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Steric effects in controlling co-ordination environment in zinc 2-nitrobenzoate complexes

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Abstract

A dinuclear zinc complex having exclusive bis(unidentate) carboxylato co-ordination mode is synthesized through two-step reactions, involving solid phase reaction followed by solution reaction. The formation of such dinuclear species is governed by the ligand under consideration. For example, 2-nitrobenzoate zinc complex having 1,10-phenanthroline is mononuclear whereas a similar complex with 8-aminoquinoline is dinuclear having bis(unidentate) carboxylato co-ordination mode. The reasons for the formation such complex is explained on the basis of the distance of separation of uncoordinated oxygen atoms of the carboxylate oxygen of mononuclear and dinuclear complexes. Zinc 2-nitrobenzoate complexes having 2,2′-bipyridine is mononuclear but with 2-aminopyrimidine has a dinuclear paddle wheel structure. Solution phase reaction of 2-nitrobenzoic acid with zinc(II)acetate in the presence of 8-aminoquinoline gives bis-(8-aminoquinoline)zinc(II) 2-nitrobenzoate.

Keywords: Paddle wheel structure; Bis-unidentate-carboxylate bridge; Mononuclear zinc complexes; Binuclear zinc complexes; Solid phase synthesis; Crystal structure

1. Introduction

Carboxylate chemistry is indispensable for the construction of inorganic motifs having interesting material properties [1]. The success in designing the target metal carboxylate synthon/s depends on the modulation of various co-ordination modes of carboxylates for synthetic [2] and biologically occurring molecules [2f,2g]. Among the different co-ordination modes chelating, monodentate, and bridging are the three modes which generally decide the structural features of inorganic carboxylate complexes [3], and they are also studied from the theoretical point of view also [3f]. Some possible bridging modes for metal carboxylate complexes are shown in Fig. 1. Bridging through two oxygen atoms of carboxylato group (bidentate) generally leads to paddle wheel structure or polymeric structures [2a,4]. But the carboxylato group having bis(unidentate) bridged complexes is known as the secondary part in polynuclear carboxylate complexes [3d,4]. Mode **II** of Fig. 1 is not independently observed. In fact the literature examples on such bridges are part of other bonding mode, arising out of steric requirements [4]. Thus, it is essential to understand the condition to achieve such bis(unidentate) carboxylato complex (Mode **II** of Fig. 1) in simple metal carboxylate and also as an independent co-ordination mode. We have recently shown that depending on the method of synthesis mono-nuclear and dinuclear metal carboxylate complexes can be prepared [5]. In the case of 2-nitrobenzoate complexes polymorphs as well as pseudo-polymorphs are also established [5a–i]. In these cases it was illustrated that the nitro groups can be oriented in different directions and that it is sensitive to environment. Recently competitive reactivity of pyrazole with carboxylate ligands is used to synthesize interesting zinc complexes [1i]. In this study we report a novel example of bis(unidentate) carboxylato bridged dinuclear zinc carboxylate complex, which is much different from the conventional

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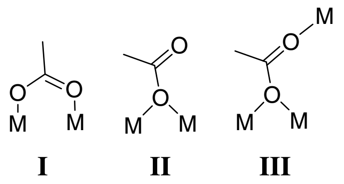


Fig. 1. Different bridging modes of carboxylate group.

paddle wheel structure by using 8-aminoquinoline (AQ) as ancillary ligand, and compare its structure with different mono-nuclear and paddle wheel zinc(II) complexes.

2. Experimental

The 8-aminoquinoline (AQ), 2-nitrobenzoic acid (oNBz), PHEN = 1,10-phenanthroline, 2-aminopyrimidine (AMP), 2,2′-bipyridine were obtained from Aldrich Chemical Co. USA and used as received.

2.1. Synthesis of complexes

2.1.1. Synthesis of complex $[Zn_2(oNBz)_4(AQ)_2(H_2O)_2]$ (***1***)

In a typical procedure a mixture of zinc(II) acetate dihydrate (0.219 g, 1 mmol) and 2-nitrobenzoic acid (0.334 g, 2 mmol) was ground in a mortar and pestle and heated at 80 °C for 20 min. The mixture was then transferred to a round-bottom flask and methanol (10 ml) was added and stirred for half an hour. To this reaction mixture a solution of 8-aminoquinoline (0.288 g, 2 mmol) dissolved in a mixture of toluene (5 ml) and methanol (5 ml) was added dropwise. A clear solution was observed. The clear solution was kept for crystallization and after 3 days white needle-like crystals appeared and were filtered. Yield: 82%. For the synthesis of other complexes **2**, **4** and **5** identical reaction conditions except the nitrogen donor ligands namely 1,10-phenanthroline, 2,2′-bipyridine and 2-aminopyrimidine, respectively, are used. Isolated yield of pure crystalline compounds of **2**, **4** and **5** are 86%, 90%, 94%, respectively.

