Studies on cluster, salt and molecular complex of zinc-quinolinate

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Abstract. Reactions of zinc halides with 8-hydroxyquinoline (hydroxQ) in equimolar ratio were carried out in different solvents. Respective solvates of tetranuclear clusters, namely $[\text{Zn}_4(\text{oxyQ})_6\text{X}_2](\text{solvent})_2$, (when $\text{X} = \text{Cl}$, Solvent = dimethylformamide (**1**), dimethylacetamide (**2**) and dimethylsulphoxide (**3**); $\text{X} = \text{Br}$, solvent = dimethylformamide (**4**), oxyQ = quinolinate anion) were obtained. Bond parameters of these isostructural clusters **1–4** are compared from their single crystal structures. Anhydrous form of the cluster have porous packing and is thermally stable below 250°C. Surface area of the clusters **1** and **4** are 8.933 and 6.172 m²/g, respectively. Complexes **1** and **4** can be reversibly hydrated, which is reflected in colour changes. The reaction of zinc chloride with 8-hydroxyquinoline in equimolar ratio followed by crystallization from water gave salt $(\text{HhydroxQ})_2[\text{ZnCl}_4]$ (**5**) and a similar reaction followed by crystallization from 3-methylpyridine (3mepy) resulted in the molecular complex $[\text{Zn}(\text{oxyQ})_2(3\text{mepy})]$. $[\text{Zn}(\text{oxyQ})_2(3\text{mepy})_2] \cdot 3\text{H}_2\text{O}$ (**6**). Complex **5** is formed from a hydrolytic equilibrium of water with zinc chloride yielding tetrachloro zinc anion and zinc hydroxide. Taking advantage of this reaction, a composite material of $\text{ZnO}@\text{complex 5}$ exhibiting dual fluorescence at 450 and 575 nm on excitation at 390 nm was prepared. Fluorescence emission properties of all the complexes in solid state are compared with fluorescence emission of the ligand.

Keywords. Zinc-clusters; molecular complex; hydrolytic equilibrium; zinc oxide; porous material.

1. Introduction

Zinc carboxylates are widely used as metallo-organic frameworks^{1–10} for gas absorption. Such studies require information on the ability to retain framework structure under drastic conditions after removal of solvated species. Covalently linked compounds of zinc carboxylates with giant structures are useful in these studies.^{11,12} However, an understanding of the packing of solvates of large zinc clusters is essential as solvents may act as filler of voids between molecules. This effect may help in reversible exchange to pave way for preparing useful porous materials. Since zinc ions can form varieties of neutral clusters^{13–16} and zinc quinolinate complexes are useful as optical material,^{17–19} we report here a series solvates of tetra-nuclear zinc 8-oxyquinolinate clusters along with their hydration and determination of surface area. We prepared a series of solvates of tetra-nuclear clusters of zinc with halide as the terminal ligand as shown in figure 1. The advantage of the 8-hydroxyquinoline as ligand is due to its reported ability to form tetra-nuclear clusters having carboxylate terminal groups.^{20,21} Moreover, while understanding the hydrolytic equilibrium of zinc chloride in presence of 8-hydroxyquinoline we are able to

encapsulate zinc oxide by a zinc complex, which in turn displays novel fluorescence property.

2. Experimental

All reagents were obtained from Sigma Aldrich (USA) and used as received. IR spectra were recorded on a Perkin-Elmer Spectrum One FT-IR spectrometer with KBr pallets in the range of 4000–400 cm^{–1}. ¹HNMR data were recorded with a Varian 400 MHz FTNMR spectrometer. Powder X-ray diffraction (XRD) patterns were recorded on a Bruker D8 Advance (Germany) diffractometer with Cu K α (1.542 Å) radiations operated at 40 kV and 40 mA on glass surface of an air-dried sample. Solid state fluorescence emission spectra were measured on a Horiba Jobin Yvon Fluoromax-4 spectrofluorimeter. Surface analysis was performed using a Quantachrome, Model: Autosorb-IQ MP surface analyser.

2.1 X-ray crystallography

X-ray single crystal diffraction data for all the compounds were collected on Oxford SuperNova diffractometer. Data refinement and cell reductions were carried out by CrysAlisPro.⁴¹ Structures were solved by direct methods and refined by full-matrix least-squares

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where X = Cl or Br, solvent = DMF, DMA or DMSO

Figure 1. Tetra-nuclear zinc-8-oxyquinolate cluster.

calculations using SHELXTL software.⁴² All the non-H atoms were refined in the anisotropic approximation against F^2 of all reflections. Crystal parameters of the crystals are shown in table 1.

