



Synthesis, characterization, and reactivity of zinc carboxylate complexes of 2,3-pyridine dicarboxylic acid and (3-oxo-2,3-dihydro-benzo[1,4]oxazin-4-yl)acetic acid

W. Marjit Singh, Bigyan R. Jali, Babulal Das, Jubaraj B. Baruah *

Department of Chemistry, Indian Institute of Technology Guwahati, Guwahati 781 039, Assam, India

ARTICLE INFO

Article history:

Available online 3 September 2010

This article is dedicated to Prof. S.S. Krishnamurthy on the occasion of his 70th birthday

Keywords:

2,3-Pyridine dicarboxylic acid
(3-Oxo-2,3-dihydro-benzo[1,4]oxazin-4-yl)acetic acid
Carboxylate complex
Zinc
Sodium
Coordination polymer

ABSTRACT

Ethylenediammonium *tris*-2,3-pyridine dicarboxylato zinc(II) trihydrate ($(\text{enH}_2)_2[\text{ZnL}_3]\cdot 2\text{H}_2\text{O}$ (**1**) (where H_2L = 2,3-pyridine dicarboxylic acid, en = ethylenediamine) and a mixed metal coordination polymer with composition $[\text{Na}_2\text{ZnL}_3(\text{OAc})(\text{H}_2\text{O})_3]_n$ (**2**) {where L' = anion of (3-oxo-2,3-dihydro-benzo[1,4]oxazin-4-yl)acetic acid} are synthesized and characterized. The complex **1** is mono nuclear complex with three coordinating carboxylate anion along with nitrogen chelating zinc ion and there is three uncoordinated carboxylate group one each from three ligand molecules making a complex anion of zinc(II). The zinc(II) ion are in distorted octahedral coordination geometry. In this complex diprotonated ethylenediamines serve as cations. The complex **2** has a polymeric structure with one acetate and three carboxylate of L' binding to zinc ion provides a tetrahedral environment and these ligands further hold dinuclear units of tri-aquated sodium ions; each dinuclear sodium units are bridged by one water molecule make the coordination polymer. The catalytic ability of these two complexes **1** and **2** towards carbon–carbon bond formation reaction between 3,4-dimethoxy benzaldehyde and acetone are studied. Both the complexes as well as sodium salt of L' are found to be catalyst for such reactions.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

Zinc carboxylate complexes are useful catalyst for C–C bond formation reactions [1]. Some of the zinc carboxylate complexes find place in carbon-dioxide activation [2–6]. Binuclear zinc carboxylate complexes are useful as biological mimic [7,8]. There is need for studying structural and reactivity of carboxylate complexes that have additional functional groups or binding sites so that they provide extra supramolecular interactions [9]. Moreover, when such units are attached to chiral units, they should cause chiral transformations [1]. Thus, there is a need to synthesize new carboxylate complexes with pendant functional groups having scope for synthetic modifications. Further to this amino acid containing heterocycle such as proline and its zinc complexes are active catalyst for carbon–carbon bond formation reactions [15–18]. So, we have chosen two carboxylic acid compound having heterocycle attached to them and prepared zinc complexes for such studies. The two acids chosen are 2,3-pyridine dicarboxylic acid (H_2L) and (3-oxo-2,3-dihydro-benzo[1,4]oxazin-4-yl)acetic acid (HL') (Fig. 1). The complex derived from them are characterized by

determining their crystal structures and their catalytic activity towards condensation reaction between 3,4-dimethoxy benzaldehyde with acetone is described.

2. Experimental

Synthesis of ethylenediammonium *tris*-2,3-pyridine dicarboxylato zinc(II) trihydrate (**1**): to a methanolic solution (20 ml) of H_2L (0.516 g, 3 mmol), zinc(II) acetate dihydrate (0.219 g, 1 mmol) was added and stirred for half an hour. A white precipitate was formed. Ethylenediamine (140 μl , 2 mmol) was added dropwise at room temperature to dissolve the precipitate. The solution was filtered, and kept for crystallization. Colourless blocks were formed in 2–3 days after keeping them in a beaker suitable for X-ray crystallography. Isolated yield, 45%. IR (KBr, cm^{-1}): 3418 (b), 2924 (s), 2852 (w), 1609 (s), 1578 (s), 1392 (m), 1362 (s), 1268 (m), 1232 (w), 1103 (s), 828 (m), 709 (w). ^1H NMR (D_2O , 400 MHz, ppm): 8.31 (3H, d, $J = 4.0$ Hz), 7.89 (3H, d, $J = 7.60$ Hz), 7.61 (3H, dd, $J = 2.40$ Hz, 5.20 Hz), 3.23 (8H, s). Molar conductance: 207.0 $\text{S cm}^2 \text{mol}^{-1}$ in water.