2.1.2. Synthesis of complex $[Zn\,(oNBz)_2(AQ)_2]$ (*3*)

To a solution of zinc(II)acetate dihydrate (0.219 g, 1 mmol) and 2-nitrobenzoic acid (0.334 g, 2 mmol) in methanol (25 ml) a solution of 8-aminoquinoline (0.288 g, 2 mmol) in methanol (10 ml) was added dropwise. A homogeneous solution was obtained. The solution was stirred at room temperature for 2 h. The solution was filtered through an ordinary filter paper to remove any undissolved residue. The filtrate was kept standing for two days and then a white crystalline product of **3** was obtained. Yield was 92% with respect to 8-aminoquinoline.

2.2. Spectroscopic data for complexes ***1–4***

2.2.1. $[Zn_2(oNBz)_4(AQ)_2(H_2O)_2]$ (***1***)

^{1}H NMR (DMSO-d_6) 5.89 (br s, 2H), 6.85 (dm, $J = 7$ Hz, 1H), 7.04 (dt, $J = 8$ Hz, 1H), 7.29 (t, $J = 8$ Hz, 1H), 7.44 (dd, $J = 4$ Hz, 1H), 7.57–7.67 (m, 4H), 7.75–7.80 (m, 4H), 8.15 (dm, $J = 8$ Hz, 1H), 8.71 (dm, $J = 4$ Hz, 1H). IR (KBr, cm^{-1}) 3448(bw), 3027(w), 1659(s), 1576(s), 1526(s), 1512(s), 1409(s), 1360(s), 1379(s), 1318(m), 1145(w), 808(m), 783(s), 742(s), 698(s). Elemental *Anal.* Calc. for $C_{46}H_{36}N_8O_{18}Zn_2$: C, 49.30; H,3.22. Found: C, 49.46; H, 3.28%.

2.2.2. $[Zn(oNBz)_2(PHEN)(H_2O)]$ (***2***)

^{1}H NMR (DMSO-d_6) 7.44 (t, $J = 8$ Hz, 2H), 7.53 (t, $J = 8$ Hz, 2H), 7.55–7.63 (m, 4H), 8.08 (br s, 1H), 8.87 (d, $J = 8$ Hz, 1H), 9.20 (br s, 1H). IR (KBr, cm^{-1}) 3186(br s), 3085(s), 1599(br s), 1481(s), 1391(s), 1351(s), 1307(s), 1266(s), 1150(s), 1090(w), 1076(s), 866(m), 785(s), 726(s), 702(s), 649(s). Elemental *Anal.* Calc. for $C_{26}H_{18}N_4O_9Zn$: C, 52.42; H, 3.02. Found: C, 52.38; H, 3.05%.

2.2.3. $[Zn\,(oNBz)_2(AQ)_2]$ (***3***)

^{1}H NMR (DMSO-d_6) 5.89 (br s, 4H), 6.85 (dm, $J = 7$ Hz, 2H), 7.04 (dt, $J = 8$ Hz, 2H), 7.29 (t, $J = 8$ Hz, 2H), 7.44 (dd, $J = 4$ Hz, 2H), 7.57–7.67 (m, 4H), 7.75–7.80 (m, 4H), 8.15 (dm, $J = 8$ Hz, 2H), 8.71 (dm, $J = 4$Hz, 2H). IR (KBr, cm^{-1}) 3309(s), 2971(br s), 1634(s), 1501(w), 1393(wb), 1219(m), 1040(m), 825(s), 789(s), 692(s). Elemental *Anal.* Calc. for $C_{32}H_{24}N_6O_8Zn$: C, 55.98; H,3.50. Found: C, 56.01; H, 3.54%.

2.2.4. $[Zn\,(oNBz)_2(bpy)]$ (***4***)

^{1}H NMR (DMSO-d_6) 7.50 (t, $J = 8$ Hz, 2H) 7.58 (t, $J = 8$ Hz, 2H), 7.67 (dd, $J = 8$ Hz, 4H), 8.18 (s, 2H), 8.57(s, 2H), 8.75 (s, 2H). IR (KBr, cm^{-1}) 3533(s), 3445(s), 1579(s), 1571(s), 1525(s), 1492(m), 1442(s), 1399(s), 1371(s), 1316(s), 1020(s), 774(s), 736(s), 694(s). Elemental *Anal.* Calc. for $C_{24}H_{16}N_4O_8Zn$: C, 52.01; H, 2.89. Found: C, 52.07; H, 2.90%.

2.2.5. $[Zn_2(\mu\text{-}oNBz)_4(AMP)_2]$ (***5***)