2.2 Synthesis of zinc complexes

To a solution of 8-hydroxyquinoline (0.31 g, 2 mmol) in methanol (20 ml) zinc chloride (0.28 g, 2 mmol) was added and stirred for 15–20 min. A white precipitate was formed which was filtered and recrystallized from DMF to obtain complex **1**. Similar recrystallization of the white precipitate from DMA and DMSO yielded their corresponding solvates. DMF solvate (**1**): Yield ~45% (with respect to zinc). IR (KBr, cm^{-1}): 3392(s), 2919(w), 2851(w), 1624(m), 1577(m), 1499(s), 1467(s), 1421(w), 1389(s), 1371(s), 1327 (s), 1283 (w), 1240 (w), 1109(s), 1033(w), 820(w), 783(w), 742 (m), 620 (w). DMA solvate (**2**): yield ~48% (with respect to zinc). IR (KBr, cm^{-1}): 3372(s), 2919(w), 2851(w), 1628 (m), 1602 (m), 1577 (m), 1499 (s), 1466 (s), 1421(w), 1389 (s), 1371(s), 1327 (s), 1282 (w), 1240 (w), 1109(s), 1031(w), 820(w), 785(w), 742 (m), 640 (w), 596 (w), 502 (w). DMSO solvate (**3**): Yield ~45% (with respect to zinc). IR (KBr, cm^{-1}): 3378 (s), 2918 (w), 1618(m), 1603 (m), 1577 (m), 1500 (s), 1467 (s), 1399 (w), 1390 (s), 1371(s), 1327(s), 1283 (w), 1241(w), 1110 (m) 1033 (w), 850 (w), 820 (w), 780 (w), 743 (s), 640 (w), 502(w). ¹HNMR (DMSO- d_6 , 400 MHz), 8.60 (s, 3H), 8.33 (d, $J = 8$ Hz, 3H), 7.47 (s, 3H), 7.30 (s, 3H), 6.93 (q, $J = 6.8$ Hz, 6H), 2.04 (s, 6H).

A procedure similar to that of **1** was used for preparation of complex **4** in which zinc bromide was used in place of zinc chloride in DMF (10 ml). Yield ~45% (with respect to zinc). IR (KBr, cm^{-1}): 3190 (s), 1644 (m), 1601(m), 1577 (m), 1499 (s), 1456 (s), 1421(w), 1373(s), 1325(s), 1280 (w), 1137 (w), 1105(s), 1067 (w), 1032 (w), 909 (w), 821(m), 787 (m), 742 (m), 641(w), 600 (w), 545 (w), 499 (w).

Salt **5** was obtained by a procedure similar to that of **1** but water was used as solvent to dissolve the precipitate. Yield ~35% (with respect to zinc). IR (KBr, cm^{-1}): 3453(w), 3056(w), 2933(w), 2539(w), 1627(w), 1581(m), 1531(w), 1499(s), 1467(s), 1428(w), 1382(s), 1359(s), 1324(s), 1276(m), 1241(m), 1228(w), 1180(w), 1106(s), 1022(s), 916(w), 823(s), 786(s), 755(s), 646(w), 553(w), 514(m).

A procedure similar to that of **1** was used to prepare molecular complex **6**. However, 3-picoline was used in excess to dissolve the precipitate. Yield ~60% (with respect to zinc). IR (KBr, cm^{-1}): 3323 (s), 3044 (w), 1581(m), 1495 (m), 1464 (s), 1422 (w), 1389 (s), 1327 (s), 1283 (w), 1232 (w), 1109 (m), 1056 (w), 1031 (w), 821 (m), 791 (m), 735 (m), 705 (w), 640 (w), 500 (w). ¹HNMR (DMSO- d_6 , 400 MHz), 8.78 (t, $J = 2.8$ Hz, 3H), 8.36 (q, $J = 1.6$ Hz, 4H), 7.57 (q, $J = 4$ Hz, 3H), 7.44 (q, $J = 8$ Hz, 2H), 7.29 (d, $J = 8$ Hz, 2H), 7.02 (d, $J = 7.2$ Hz, 3H), 2.29 (s, 6H).

3. Results and Discussion

Tetra-nuclear zinc 8-oxyquinolate clusters possessing chloride and bromide as terminal ligands were synthesised by reacting corresponding salt of zinc with 8-hydroxyquinoline in different solvents which is shown in equation 1. The structure of each solvated cluster was determined to ascertain the identity of the complexes and packing patterns.

(1)

when X = Cl, solvent = DMF (**1**); X = Cl, solvent = DMA (**2**); X = Cl, solvent = DMSO (**3**); X = Br, solvent = DMF(**4**).