The (3-oxo-2,3-dihydro-benzo[1,4]oxazin-4-yl)acetic acid was prepared by reported procedure [10].

Synthesis of the complex $[\text{Na}_2\text{ZnL}_3(\text{OAc})(\text{H}_2\text{O})_3]_n$: to a solution of sodium salt of the ligand (3-oxo-2,3-dihydro-benzo[1,4]

* Corresponding author. Tel.: +91 361 2582082; fax: +91 361 2690762.

E-mail address: juba@iitg.ernet.in (J.B. Baruah).

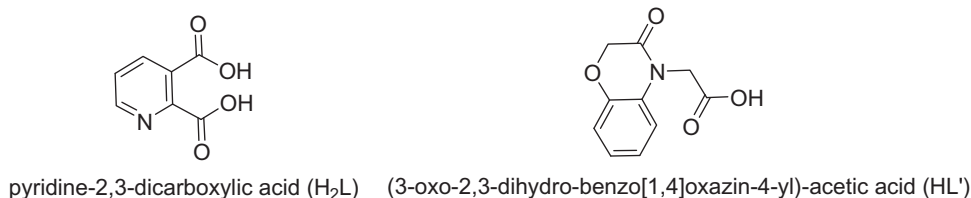


Fig. 1. Structure of ligands.

oxazin-4-yl)-acetic acid (HL') (0.229 g, 1 mmol) dissolved in methanol/water (15 ml of 2:1 by volume), a solution of zinc(II) acetate dihydrate (0.110 g, 0.5 mmol) in methanol (5 ml) was added. A colorless solution was observed, the solution was kept undisturbed for crystallization. After four days, colorless crystals of the complex were obtained. Yield 78%, FT-IR (KBr, cm^{-1}): 3450 (bs), 2960 (w), 1660 (s), 1614 (s), 1504 (m), 1471 (w), 1323 (s), 1388 (s), 1316 (w), 1281 (s), 1243 (m), 1135 (m), 1088 (w), 1056 (m), 902 (m), 755 (s). 1H NMR (DMSO- d_6): 6.93 (4H, m, aromatic protons), 4.60 (2H, s, cyclic aliphatic $-CH_2-$), 4.30 (2H, s, $-CH_2-$ group), 3.16 (s, from H_2O), 1.77 (3H, s, $-CH_3$ of acetate). ^{13}C NMR (DMSO- d_6): 176.2, 170.9, 163.8, 144.6, 129.4, 123.1, 122.6, 116.2, 115.8, 67.1, 44.7, 23.7.

The X-ray crystallographic data were collected at 296 K with Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) 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 [11]. The structures were solved by direct methods and refined by full-matrix least-squares calculations using SHELXTL software. All the non-H atoms were refined in the anisotropic approximation against F^2 of all reflections. The H-atoms, except those attached to O were placed at their calculated positions and refined in the isotropic approximation; those attached to hetero-atoms (O) were located in the difference Fourier maps, and refined with isotropic displacement coefficients. Some of the hydrogen atoms of oxygen atoms of water of crystallization could not be

located in both the structures **1** and **2**. The crystallographic parameters are given in Table 1.

Typical catalytic reaction for preparation of (E)-4-(3,4-dimethoxyphenyl) but-3-en-2-one: to a solution of 3,4-dimethoxy benzaldehyde (0.33 g, 2 mmol), and sodium hydroxide (0.002 g, 5 mol%) in acetone (15 ml), complex **1** (0.007 g, 1 mol%) was added. The resulting solution was kept stirring for 4 h at room temperature. After slow evaporation of the filtrate, a yellow color semi solid was obtained, which was purified by column chromatography and characterized by recording its 1H NMR, IR and comparing with authentic sample.

Catalyst optimization: to the above reaction mixture naphthalene (0.126 g) was added and the consumption of the 3,4-dimethoxybenzaldehyde with time during the reaction was monitored by GC-MS. The GC-MS were recorded in a Perkin-Elmer Clarus 500 with oven, temperature 200 °C, injector temperature 250 °C, inlet line a source temperature 150 °C with a capillary column of 5% phenyl 95% methyl-polysiloxane. The relative peak areas are calibrated independently by using naphthalene as a standard in each experiment. Similar reactions were performed with other catalysts namely $L'Na$, **2** and without catalyst were monitored.

3. Results and discussion

The reaction of zinc(II) acetate with 2,3-pyridine dicarboxylic acid followed by ethylenediamine gives a mononuclear complex (Fig. 2) with composition $(enH_2)_2[ZnL_3] \cdot 2H_2O$ (where H_2L = 2,3-pyridine dicarboxylic acid, en = ethylenediamine) (Eq. (1)).