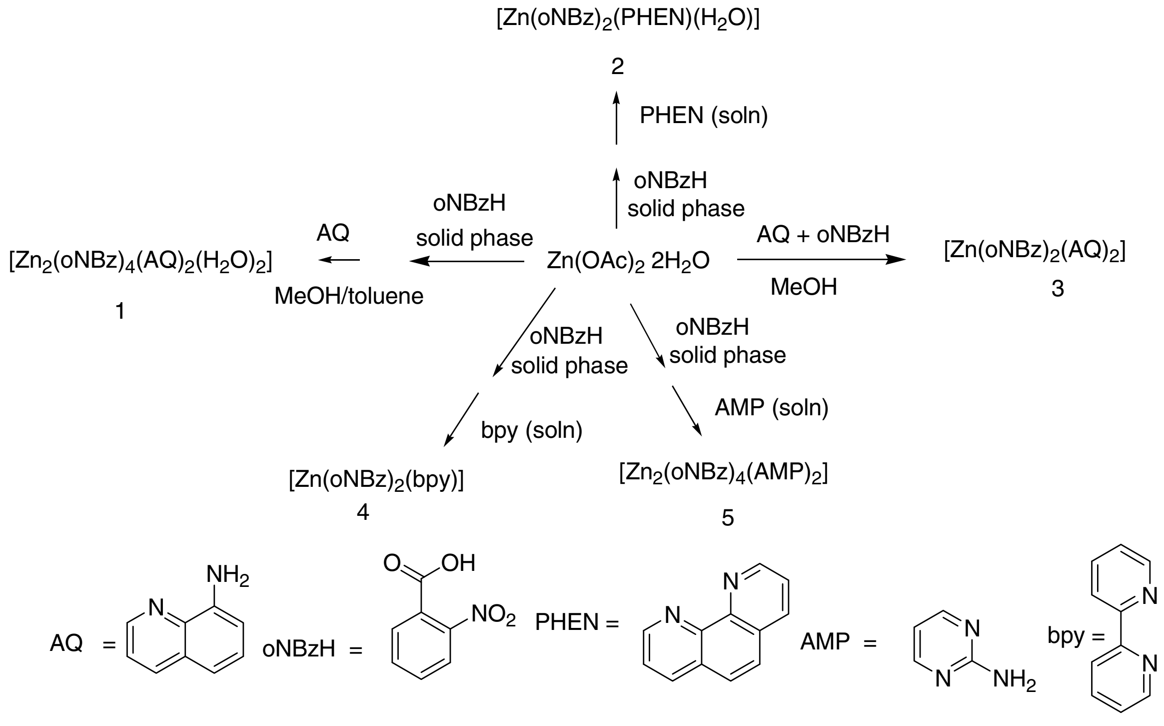
^{1}H NMR (DMSO-d_6) 6.53 (m, 1H), 6.60 (br s, 2H), 7.58 (t, $J = 8$ Hz, 2H), 7.62 (t, $J = 8$ Hz, 2H), 7.74–7.79 (m, 4H), 8.19 (br s, 1H). IR (KBr, cm^{-1}) 3443(s), 3323(s), 3181(s), 3096(s), 1568(s), 1595(s), 1569(s), 1530(s), 1485(s), 1408(s), 1363(s), 1344(s), 1228(s), 1263(s), 1195(s), 1154(s), 1073(w), 877(m), 863(s), 839(s), 801(s), 787(s), 754(s), 740(s), 698(s) 658(s). Elemental *Anal.* Calc. for $C_{36}H_{26}N_{10}O_{16}Zn_2$: C, 43.84; H, 2.64. Found: C, 43.81; H, 2.63%.

2.3. X-ray crystallography

The X-ray diffraction data were collected at 296 K with Mo Kα radiation ($\lambda = 0.71073$ Å) using a Bruker Nonius SMART CCD diffractometer equipped with 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. The structures were solved by direct methods and refined by full-matrix least-squares calculations

Table 1
Crystallographic parameters for compounds **1**, **3**–**5**

Compound no.	**1**	**3**	**4**	**5**
Formulae	$C_{46}H_{36}\ N_8O_{18}Zn_2$	$C_{32}H_{24}N_6O_8Zn$	$C_{24}H_{16}N_4O_8Zn$	$C_{36}H_{26}N_{10}O_{16}Zn_2$
M_w	1119.57	685.94	553.78	985.41
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P2(1)/c$	$P2(1)/c$	$P2(1)/c$	$P2(1)/c$
Temperature (K)	296	296	296	296
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
a (Å)	7.6674(5)	7.6959(5)	7.6111(8)	12.1172(2)
b (Å)	21.4398(15)	20.2231(14)	17.332(2)	17.3050(4)
c (Å)	14.2719(10)	9.5743(6)	18.156(2)	10.2873(2)
α (°)	90.00	90.00	90.00	90.00
β (°)	96.484(4)	99.590(4)	98.333(7)	110.6550(10)
γ (°)	90.00	90.00	90.00	90.00
V (Å^3)	2331.1(3)	1469.27(17)	2369.8(5)	2018.47(7)
Z	2	2	4	2
D_{calc} (mg m^{-3})	1.595	1.550	1.552	1.621
Absorption coefficient (mm^{-1})	1.116	0.901	1.095	1.275
Absorption correction	none	none	none	none
$F(000)$	1144	704	1128	1000
Total no. of reflections	24840	19765	28473	27123
Reflections, $I > 2\sigma(I)$	5782	3597	5804	4924
Max. 2θ (°)	28.39	28.34	28.34	28.24
Ranges (h,k,l)	$-10 \leqslant h \leqslant 10$ $-28 \leqslant k \leqslant 28$ $-18 \leqslant l \leqslant 19$	$-10 \leqslant h \leqslant 8$ $-26 \leqslant k \leqslant 26$ $-12 \leqslant l \leqslant 12$	$-9 \leqslant h \leqslant 9$ $-20 \leqslant k \leqslant 23$ $-24 \leqslant l \leqslant 22$	$-16 \leqslant h \leqslant 15$ $-23 \leqslant k \leqslant 23$ $-13 \leqslant l \leqslant 13$
Completeness to 2θ (%)	98.8	98.2	98.2	98.7
Refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2
Data/restraints/parameters	5782/0/350	3597/0/214	5804/0/334	4924/0/297
Goodness-of-fit on F^2	1.148	1.008	1.026	1.021
R indices $[I > 2\sigma(I)]$	0.0717	0.0539	0.0370	0.0305
R indices (all data)	0.0992	0.0935	0.0698	0.0507