Clusters **1–4** are isostructural, each belong to P-1 space group and have unit cell volume 1457.18(14), 1482.62(15), 1445.71(18) and 1470.82(16) Å³, respectively. The respective crystal densities are 1.531, 1.536, 1.555 and 1.617 g/cm³. Clusters have similar tetra-nuclear zinc core as shown in figure 2a. Metal ions in the clusters are in two different types of environments. The zinc sites holding the halide ions are penta-coordinated while the other two zinc sites are hexa-coordinated. The metal ligand bond distances are comparable to the reported complexes with acetate as auxiliary ligands.²⁰ Comparisons of various metal ligand bond distances are listed in supporting information. Packing patterns clusters are guided by C-H $\cdots\pi$ and C-H $\cdots$ X interactions. One illustrative example is shown in figure 2b and c.

Table 1. Crystal parameters of the complexes **1–6**.

Compound No. Formulae	1 C ₆₀ H ₅₀ Cl ₂ N ₈ O ₈ Zn ₄	2 C ₆₂ H ₅₄ Cl ₂ N ₈ O ₈ Zn ₄	3 C ₅₈ H ₄₈ Cl ₂ N ₆ O ₈ S ₂ Zn ₄	4 C ₆₀ H ₅₀ Br ₂ N ₈ O ₈ Zn ₄	5 C ₁₈ H ₁₆ Cl ₄ N ₂ O ₂ Zn	6 C ₇₈ H ₆₈ N ₁₀ O ₉ Zn ₃
Mol. wt.	1343.46	1371.51	1353.52	1432.38	499.50	1485.53
CCDC No.	960180	960179	960181	960177	960182	960178
Crystal system	Triclinic	Triclinic	Triclinic	Triclinic	Monoclinic	Monoclinic
Space group	<i>P</i> – <i>I</i>	<i>P</i> – <i>I</i>	<i>P</i> – <i>I</i>	<i>P</i> – <i>I</i>	<i>C</i> 2/ <i>c</i>	<i>P</i> 2/ <i>c</i>
Temperature (K)	296 (2)	296 (2)	296 (2)	296 (2)	296 (2)	296 (2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
<i>a</i> (Å)	11.4278(7)	11.2931(7)	11.5945(6)	11.3662(7)	15.2315(10)	22.9887(12)
<i>b</i> (Å)	12.5311(6)	12.6163(8)	12.4479(9)	12.5613(8)	8.1375(9)	8.3971(4)
<i>c</i> (Å)	12.6744(7)	12.7410(7)	12.5482(10)	12.6119(8)	16.742(2)	18.0997(8)
α (°)	101.688(4)	102.346(5)	99.560(7)	101.500(5)	90.00	90.00
β (°)	110.189(5)	111.205(5)	114.464(7)	109.660(6)	91.413(9)	93.958(4)
γ (°)	112.178(5)	109.004(5)	109.975(6)	111.242(6)	90.00	90.00
<i>V</i> (Å ³)	1457.18(14)	1482.62(15)	1445.71(18)	1470.82(16)	2074.5(4)	3485.6(3)
<i>Z</i>	1	1	1	1	4	2
Density/gcm ^{–3}	1.531	1.536	1.555	1.617	1.599	1.415
Abs. Coeff. /mm ^{–1}	1.780	1.751	1.863	3.031	1.715	1.091
Abs. correction	multi-scan	None	multi-scan	multi-scan	multi-scan	none
<i>F</i> (000)	684	700	688	720	1008	1536
Total No. of reflections	5259	5364	5231	5323	1870	6301
Reflections, <i>I</i> > 2σ(<i>I</i>)	4012	4054	3572	3993	1126	4013
Max. 2θ (°)	50.50	50.50	50.50	50.50	50.48	50.50
Ranges (<i>h</i> , <i>k</i> , <i>l</i>)	–13 ≤ <i>h</i> ≤ 13	–13 ≤ <i>h</i> ≤ 13	–13 ≤ <i>h</i> ≤ 13	–13 ≤ <i>h</i> ≤ 13	–18 ≤ <i>h</i> ≤ 9	–27 ≤ <i>h</i> ≤ 27
	–15 ≤ <i>k</i> ≤ 11	–15 ≤ <i>k</i> ≤ 15	–14 ≤ <i>k</i> ≤ 14	–15 ≤ <i>k</i> ≤ 14	–9 ≤ <i>k</i> ≤ 9	–10 ≤ <i>k</i> ≤ 7
	–15 ≤ <i>l</i> ≤ 15	–15 ≤ <i>l</i> ≤ 15	–15 ≤ <i>l</i> ≤ 15	–15 ≤ <i>l</i> ≤ 13	–20 ≤ <i>l</i> ≤ 8	–21 ≤ <i>l</i> ≤ 20
Completeness to 2θ (%)	0.999	0.999	0.999	0.999	0.992	0.998
Data/Restraints/Parameters	5259/0/372	5364/32/382	5231/0/363	5323/0/372	1870/0/128	6301/7/467
Goof (<i>F</i> ²)	1.035	1.034	1.049	1.028	1.043	1.052
<i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	0.0422	0.0548	0.0615	0.0421	0.0413	0.0647
<i>R</i> indices (all data)	0.0610	0.0751	0.0936	0.0638	0.0663	0.1058

