tetra nuclear complex have six co-ordination geometry. Polymeric cadmium complexes having seven co-ordination is common in co-ordination chemistry of cadmium [1a], however the complex **5** is a rare example of tetra nuclear complex having eight co-ordination. It is interesting to note that each of the tetra nuclear complex possesses aqua-ligand at the end cadmium atoms; each and these aqua ligands interacts with

Table 3
Hydrogen bonding geometry (distances and angles) in complexes **1**–**4**

D–H···A	$d_{\mathrm{D–H}}$ (Å)	$d_{\mathrm{H\cdots A}}$ (Å)	$d_{\mathrm{D\cdots A}}$ (Å)	∠D–H···A (°)
*For **1***				
C23–H···O2	0.960	2.470	3.412	187.02
O4–H···N2	0.926	2.242	2.990	158.24
N6–H···O2	0.817	1.935	2.737	166.98
*For **2***				
N2–H···O1	0.880	1.961	2.821	165.57
*For **3***				
O3–H...O2	0.730	1.963	2.683	168.42
O6–H...O4	0.803	1.933	2.729	171.25
N2–H... O5	0.854	2.062	2.864	156.08
*For **4***				
O6–H···O2 (intramolecular)	0.889	1.788	2.589	148.63
N2–H···O1	0.832	2.280	3.041	152.41
N3–H···O3	0.832	2.188	2.954	153.05

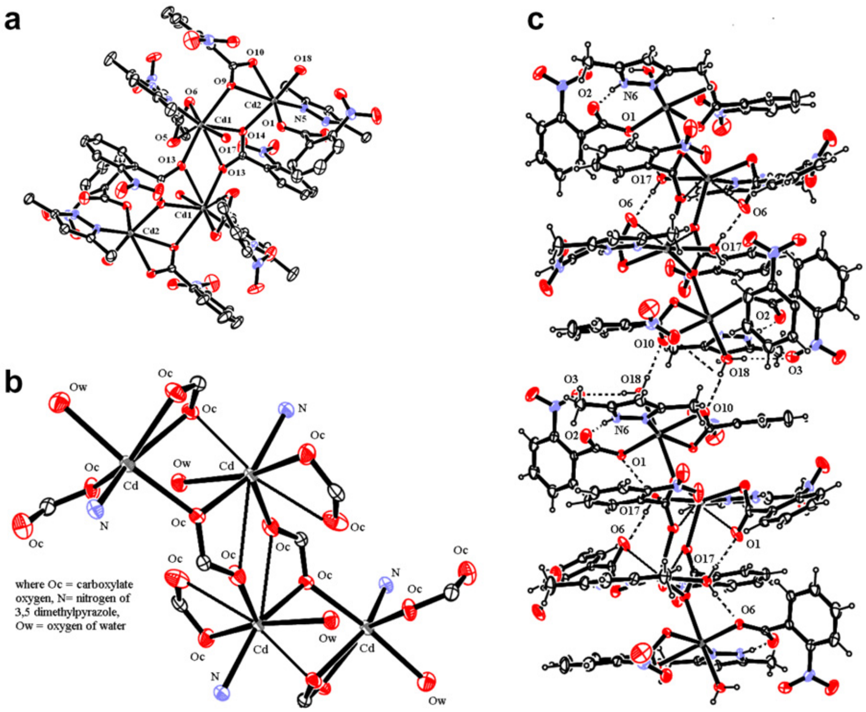

Fig. 2. (a) Structure of tetra nuclear complex **5** (hydrogen atoms are omitted for clarity). (b) The arrangement of ligands around the cadmium in the tetra nuclear complex. (c) Hydrogen bonding interactions in the self assembled structure (drawn with 20% thermal ellipsoids).