Scheme 1.

using SHELXTL software. All the non-H atoms were refined in the anisotropic approximation. The crystallographic parameters of the compounds studied are given in Table 1.

3. Results and discussion

It is observed that depending on the reaction condition different types of co-ordination environments in zinc 2-nitrobenzoate complexes having different nitrogen donor ligands could be obtained as illustrated in Scheme 1.

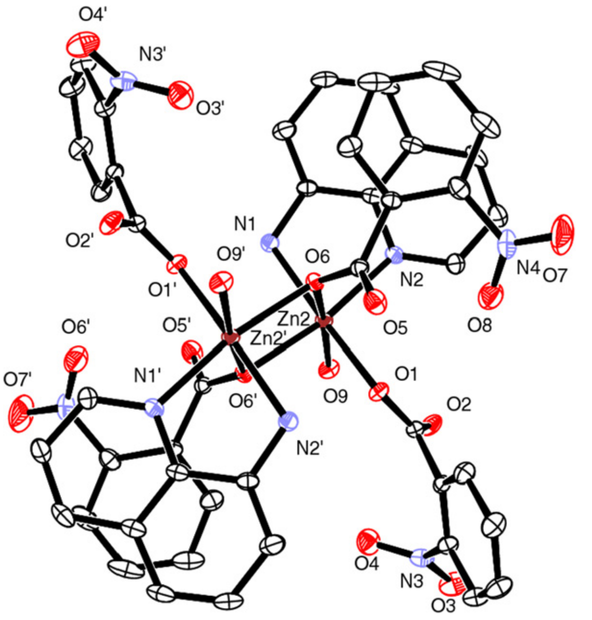


Fig. 2. The ORTEP diagram of complex **1** (20% thermal ellipsoid, hydrogen atoms are omitted for clarity) The bond distances (Å) and bond angles (°) for [Zn$_2$(oNBz)$_4$(AQ)$_2$(H$_2$O)$_2$] (**1**) are Zn2–N1, 2.12; Zn2–N2, 2.13; Zn2–O9, 2.11, Zn2–O1, 2.61 Zn2–O6, 2.25; <O9–Zn2–O6, 91.35; <N1–Zn2–O9, 100.96; <O1–Zn2–O9, 88.80; <N2–Zn2–O6, 92.72; <N1–Zn2–O6, 92.58; <N1–Zn2–N2, 79.09.

The reaction of 2-nitrobenzoic acid with zinc(II)acetate dihydrate followed by treatment with 8-aminoquinoline gave a dinuclear zinc complex having composition [Zn$_2$(oNBz)$_4$(AQ)$_2$(H$_2$O)$_2$] (**1**) where AQ is 8-aminoquinoline and oNBz is 2-nitrobenzoato anion. The structure of the complex determined by crystallography is shown in Fig. 2. The complex has monodentate carboxylate, chelating 8-aminoquinoline, water, and bridging carboxylate, one each per zinc center. The co-ordination mode of carboxylate group in the bridge is mediated by one oxygen of the carboxylate group to have a bis(unidentate) carboxylate bridge. Such binding modes are reported in polycarboxylic acids, in which it occurs due to steric reasons [2e]. However, in isolated molecules such interactions are not preferred [2e,3d,4b] and to the best of our knowledge they are not isolated as exclusive bridging mode in dinuclear systems. Even when such bis(unidentate) co-ordination of carboxylate group is present they generally occur complementary to a commonly occurring bidentate bridging mode [2e]. The distance between two zinc atoms in the dinuclear motif is 3.31 Å, which is higher than 3.03 Å for complexes of zinc having paddle wheel structure [5d,5i].

The complex is highly symmetric and may be considered as a self-assembly of two mono-nuclear halves with a composition [Zn(oNBz)$_2$(AQ)(H$_2$O)] and having a structure as shown in Fig. 3a. This part has structural similarity with a mononuclear [Zn(oNBz)$_2$(PHEN)(H$_2$O)] (**2**) complex [5i] (where PHEN = 1,10-phenanthroline). The structure of [Zn(oNBz)$_2$(PHEN)(H$_2$O)] (**2**) is shown in Fig. 3b. This compound **2** is mono-nuclear and we have not been able to get a dinuclear counterpart of this composition when synthesis is carried out in solid phase followed by solution