Figure 2. (a) Two different coordination environment in $[Zn_4(oxyQ)_6Cl_2]$ core; (b) C-H... π interactions and (c) C-H...Cl interactions in complex **1**.

The C11-H11...Cl1 has the hydrogen bond donor–acceptor distance $d_{H11 \dots Cl1}$ $2.819 \text{ \AA}$ and angle $\angle C11-H11 \dots Cl1$, 130.1° . Distance between the centroid of the π -cloud of quinoline and the H of C3-H3 bond is $2.92 \text{ \AA}$. The

solvent molecules are held loosely by weak interactions; in the case of dimethylformamide (DMF), the interactions are through C-H...O interactions; whereas DMA are held by C-H... π interactions. Due to loose

Table 2. Comparison of bond lengths and bond angles of complexes **1–3**.

Bond	Length (Å)	Length (Å)	Length (Å)	Bond angle	Angle (°)	Angle (°)	Angle (°)
	Complex 1	Complex 2	Complex 3		Complex 1	Complex 2	Complex 3
Zn1-Cl1	2.283(11)	2.287(2)	2.284(2)	Cl1-Zn1-O1	108.47(8)	108.02(14)	109.83(13)
Zn1-O1	2.004(4)	2.001(5)	1.993(5)	Zn1-O2-Zn2	95.66(9)	95.63(17)	106.8(2)
Zn1-O2	2.313(2)	2.303(4)	2.324(4)	Cl1-Zn1-O2	171.98(8)	171.73(12)	171.33(12)
Zn1-O3	2.007(3)	2.013(5)	2.018(5)	Cl1-Zn1-O3	106.40(8)	106.65(14)	105.23(13)
Zn1-N2	2.101(4)	2.108(6)	2.105(5)	Zn1-O2-Zn2a	96.99(10)	97.00(16)	97.82(15)
Zn2-O1	2.103(2)	2.103(4)	2.106(4)	Cl1-Zn1-N2	97.56(10)	97.26(18)	77.41(17)
Zn2-O2	2.136(3)	2.141(5)	2.126(5)	Zn2-O2-Zn2a	100.30(11)	100.29(15)	99.96(14)
Zn2-N1	2.089(4)	2.082(6)	2.091(6)	Zn1-O3-Zn2a	107.04(13)	106.8(2)	96.68(16)
				Zn1-O1-Zn2	106.93(13)	106.9(2)	107.0(2)

Figure 3. Thermogravimetry of (a) Cluster **1**; (b) cluster **1** heated at 200°C; (c) desolvated cluster **1** after exposing to moisture (heating rate in each case 5°C per minute). **Scheme 1.** Thermal decomposition of the clusters **1–3**.

binding of the solvent, these clusters lose their solvent molecules at relatively low temperature. We have compared the bond distances and bond angles of zinc

atoms in clusters **1–4**. Table 2 presents a comparison of the effect of solvents in the geometry of the tetra-nuclear clusters **1,3**. Clusters **1** and **2** have DMF and DMA as the solvent of crystallization, both are homologous, and accordingly we do not see much difference in the structure of the host. However, cluster **3** has DMSO as solvent of crystallization; it has a clear difference in the Zn1-O2-Zn2 bond angle at one face without significantly affecting the analogous bond on the other face. Thus, the solvent causes slight distortion of one face of the cluster. On the other hand, clusters **1** and **4** have DMF as solvent of crystallization but have different anions; former has two chlorides, whereas latter has two bromides. The comparison of the bond parameters between these two clearly shows that the difference in metal halogen bonds is obvious from the difference in atomic radius of the halides. There are differences between the Zn1-O2 and Zn1-O3 distances, in the case of cluster **4**. In both cases, the halogens project away and do not interfere in the knitting of the cluster, in spite of the change in metal–oxygen bond distances of the site where the halides are attached. This indicates that the packing effect as well as electro-negativity difference between the halides play a role in giving shape to the geometry of the clusters.