the carbonyl group of another tetra-nuclear complex making an one dimensional self-assembled polymeric structure. Some of the important hydrogen bonding interactions present in the hydrogen bonded assembly is listed in Table 4. This structure is also important from another point of view is that it is an exception to the structure that is observed as mononuclear complex from 2-chlorobenzoic acid and 2-hydroxybenzoic acid which are *ortho*-substituted aromatic carboxylates. However, it is observed that the solid phases reaction of 2-nitrobenzoic acid with cadmium acetate with (L_a) results in the formation of mononuclear hexa-coordinated species namely tetra (3,5-dimethylpyrazole) cadmium(II) (2-nitrobenzoate). In the case of solid phase reaction we did not observe tetra nuclear species rather observed a mononuclear species; this suggests that tetra nuclear species may be a kinetic control product. In fact tetra-nuclear complex on heating transforms to mononuclear hexa-coordinated complex.

Table 4
Hydrogen bonding geometry (distances and angles) in complex **5**

D–H···A	$d_{\mathrm{D-H}}$ (Å)	$d_{\mathrm{H\cdots A}}$ (Å)	$d_{\mathrm{D\cdots A}}$ (Å)	∠D–H···A (°)
N6–H···O2	0.817	1.935	2.737	166.98
O1–H···O17	0.748	2.092	2.831	169.24
O6–H···O17 (2−*x*, 1−*y*, *z*)	0.781	1.998	2.766	167.41
O3–H···O18	0.784	2.274	3.035	160.76

The complex **6** has a polymeric structure with the carboxylate oxygen atoms as bridging atoms to the cadmium ions. The structure of the complex **6** is shown in Fig. 3a. The 4-nitrobenzoate complex **6** does not have aqua ligand as compared to that of **5**. Thus, it may be said that the position of water molecule is occupied up by bridging oxygen atom of a carboxylate group leading to co-ordination polymer. In the one-dimensional polymer all the cadmium are in seven co-ordination environment. The metal–ligand bond geometries are listed in Table 5. Similar structures are obtained in the case of 4-chlorobenzoate complex **7** as well as in the 1-naphthoate complex **8**. Important bond distances are listed in Table 5. In these two cases the metal–ligand composition of the complex is identical to that of **6**. A similar reason may be put forward in these cases for explaining polymer formation. The attack of one nitrogen donor ligand is favored in these three complexes due to steric reasons and this makes approach of another molecule to form bridging carboxylate bonds between two discrete units. Careful analysis of the structure shows (Fig. 3b) that every carboxylate can be a bridging as well as chelating in the polymeric system. Such system can be constructed from the dinuclear building blocks as depicted in Fig. 3f. Support to this fact arises from the fact that there are two different Cd–Cd distances in each of these complexes in alternating manner. For example the Cd–Cd distances in 4-nitrobenzoate, 4-chlorobenzoate and 1-naphthoate complexes are 4.138 Å, 3.748 Å; 4.119 Å, 3.745 Å and 4.152 Å, 3.801 Å respectively. The observation of long and short separation clearly indicates that there is a part of the poly-