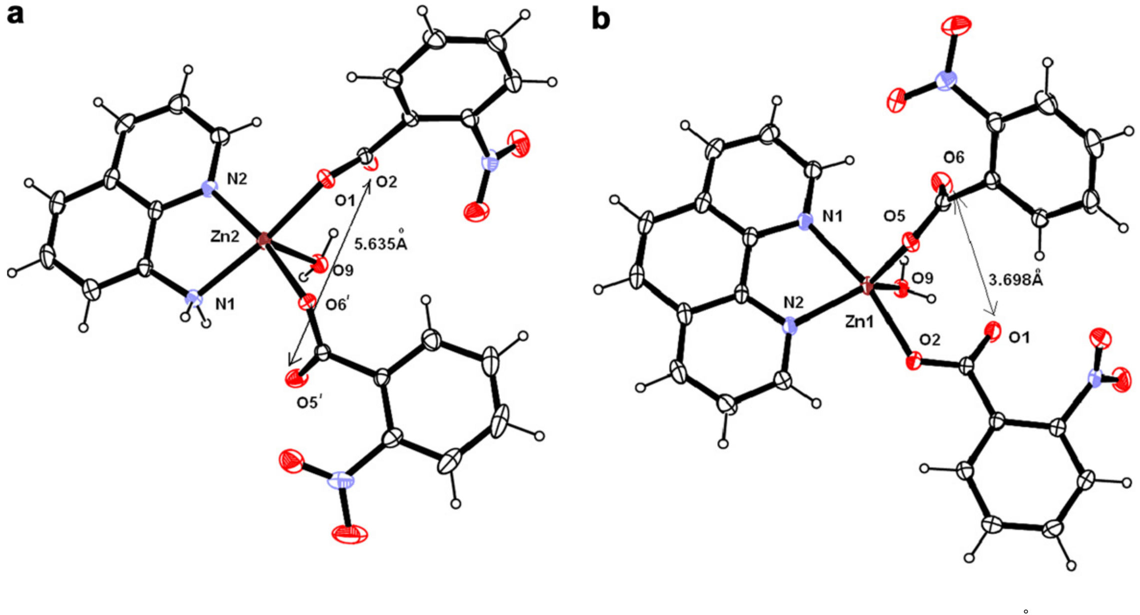


Fig. 3. The structure of (a) symmetric half of dinuclear zinc complex **1**; (b) mononuclear complex **2** [5i]. The bond distances (Å) and bond angles (°) for **2** are Zn1–N2, 2.08; Zn1–N1, 2.17; Zn1–O9, 2.04; Zn1–O2, 2.08; Zn1–O5, 1.99; <O9–Zn1–O2, 87.71; <N1–Zn1–O9, 93.62; <O2–Zn1–O9, 87.71; <N2–Zn1–O5, 117.59; <N1–Zn1–O5, 99.53; <N1–Zn1–N2, 78.02.

chemistry or completely in solution. On comparison of these two structures, it is observed that the bite angle between the two nitrogen donor atoms and the zinc atom is comparable. Same is the case with the other bond distances and the bond angles around the zinc in the two zinc complexes. But there is a significant difference in the distance of separation between the oxygen atoms involved in bridging between the zinc ions and the un-coordinated oxygen atoms of the monodentate 2-nitrobenzoate ligand of complex **1**, with the distance between the oxygen atoms of the two un-coordinated oxygen atoms of the monodentate benzoate group of **2**. These distances of separations are found to be 5.64 Å and 3.70 Å, respectively (Fig. 3a and b). This difference in distances arises from the twist conferred to the benzoate group due to the orientations of the nitro groups. Such comparatively large separation between the two oxygens in compound **1** is facilitated by the inter-molecular hydrogen bonding between the N1–H ··· O5 ($d_{\text{D–A,inter}}$ 3.06Å; <D–H ··· A, 142.95°) and also by intra-molecular hydrogen bonding O9–H ··· O2 ($d_{\text{D–A}}$ 2.69 Å; <D–H ··· A 150.1°) and inter-molecular hydrogen bonding between O9–H ··· O5 ($d_{\text{D–A}}$ 2.65 Å, <D–H ··· A 154.29°). Thus, in the case of **1** the orientation of the oxygen atom is such that it becomes easy to form dinuclear complex, whereas in the case of **2** it is not the case. The dinuclear complex formation in **1** is also facilitated by the separation between the free oxygens of carboxylate group; it allows another molecule to come close to form a dinuclear structure through bis(unidentate) bridging co-ordination. In complex **1** Zn2–O6 distance is 2.25 Å which is well in the permissible limit to have a dative bond. In a paddle wheel

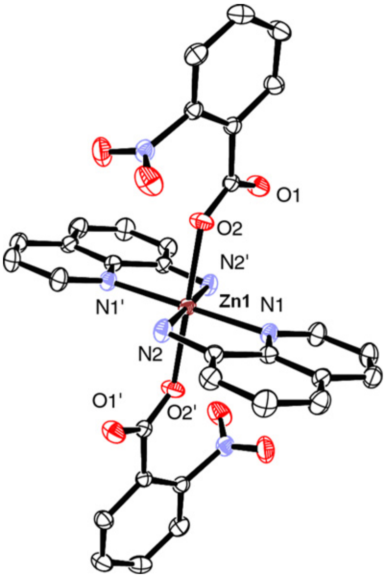


Fig. 4. The structure of bis (8-aminoquinoline) zinc(II) 2-nitrobenzoate (**3**) (drawn with 20% thermal ellipsoid, hydrogen atoms are omitted for clarity). The bond distances (Å) and bond angles (°) are Zn1–N2, 2.13, Zn1–N1, 2.15, Zn1–O2, 2.14, <N1–Zn1–N2, 79.71, <N1–Zn–O2, 89.59, and <N2–Zn–O2, 92.43.