Thermogram of the DMF solvate **1** is shown in figure 3a. Weight loss at 90–137°C occurs due to loss of two molecules of DMF (theoretical 10.9% and found 8.9%) and the compound is thermally stable up to 350°C. Thermal decomposition of the clusters can be correlated by scheme 1. It involves two steps; first is loss of solvent, followed by decomposition of the complex to lose three 8-hydroxyquinolates. For complex **1**, the calculated weight loss to form a composition $[\text{Zn}_4(\text{oxyQ})_3(\text{OH})(\text{O})\text{Cl}_2]$ is 41.1%, whereas weight loss at 350–450°C was found to be 42.7%. Cluster **4** also has shown a similar trend of thermal decomposition. The IR spectra of cluster **4** after heating at 480°C was recorded, which showed the IR-stretching frequencies of the

Figure 4. Nitrogen gas adsorption isotherm at standard temperature and pressure for complex **1** and pore size distribution (inset).

oxyquinolate part (refer to supplementary figure 6S). This suggests that at 480°C, a portion of the oxyquinolate ligand remains with zinc ions. Since clusters on heating led to partial loss of quinolate ligands, we investigated synthesis of new complexes through thermochemical reactions. Cluster **1** on heating at 200°C resulted in the formation of de-solvated complex, which on standing at ordinary atmospheric condition at room temperature, slowly absorbs moisture to yield hydrated form. The water absorption process is reversible. The process is illustrated in the three thermograms of the complex after and before heating at 200°C (figure 3). Since, relatively high thermal stability and reversibility of water binding were observed in these clusters, we determined surface areas of clusters **1** and **4**. The nitrogen adsorption plot of type 2 showing reversibility in nitrogen adsorption were observed.²² An illustrative example of the nitrogen adsorption study is shown for the Cluster **1** in figure 4. A similar plot for Cluster **4** is available as supplementary figure. The surface area for Cluster **1** is 8.933 m²/g; whereas for Cluster **4**, the surface area is 6.172 m²/g (figure 4).

De-solvation of the Cluster **4**, and exchange of solvent by water molecules can be monitored by colour

changes in the sample. For example, initial brownish-green colour of the sample changes to orange on heating which returns to greenish colour on accepting water as illustrated in the photograph of the sample shown in figure 5. Visible spectra of solid samples of **4** were recorded and shown as supplementary information figure S12. The anhydrous form has a shoulder at 475 nm in addition to the parent absorption of solvated form at 400 nm. In a recent study, it has been shown that removal of guest molecules from zinc carboxylate metallo-organic frameworks drastically changes colour.²³ Such phenomenon arises due to changes in the π -stacking interactions between the included guests in the host framework, which are involved in ligand to ligand charge transfer transitions. Here, clusters **1–4** have strong C-H $\cdots\pi$ interactions, which may be affected by removal of solvent of crystallization, resulting in the observed colour changes. Generally, formation of zinc complexes are guided by solvents;^{16,27} thus, the stability of solvated tetranuclear clusters **1–4** is of synthetic interest.^{24–28} On the other hand, the formation of the clusters **1–4** were from 1:1 ratio of ligand and metal ion (eq. 1). In an earlier study oxalate-bridged tetra-nuclear zinc oxyquinolate cluster was also prepared from a reaction of zinc(II) ions and 8-hydroxyquinoline in 1: 1 molar ratio.²¹ Thus, another product is possible during synthesis of the clusters. The identity of the uncharacterised part in those reactions became obvious when water was used as solvent. When we carried out the reaction of zinc chloride with 8-hydroxyquinoline in aqueous medium, we obtained a complex (HhydroxQ)₂ [ZnCl₄] (**5**), which has hydroxyquinolinium cation. In aqueous medium, the reaction probably follows eq. (2).

The entire reactions are thus guided by solvents and based on hydrolytic equilibrium of zinc chloride in different solvents. To show the formation of zinc hydroxide in the reaction, we have taken the crude precipitate from the reaction mixture of zinc chloride with 8-hydroxyquinoline. The precipitate is supposed to comprise complex **5** and zinc hydroxide. The crude precipitate was heated at 150°C for

Figure 5. Photographs of powder samples of (a) cluster **4**; (b) desolvated cluster **4**; (c) desolvated cluster **4** after absorbing moisture.

Figure 6. Powder XRD pattern of complex; bottom: **5**, top: crude precipitate from the reaction of zinc chloride with 8-hydroxyquinoline in water heated at 150°C for 12 h showing the formation of ZnO@complex **5**.