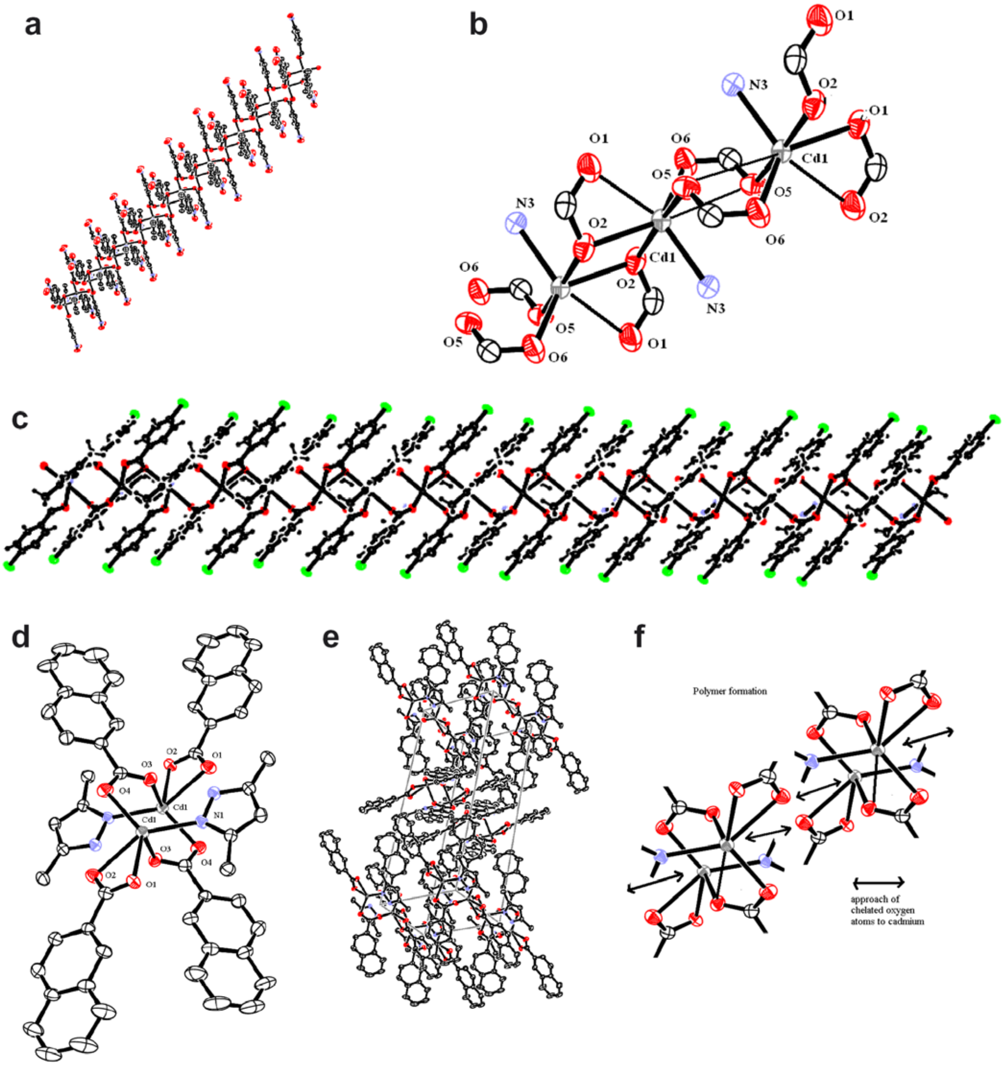

Fig. 3. The structure of (a) **6** (b) ligand environment in the co-ordination polymer of **6**, (c) the structure of **7** (d) the repeated units in the co-ordination polymer **8** (e) unit cell of **8** (f) representation showing a route for formation of co-ordination polymers in **6**–**8**.

mer having paddlewheel type structure and another unit has features of mononuclear structure and combination of which is leading to the co-ordination polymers. Thus, formation of mononuclear complexes may be imagined to be from cleavage of such polymeric species. It may be proposed that that the polymeric units are having mononuclear and dinuclear paddlewheel structure and each paddlewheel can be squeezed to give mononuclear species if the diagonal bridging atoms can be connected to the cadmium atom. Such distortion in paddlewheel would preferentially take the system to a mononuclear species. This is illustrated in Scheme 1, where arrows are indicating the approach of an oxygen atom to cause distortion to a limiting case and beyond which distortion would make two mononuclear chelate from one parent bridged binuclear system. We have observed in the case of copper [6a] and cobalt [6e] and in nickel [6b,6c] that similar reactions are highly sensitive to the reaction conditions. However, the present study is designed such a way that all the reactions are carried out under identical molar ratios and identical condition. The driving force in the case of cadmium complexes to have polymeric form thus arises from the competition between the steric factor and attack of a bridging ligand to form co-ordination polymer. The (4-chloro-2-methylphenoxy) acetate complex of cadmium(II) complex has polymeric structures having six coordination number of cadmium [8]. In this complex, two water molecules and a carboxylate group serves as bridging ligand [8]. All the complexes presented in this manuscript are also characterized by recording their proton-NMR. The integration of protons confirmed that they have the same composition in solution and solid state. However, it is found that for complex **5** and **9** in DMSO the water signals of the complexes are merged with the water signal from dissolved water in the solvent. Each of the complexes has characteristic N–H stretching frequency from the 3,5-dimethylpyrazole ring however, at a different position. For example, complex **1** has absorption at 3434 cm^{-1} for N–H stretching whereas the 3,5-dimethyl pyrazole has absorption at 3201 cm^{-1}. The compound has absorption frequencies that have