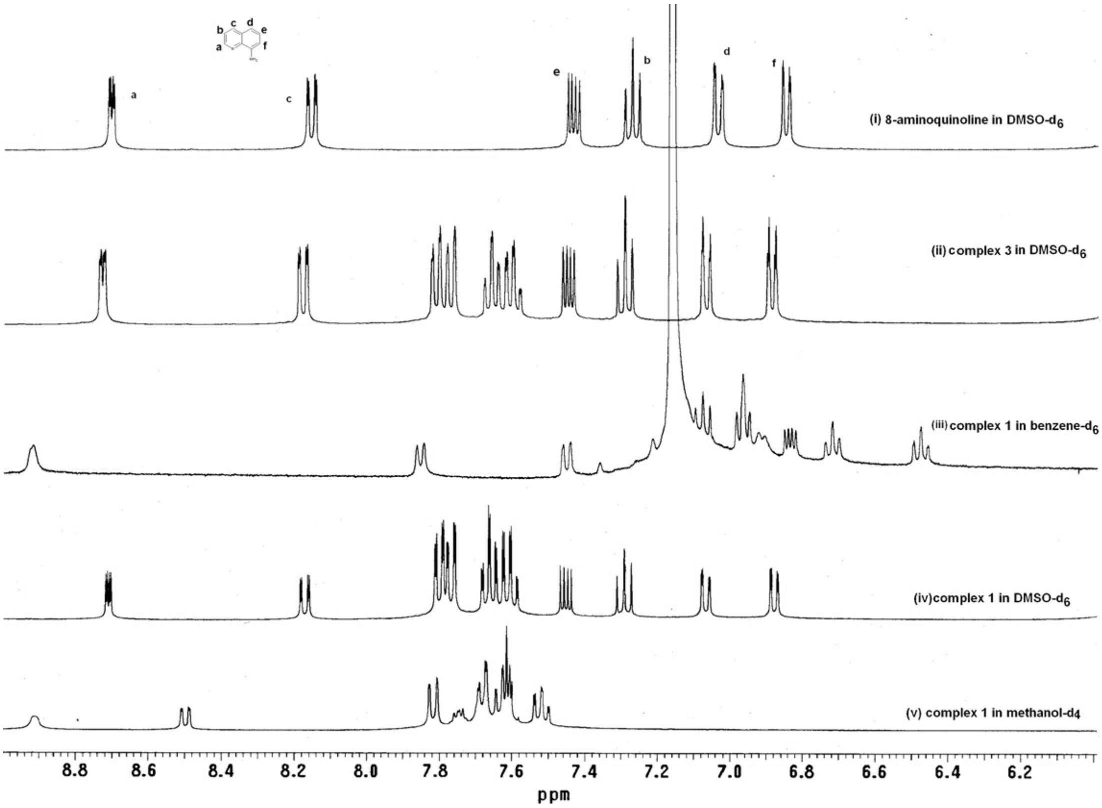


Fig. 5. ^{1}H NMR spectra of (i) 8-aminoquinoline (ii) complex **3** in DMSO-d_6 and (iii)–(v) complex **1** in different solvents in the range of 6–9 ppm.

structure such distances are large, for example the bis-pyridine tetra (μ-benzoato)zinc(II) complex has a paddle wheel structure [5i] and has such distance to be 3.33 Å (see Fig. 4).

The reaction between zinc(II) acetate 8-aminoquinoline and 2-nitrobenzoic acid in 1:1:2 molar ratio in methanol solution gives bis (8-aminoquioline) zinc(II) 2-nitrobenzoate (**3**). The side product in the reaction is found to be zinc(II) 2-nitrobenzoate. The formation of side product can be decreased by using 1:2:2 stoichiometry; in which case only **3** is formed. The solvents have a profound effect in the chemical shifts of the protons in the ^{1}H NMR spectra of complex **1** (Fig. 5). The ^{1}H NMR spectra recorded in DMSO-d_6 solution shows that both complexes **1** and **3** dissociate in dimethyl sulfoxide. In these two cases ^{1}H NMR signals arising from 8-aminoquinoline ligand of the complexes resemble the parent ligand [Fig. 5i, ii and iv]. However, complex **1** shows entirely different spectra in methanol-d_4 and benzene-d_6. The solution of complex **1** in benzene-d_6 has 10 aromatic proton signals (six from 8-aminoquinoline and two each from bridging and terminal 2-nitrocraboxylate) in contrast to eight aromatic proton signals (six from 8-aminoquinoline and two from 2-nitrobenzoate) that are observed from the solution of complex **1** in DMSO-d_6. This suggests that the protons in the aromatic ring of the bridging and the terminal carboxylate are not magnetically equivalent. In the case of methanol-d_4 solution of complex **1** there are eight aromatic proton