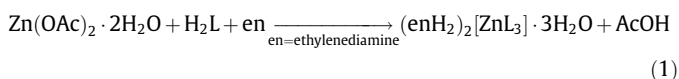


Table 1
The crystallographic parameters for complex **1** and **2**.

Compound	1	2
Empirical formula	$C_{25}H_{33}N_7O_{14}Zn$	$C_{32}H_{27}N_3Na_2O_{19}Zn$
M_r	720.92	868.92
Temperature (K)	296	296
Crystal size (mm^3)	$0.40 \times 0.28 \times 0.16$	$0.44 \times 0.26 \times 0.20$
Crystal systems	orthorhombic	monoclinic
Space group	$P2_12_12_1$	$P2_1$
a (\AA)	8.0064(4)	8.0001(4)
b (\AA)	16.0942(10)	14.7338(7)
c (\AA)	23.1032(13)	16.1445(8)
α ($^\circ$)	90.00	90.00
β ($^\circ$)	90.00	103.673(3)
γ ($^\circ$)	90.00	90.00
V (\AA^3)	2977.0(3)	1849.05(16)
Z	4	2
D_{calc} ($g\ cm^{-3}$)	1.600	1.561
μ (Mo $K\alpha$) (mm^{-1})	0.908	0.120
$F(0\ 0\ 0)$	1480	888
θ ($^\circ$)	27.00	28.32
Reflections collected	35390	19747
Independent reflections (R_{int})	6201	8422
Data/restraints/parameters	6201/0/428	8422/0/515
GOF on F^2	1.012	0.929
R_1, wR_2 [$I > 2\sigma(I)$]	0.0599, 0.1452	0.0816, 0.1596
R_1, wR_2 (all data)	0.0821, 0.1600	0.1986, 0.2471
Flack parameter	–	0.04(3)

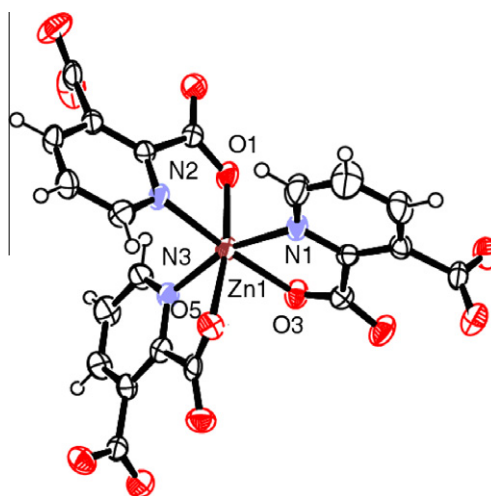


Fig. 2. Structure of tris-(2,3-pyridine dicarboxylato) zinc anion (the cations of the complex are removed for clarity).

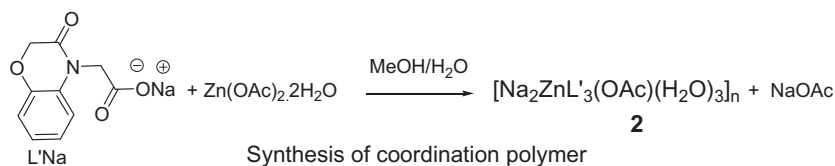
Table 2
Selected bond distances (Å) and bond angles (°) of complex **1**.

Bond parameter	For 1	Bond parameter	For 1
Zn(1)–N(1)	2.123(4)	<O(3)–Zn(1)–N(2)	175.36(15)
Zn(1)–N(2)	2.149(4)	<N(2)–Zn(1)–N(3)	93.46(16)
Zn(1)–N(3)	2.124(4)	<N(3)–Zn(1)–O(5)	77.64(14)
Zn(1)–O(5)	2.144(3)	<O(1)–Zn(1)–O(3)	100.21(15)
Zn(1)–O(1)	2.076(3)	<O(5)–Zn(1)–O(3)	86.60(14)
Zn(1)–O(3)	2.136(4)	<N(3)–Zn(1)–O(1)	96.54(16)
<N(3)–Zn(1)–N(1)	162.30(16)	<N(1)–Zn(1)–O(3)	77.11(15)
<N(2)–Zn(1)–N(1)	98.86(16)	<N(3)–Zn(1)–O(3)	90.98(15)
<N(2)–Zn(1)–O(5)	95.64(14)	<O(5)–Zn(1)–O(1)	171.20(14)
<N(1)–Zn(1)–O(5)	88.50(15)	<N(1)–Zn(1)–O(1)	98.41(17)
<N(2)–Zn(1)–O(1)	77.98(14)		

The complex has characteristic infra-red stretching at 3418 cm^{-1} due to N–H stretching with a strong overtone band at 1609 cm^{-1} . The carboxylate carbonyl frequency appears at 1578 cm^{-1} . The molar conductance is found to be $207.0\text{ S cm}^2\text{ mol}^{-1}$ corresponds to the 1:2 electrolyte. The proton NMR spectrum of the complex shows the corresponding peaks for the ligands and the ethylene diammonium cations. The crystal structure of the complex, reveals it to have an octahedral geometries around the zinc ion. The complex **1** is obtained either from the reaction of zinc(II) acetate to dicarboxylic acid (H_2L) ratio (1:2) or in (1:3); later composition gives the best yield. This suggests that the reaction to be thermodynamically controlled. The zinc ions are in octahedral geometry and the some of the metal–ligand bond distances and bond angles of the zinc complex are listed in Table 2.