Table 5
Cadmium–ligand bonding geometry (distances and angles) in complex **6**, **7**, **8** and **9**

Cd–L	Co–L (Å)	L–Cd···L	∠L–Cd···L (°)	Cd–L	Co–L (Å)	L–Cd···L	∠L– Cd···L (°)
*For **6***				*For **7***			
Cd–O1	2.219	O6–Cd–O1	87.71	Cd–O1	2.293	O1–Cd–O2	101.99
Cd–O2	2.767	O5–Cd–N3	87.65	Cd–O3	2.479	O4–Cd–O3	97.75
Cd–O5	2.291	O5–Cd–O5′	75.37	Cd–O2	2.383	O1–Cd–N1	104.08
Cd–O6	2.524	O2–Cd–N3	77.78	Cd–O4	2.209	O2–Cd–N1	78.11
Cd–N3	2.279	O6–Cd–N3	148.02	Cd–N1	2.271	O2–Cd–O3	77.78
				*For **9***			
				Cd–O1	2.430	O4–Cd–N2	97.23
*For **8***				Cd–O2	2.384	O4–Cd–N2	91.47
Cd–O2	2.302	O1–Cd–O3	77.52	Cd–O3	2.484	O4–Cd–N1	85.40
Cd–O1	2.461	O2–Cd–O2′	75.44	Cd–O4	2.363	O3–Cd–O2	84.51
Cd–O3	2.402	O3–Cd–N1	77.85	Cd–N1	2.358	O4–Cd–O5(aq)	81.35
Cd–O4	2.212	O1–Cd–O4	89.25	Cd–N2	2.356	O5–Cd–N2(aq)	88.37
Cd–N1	2.253	O2–Cd–N1	104.59	Cd–O5(aq)	2.328	O5–Cd–N1(aq)	95.21

characteristic features of bi-dentate carboxylate ligand [9]. For example the complex **1** has absorption at 1538(v_{as}) and 1404(v_s) cm^{-1} due to the bidentate carboxylic acid group. The parent benzoic acid has absorptions at 1682 and 1421 cm^{-1}. The other mono-nuclear complexes also have similar trends in absorptions over the parent carboxylic acid, confirming bi-dentate nature of the carboxylate groups. The complexes **6**, **7**, **8** have both bidentate and bridging carboxylates from crystallographic study. Although, in these cases clear distinction could not be made between the two type of binding mode from the IR-absorptions but some inference can be made; for example in the case of **7**, the absorptions from carboxylate groups occurs at 1590, 1500, 1411 and 1390 cm^{-1} in contrast to the parent carboxylic acid namely 4-chlorobenzoic acid, which has absorptions at 1683, 1592, 1424 cm^{-1}.

Since we have obtained a polymeric structure for the 1-naphthoate complex **8**, we extended our study to the reaction of cadmium acetate with 1-naphthoic acid and pyridine

$$\mathrm{Cd(OAc)_2 2H_2O + 1\text{-}C_{10}H_7COOH + L_b} \rightarrow \underset{\mathbf{9}}{\mathrm{[Cd(C_{10}H_7COO)_2(L_b)_2(H_2O)]}} \quad (1)$$

where Lb = pyridine

This reaction led to complex having composition $[M(L)_2(L_b)_2(H_2O)]$ (**9**) where L is 1-naphthoate and L_b is pyridine. As expected from the trend from the composition that in this class of compound there is no polymeric structure, we have found it to be so for the complex. It is found that the complex has a distorted pentagonal bipyramidal seven co-ordination geometry as shown in Fig. 4a. Four oxygen atoms from naphthoate groups and oxygen atom of the aqua ligand form the basal plane. The axial positions are taken up by two pyridine ligands. The complex in solid state has extensive hydrogen bonded structure through the interaction of the aqua