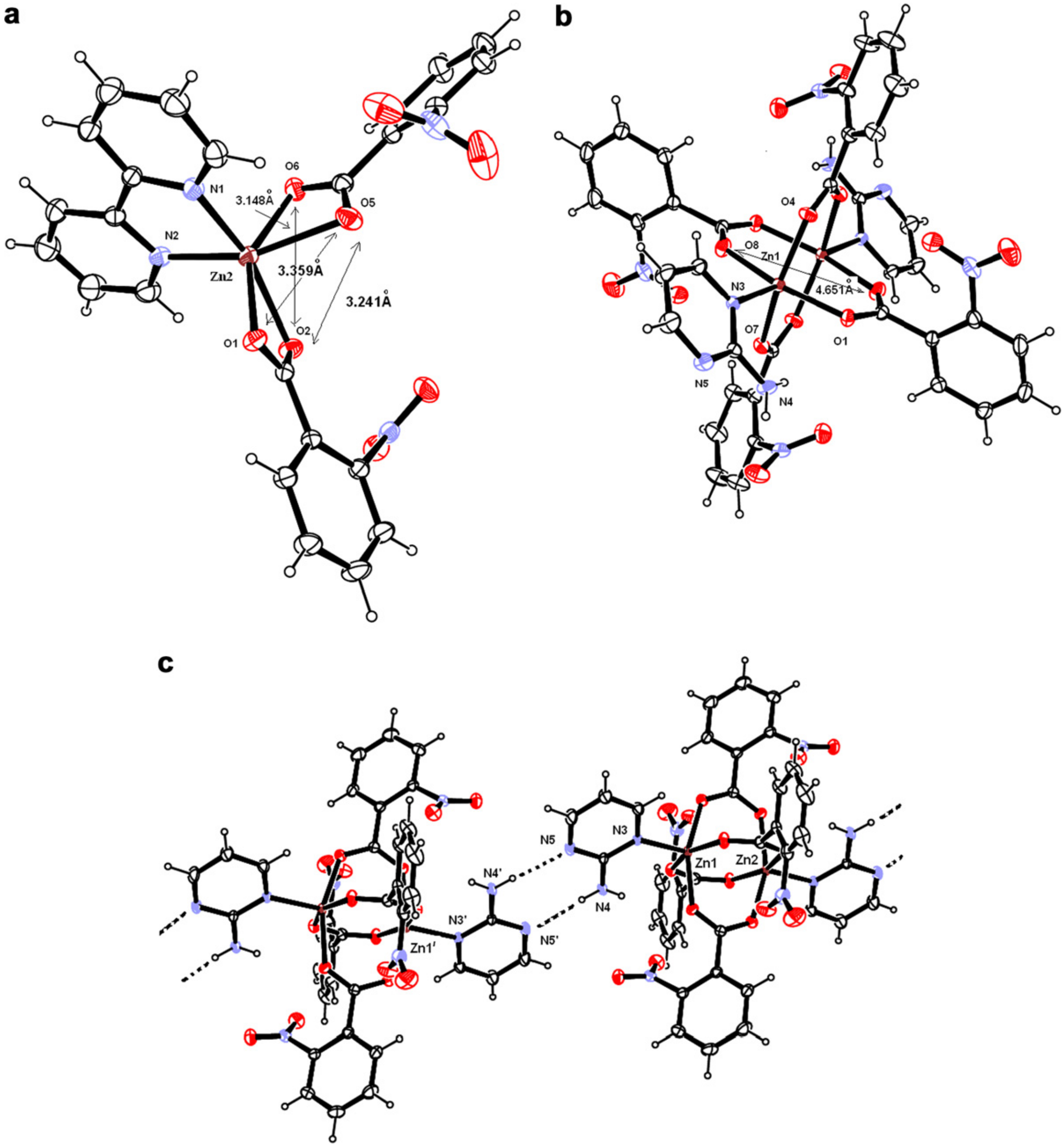


Fig. 6. The structure of complex (a) [Zn(oNBz)$_2$(bpy)] (**4**) and (b) [Zn$_2$(μ-oNBz)$_4$(AMP)$_2$] (**5**); (c) the self-assembling of **5** through hydrogen bonding interactions (the figures are drawn with 20% thermal ellipsoids).

signals corresponding to the ligands but the aromatic signals appear at much different chemical shift positions from the parent 8-aminoquinoline. This result supports the fact that the compound does not remain in dinuclear form and most likely it occurs as mono-nuclear species. Recrystallisation of compound **1** from methanol gave a mixture of compounds **1** and **3**. Formation of mixture of a **1** and **3** on re-dissolution in methanol is confirmed by recording the powder X-ray diffraction of the residue from methanolic solution (Supplementary material) and also by picking up crystals from the mixture and determining the X-ray structure. It may be noted that the dinuclear complex **1** can be crystallized only when the aromatic solvent such as toluene or benzene is used along with methanol.