12 h and the powder XRD was recorded. The powder XRD was compared with that of complex **5** and zinc oxide (figure 6). It was found that powder diffraction pattern contains peaks of zinc oxide. Zinc oxide peaks in the powder XRD patterns are marked with downward arrows. Zinc oxide is generally

prepared by overnight heating of zinc hydroxide at around 100°C.²⁹ On the other hand, complex **5** as well as zinc oxide have discernable non-overlapping peaks. Besides, we have also confirmed from thermogram of complex **5** that it does not decompose at 150°C. The $[\text{ZnCl}_4]^{2-}$ anions are often observed in the reactions of zinc chloride with hydrochloric acid. However, isolation of tetrachloro zinc in the reaction of zinc chloride with quinoline without additional acid is noteworthy. The $\text{Cs}_2[\text{ZnCl}_4]$ anion³⁰ has Zn–Cl bond distances $\sim 2.25 \text{ \AA}$ with Cl–Zn–Cl angles varying from 106–115°. The structure of complex **5** is shown in figure 7a has similar metal halogen bond parameters as that of the cesium complex reported earlier. In the complex, 8-hydroxyquinolinium cations are held to the anions through $\text{N-H}\cdots\text{Cl}$ ($d_{\text{H}\cdots\text{Cl}}$, 2.35 Å) and $\text{O-H}\cdots\text{Cl}$ ($d_{\text{H}\cdots\text{Cl}}$, 2.30 Å) interactions. The bond distances are Zn1–Cl1, 2.2632(14); Zn1–Cl2, 2.2771(13); and bond angle of Cl1–Zn1–Cl2 is 111.88(5)°. Thermal stability of the complex **5** was studied by analysing its thermogram. It is found that the complex is less thermally stable than the cluster and decomposes at about 250°C. The thermogram of complex **5** (Supporting figure S10)

Figure 7. (a) Structure of $(\text{HQ})_2[\text{ZnCl}_4]$ (ORTEP drawn with 30% probability); (b) structure of the molecular complex $[\text{Zn}(\text{oxyQ})_2(3\text{mepy})].[\text{Zn}(\text{oxyQ})_2(3\text{mepy})_2].3\text{H}_2\text{O}$ (**6**); Some of the selected bond distances (Å) Zn1–O1, 2.053(3); Zn1–N1, 2.145(4); Zn1–N2, 2.275(4); Zn2–N3, 2.076(4); Zn2–O2, 2.062(4); Zn2–O3, 2.059(4); Zn2–N4, 2.903(4); Zn2–N5, 2.080(5); and selected bond angles (°) are O1–Zn1–N1, 80.90(17); O1–Zn1–N2, 88.99(17); N1–Zn1–N2, 91.33(15); N3–Zn2–N5, 103.22(19); N4–Zn2–N5, 115.0(1); O2–Zn2–O3, 162.20(16); O2–Zn2–N3, 80.97(18); O2–Zn2–N4, 91.20(17); O2–Zn2–N5, 101.5(1); O3–Zn2–N3, 96.26(17); O3–Zn2–N4, 80.08(17); O3–Zn2–N5, 96.26(19); N3–Zn2–N4, 141.80(17). Molecular complex **6** (ORTEP drawn with 30% thermal ellipsoids); (c) hexa-coordinated molecules of **6**; and (d) penta-coordinated molecules of **6**.

shows that it loses 45.8% weight in the range of 250–350°C. This weight loss corresponds to loss of a hydroxyquinoline and two hydrochloric acid molecules (theoretical 43.7%). On further heating, the complex loses weight in the region from 450°C to 700°C and gives a residue having composition $\text{ZnClO}_{0.5}$ (theoretical weight loss 78.9%, experimental weight loss 79.2%). This suggests that when $(\text{HhydroxQ})_2[\text{ZnCl}_4]$ is heated, it initially forms $[(\text{hydroxQ})\text{ZnCl}_2]$ which is above 450°C forms dinuclear Zn_2OCl_2 .