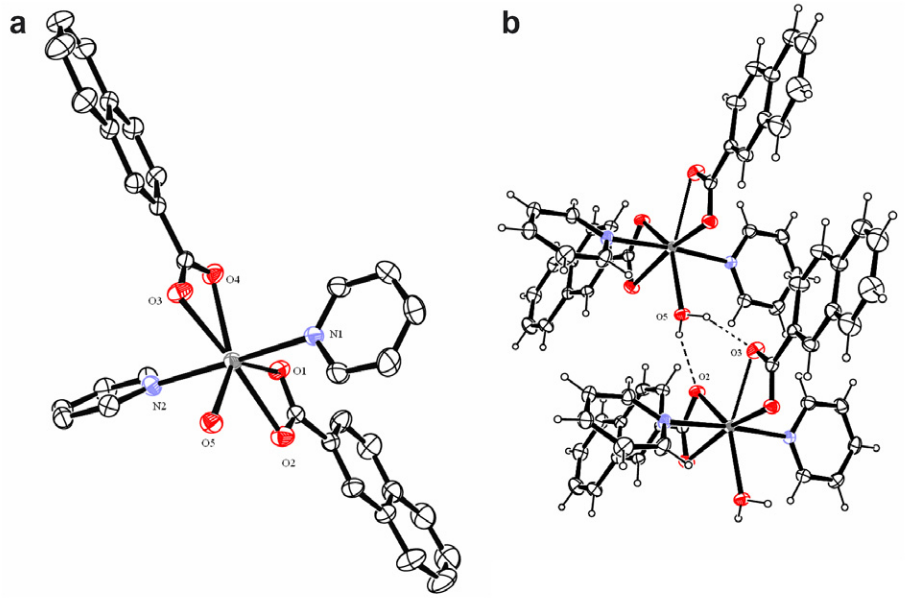

Fig. 4. (a) The structure of **9** (hydrogen atoms are omitted for clarity). (b) The hydrogen bond interactions between two molecules of **9** (drawn with 20% thermal ellipsoid).

ligand with the oxygen of carboxylate groups. The hydrogen bonded chain like structures are formed from O5–H···O3 with 0.901 ($d_{D–H}$), 1.934 ($d_{H\cdots A}$), 2.766 ($d_{D\cdots A}$), 152.759 (∠D–H···A/°) and O5–H···O2 with 0.809 ($d_{D–H}$), 1.995 ($d_{H\cdots A}$), 2.727 ($d_{D\cdots A}$) 150.18 (∠D–H···A/°). The hydrogen bonding between two molecules of **9** is shown in Fig. 4b.

In conclusion it has been possible to rationalize the relation between composition and structure in 3,5-dimethypyrazole containing cadmium carboxylates. The cadmium carboxylate complex having composition $[Cd(L)_2(L_a)_2]$ leads to mononuclear structure and the composition $[Cd(L)_2(L_a)]$ leads to polynuclear co-ordination polymers, whereas the complex having the composition $[Cd(L)_2(L_a)(H_2O)]$ leads to tetranuclear complex. It is also observed that the compositions are more important than the substituent at the *ortho* or *para*-position of the aromatic carboxylate ligands, however, to a great extent the composition of L_a containing cadmium carboxylates are decided by the substituents; keeping a close correlation between the steric factor with thermodynamic control of synthesis. The overall structure in solid state is stabilized by various weak interactions. The cadmium complex having the composition $[M(L)_2(L_b)_2(H_2O)]$ leads to mononuclear pentagonal bipyramid structure.

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Appendix A. Supplementary material

CCDC 626304, 626305, 626306, 626307, 626308, 626309, 6263010, 6263011 and 626312 contain the supplementary crystallographic data for this paper. 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 doi:10.1016/j.poly.2007.01.005.

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