It is obvious that the X-ray powder diffraction patterns of products **1** and **3** are different (Supplementary material), and each of them could be prepared in pure state in good yield. Analysis of powder X-ray shows that the product obtained from the solid phase reaction followed by solution chemistry does not possess super-imposable peaks of the product obtained from only solution route. This suggests that product **3** is not formed in the solid phase reaction followed by solution reaction. The ^{1}H NMR integration of complex **3** confirms the composition of the complex in solution. The structure determined by X-ray crystallography shows that complex **3** has a distorted octahedral geometry around zinc(II)ion and that the 2-nitrobenzoate groups are located *trans* to each other. The 8-aminoquinoline ligand occupies the rest of the four co-ordination positions. The nitrogen atoms of the pyridine ring of 8-aminoquinoline are *trans* to each other.

The structural study on related compounds shows the role of the bite angles of ligands or the co-ordination of amino group in the formation of bis(unidentate) carboxylate bridged dinuclear complex. Two other zinc(II) 2-nitrobenzoate complexes, one having 2,2′-bipyridine and the other having 2-aminopyrimidine ligand were prepared. In the former case a mononuclear complex, namely 2,2′-bipyridine zinc(II) 2-nitrobenzoate (**4**) was formed, whereas in the case of 2-aminopyrimidine (AMP) a binuclear complex having composition $[Zn_2(\mu\text{-oNBz})_4(AMP)_2]$ (**5**) was obtained. The structures of the complexes were determined and the structures of the two complexes are shown in Figs. 6a and b. Some important bond lengths and bond angles are listed in Table 2.

Table 2
Selected bond distances (in Å) and angles (in °) in **4** and **5**

For 4		For 5	
Zn2–O6	2.06	Zn1–O1	2.03
Zn2–N1	2.08	Zn1–O8	2.03
Zn2–N2	2.10	Zn1–N3	2.04
Zn2–O1	2.11	Zn1–O7	2.05
Zn2–O2	2.25	Zn1–O4	2.06
Zn2–O5	2.26	O1–Zn1–O8	157.9
O6–Zn2–N1	109.1	O1–Zn1–N3	106.4
O6–Zn2–N2	101.9	O8–Zn1–N3	95.6
N1–Zn2–N2	78.7	O1–Zn1–O7	90.1
O6–Zn2–O1	148.2	O8–Zn1–O7	87.8
N1–Zn2–O1	98.7	N3–Zn1–O7	102.4
N2–Zn2–O1	98.2	O1–Zn1–O4	86.8
O6–Zn2–O2	93.6	O8–Zn1–O4	87.2
N1–Zn2–O2	157.3	N3–Zn1–O4	98.9
N2–Zn2–O2	96.0	O7–Zn1–O4	158.5
O1–Zn2–O2	59.8		
O6–Zn2–O5	60.6		
N1–Zn2–O5	100.1		
N2–Zn2–O5	161.4		
O1–Zn2–O5	100.4		
O2–Zn2–O5	91.8		

Complex **4** has six-coordination around the zinc atom. The zinc ion is in a six-coordinated environment consisting of two carboxylato groups and a bidentate 2,2-bipyridine ligand. Complex **5** has a conventional paddle wheel structure with one of the ring nitrogen atoms of 2-aminopyrimidine coordinating to the zinc atoms at the two ends. The Zn1–Zn1 distance in the complex is 3.00 Å. A square pyramidal geometry is formed around each zinc atom (Table 2). The distance between the two zincs in the paddle wheel structure is 3.01 Å, which is in very close similarity to the common binuclear zinc carboxylates having paddle wheel structures [5d]. Since only one of the nitrogen atoms of 2-aminopyrimidine is coordinating the other nitrogen gets involved in the formation of H-bonded assembly though R_2^2 (8) type of H-boned geometry (Fig. 6c) via N4–H$\cdots$N5 interactions ($d_{D\text{–}A}$, 3.05 Å; <D–H$\cdots$A 176.19°). No intra-molecular hydrogen bonding is observed in this case. The oxygen–oxygen separation in **4** and **5** is also much shorter in comparison to **1**; thus, this suggests that the orientation of the carboxylate group by the steric requirement of nitro groups decides the stability of different structures. In complex **4** the distance between the zinc and the two oxygen atoms of carboxylate groups namely Zn–O1 and Zn–O2 is 3.181 Å and 2.078 Å, respectively (Fig. 6a), whereas in the case of complex **2** similar Zn–O1 and Zn–O2 distances (Fig. 3b) are 2.252 Å and 2.108 Å respectively. These clearly suggest that in the former case the 2-nitrobenzoate group is monodentate, whereas in the later it is a bidentate chelate.

In conclusion different types of structures of the 2-nitrobenzoate complexes of zinc can be constructed depending on the reaction conditions and ancillary ligand used. The formation of dinuclear zinc complex having exclusive bis(unidentate) carboxylate bridging co-ordination mode is observed in a binuclear zinc complex and the rationality of its formation is described by the comparison of its structure with several analogous zinc complexes prepared with different ancillary ligands.

Appendix A. Supplementary material

CCDC 647910, 647911, 647912, 656163 and 639912 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. The X-ray powder pattern of complexes **1** and **3**. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2008.01.044.

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