We were interested in modifying the clusters to prepare covalently linked framework structures. Thus, various reactions of 8-hydroxyquinoline in presence of pyridine and its derivatives were carried out. We could obtain a crystalline material from the reaction of 8-hydroxyquinoline with zinc chloride and 3-methylpyridine. However, we observe a molecular complex of two mononuclear neutral complexes. The complexes were devoid of chloride. The two neutral complexes forming molecular complex has composition $[\text{Zn}(\text{oxyQ})_2(3\text{mepy})]$ and $[\text{Zn}(\text{oxyQ})_2(3\text{mepy})_2]$ (where 3mepy = 3-methylpyridine) (figure 7b). The first part adopts a five coordinate distorted square pyramid structure, whereas the other part has distorted octahedral geometry. The part having octahedral structure has a mirror plane bisecting the half of the molecule. The bond distances and bond lengths contributing to molecular complex are listed in figure 7b caption. The part of the molecular complex with octahedral geometry has two 3-methylpyridines at two apices and they are *trans* to each other. Comparing the axial Zn–N bonds in two geometries namely Zn1–N2, 2.275(4) and Zn2–N5, 2.080(5), it may be suggested that the 3-methylpyridine molecule is more tightly bound in penta-coordinate geometry than hexa-coordinate geometry. Earlier, we have shown molecular complexes of dissimilar zinc complexes between trinuclear and dinuclear combinations; and between tetra-coordinate and hexa-coordinate zinc complexes.^{31,32} Here, a penta-coordinated complex and a hexa-coordinated complex, independently self-assemble through weak interactions and are arranged in the form of layers. While forming a layer, each pair of complexes is interconnected through intervening lattice water molecules.

The coordination polymers and MOF which have connecting zinc ions, show photoluminescent properties.^{33–36} On the other hand, quinoline is a fluorescence active compound generally used for detecting metal ions and as probes.^{37,38} Fluorescence emission spectra

of each solid sample of the complexes by exciting at 390 nm were recorded (figure 8a). From the observed pattern of fluorescence emission intensity, there is no clear correlation of the emission properties with the solvent of crystallization. Among the clusters, the DMA and DMF clusters have shown quenching with respect to 8-hydroxyquinoline, whereas the DMSO containing cluster **3** shows slight enhancement of fluorescence and emission shift towards higher wavelength, which occurs at 495 nm. The 8-hydroxyquinoline in solid state has fluorescence emission at 480 nm. These observations clearly indicate the role of interstitial solvent in guiding the fluorescence. Similar observations of change of fluorescence intensities in zinc metallo-organic frameworks with inclusion of aromatic compounds were observed.²³ Molecular complex **6** shows the highest emission, whereas the DMF and DMA containing clusters **1** and **2** show the lowest emission. We have observed dual emission for the sample of ZnO doped into complex **5**, which was studied in the form of ZnO@complex **5** (figure 8b). ZnO@complex **5** exhibits emissions at 575 nm and 450 nm; 575 nm is relatively higher wavelength than parent compounds

Figure 8. (a) Fluorescence emission of the solid samples of complex (i) **6**; (ii) **3**; (iii) 8-hydroxyquinoline; (iv) **5**; (v) **4**; (vi) **2** (vii) **1** ($\lambda_{\text{ex}} = 390$ nm). (b) Fluorescence emission of ZnO@complex **5**.

and 450 nm is relatively shorter wavelength than 8-hydroxyquinoline or complex **5** (495 nm). This is an example of a composite materials showing dual fluorescence, which may have practical applications. Thus observation of dual fluorescence at such high wavelength is of definite interest.^{39,40}

4. Conclusions

We are able to show that different metal complexes are generated from 1:1 reactions of zinc chloride with 8-hydroxyquinoline. Hydrolytic instability of zinc chloride, has helped in precipitation of a tetrachlorozincate complex along with zinc hydroxide. This has enabled us to prepare zinc oxide within the matrix of complex **5**. Molecular complex **6** is a rare examples providing opening for studies of such complexes.

Supplementary Information

Experimental and simulated powder XRD patterns of all the clusters and complexes, IR spectra of cluster **4** before and after heating, nitrogen absorption isotherm of cluster **4**, Thermogravimetry of clusters, bond parameters cluster **1–4** and complex **5** are available as supporting information.

The supplementary information (figures S1–S12 and tables S1–S2) can be seen at www.ias.ac.in/chemsci.

References

1. Erxleben A 2003 *Coord. Chem. Rev.* **246** 203
2. Zheng Q, Yang F, Deng M, Ling Y, Liu X, Chen Z, Wang Y, Weng L and Zhou Y 2013 *Inorg. Chem.* **52** 10368
3. Qi Y, Che Y X and Zheng J M 2008 *Cryst. Eng. Comm.* **10** 1137
4. Granifo J, Garland M T and Baggio R 2006 *Polyhedron* **25** 2277
5. Toh N L, Nagarathinam M and Vittal J J 2005 *Angew. Chem. Int. Ed. Eng.* **44** 2237
6. Williams C A, Blake A J, Hubberstey P and Schroder M 2005 *Chem. Commun.* 5435
7. Yaghi O M, O'Keeffe M, Ockwig N W, Chae H K, Eddaoudi M and Kim J 2003 *Nature* **423** 705
8. Eddaoudi M, Moler D B, Li H, Chen B, Reineke T M, O'Keeffe M and Yaghi O M 2001 *Acc. Chem. Res.* **34** 319
9. Eddaoudi M, Li H, Reineke T, Fehr M, Kelley D, Groy T L and Yaghi O M 1999 *Top. Catal.* **9** 105
10. Kumar U, Thomas J and Thirupathi N 2010 *Inorg. Chem.* **49** 62
11. Hou L, Lin Y Y and Chen X M 2008 *Inorg. Chem.* **47** 1346
12. Gao W Y, Yan W, Cai R, Meng L, Salas A, Wang X S, Wojtas L, Shi X and Ma S 2012 *Inorg. Chem.* **51** 4423
13. He K H, Li Y W, Chen Y Q, Song W C and Bu X H 2012 *Cryst. Growth Des.* **12** 2730
14. Zhao X, Xiao B, Fletcher A, Thomas K M, Bradshaw D and Rosseinsky M J 2004 *Science* **306** 1012
15. Cui Y, Yue Y, Qian G D and Chen B L 2012 *Chem. Rev.* **112** 1126
16. Karmakar A and Baruah J B 2008 *Polyhedron* **27** 3409
17. Donze N, Pechy P, Gratzel M, Schaer M and Zuppiroli L 1999 *Chemical Physics Letters* **315** 405
18. Rawat M, Prakash S, Singh C and Anand R S 2011 *AIP Conf. Proc.* **1391** 187
19. Sokolowski K, Justyniak I, Sliwinski W, Soltys K, Tulewicz A, Kornowicz A, Moszynski R, Lipkowski J and Lewinski J 2012 *Chemistry* **18** 5637
20. Sattarzadeh E, Mohammadnezhad G, Amini M M and Ng S W 2009 *Acta Cryst.* **E65** m712
21. Wang J, Wang Q, Sun Y, Wang Y, Zhao G and Cui Y 2011 *J. Serb. Chem. Soc.* **76** 529
22. Sing K S W, Everett D H, Haul R A W, Moscou L, Pierotti R A, Rouquerrol J and Siemieniewska T 1985 *Pure and Appl. Chem.* **57** 603
23. Pramanik S, Zheng C, Zhang X, Emge T J and Li J 2011 *J. Am. Chem. Soc.* **133** 4153
24. Holland D R, Hausrath A C, Juers D and Matthews B W 1995 *Protein Sci.* **4** 1955
25. Tamilselvi A and Mughesh G 2008 *J. Biol. Inorg. Chem.* **13** 1039
26. Singh W M and Baruah J B 2009 *Dalton Trans.* 2352
27. Sarma R, Kalita D and Baruah J B 2009 *Dalton Trans.* 7428
28. Bury W, Justyniak I, Prochowicz D, Rola-Noworyta A and Lewinski J 2012 *Inorg. Chem.* **51** 7410
29. Kolodziejczak-Radzimska A and Jesionowski T 2014 *Materials* **7** 2853
30. McGinnety J A 1974 *Inorg. Chem.* **13** 1057
31. Phukan N and Baruah J B 2013 *RSC Advances* **3** 1151
32. Karmakar A, Sarma R J and Baruah J B 2006 *Inorg. Chem. Commun.* **9** 1169
33. Cui J, Lu Z, Li Y, Guo Z and Zheng H 2012 *Chem. Commun.* **48** 7967
34. Xu H, Liu F, Cui Y, Chen B and Qian G 2011 *Chem. Commun.* **47** 3153
35. Lan A, Li K, Wu H, Olson D H, Emge T J, Ki W, Hong M and Li J 2009 *Angew. Chem. Int. Ed. Eng.* **48** 2334
36. Fletcher A J, Thomas K M and Rosseinsky M J 2005 *J. Solid State Chem.* **178** 2491
37. Chen Y, Wang H, Wan L, Bian Y and Jiang J 2011 *J. Org. Chem.* **76** 3774
38. Fahrni C J and O'Halloran T V 1999 *J. Am. Chem. Soc.* **121** 11448
39. Shynkar V V, Klymchenko A S, Piemont E, Demchenko A P and Mely Y 2004 *J. Phys. Chem. A* **108** 8151
40. Klymchenko A S and Demchenko A P 2002 *J. Am. Chem. Soc.* **124** 12372
41. *CrysAlisPro* 2009 *Oxford Diffraction Ltd.* version 1, 171. 33.34d
42. Sheldrick G M 2008 *Acta Crystallogr.* **A64** 112