There are examples of 2,3-pyridine dicarboxylato complexes in which complexes in chelating mode derived from partially deprotonated acid are formed and such complexes have strong intramolecular hydrogen bonds [12]. The 2,3-pyridine dicarboxylato complexes with polymeric structures are well known [13,14]. In fact depending on the reaction procedure and cation used polymeric zinc complex of 2,3-pyridine dicarboxylato anion can be prepared [12,19–23].

The sodium salt of HL' on reaction with zinc(II) acetate dihydrate gave a complex with a composition $[\text{Na}_2\text{ZnL}'_3(\text{OAc})(\text{H}_2\text{O})_3]_n$. The ^1H NMR of the complex shows the presence of two $-\text{CH}_2-$ groups of L' in different environment. There is also signal for $-\text{CH}_3$ group of acetate. In the ^{13}C NMR, there are signals at 176.2, 170.9, and 163.8 due to the presence of three different carbonyl groups. The signals at 67.1, 44.7 corresponds to the $-\text{CH}_2-$ groups of L' and the signal appearing at 23.7 corresponds of CH_3 -group of acetate. The complex has two strong carbonyl absorptions at 1660 and 1614 cm^{-1} due to two types of carboxylate groups. The complex has broad and sharp absorption at 3450 that arises from OH-stretching of water attached to sodium ions.



This reaction is interesting as it is observed that partial ligand exchange took place but a mixed metal complex with mixed carboxylate ligand is formed. The complex can be considered to be

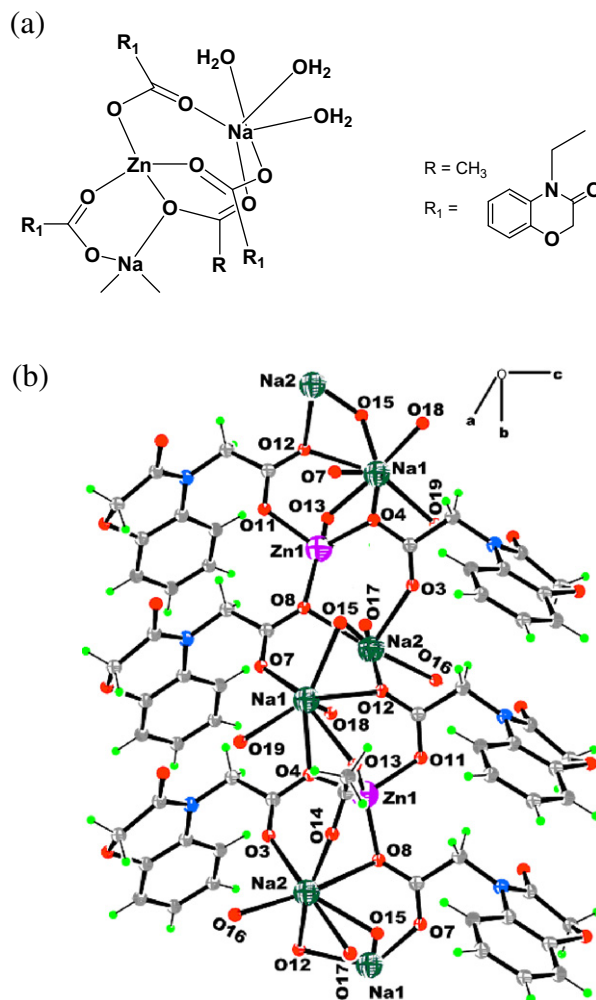


Fig. 3. (a) Representation of a portion of structural backbone of the zinc coordination polymer **2**; (b) crystal structure of the repeated units of the coordination polymer **2**.

formed by partial substitution of acetate ligand of zinc(II) acetate. The complex shows its characteristic peaks for acetate methyl group and the other CH_2 groups flanked by oxygen and nitrogen of the ligand L' . The repeated units of the polymeric structure is shown in Fig. 3a, the structure of the coordination polymer is shown in Fig. 3b. The coordination polymer is formed by zinc anions coordinated to three carboxylate oxygen atoms of the ligand L' and one oxygen atom of acetate group. The zinc ions are in distorted tetrahedral environment. Each of the carboxylate group is

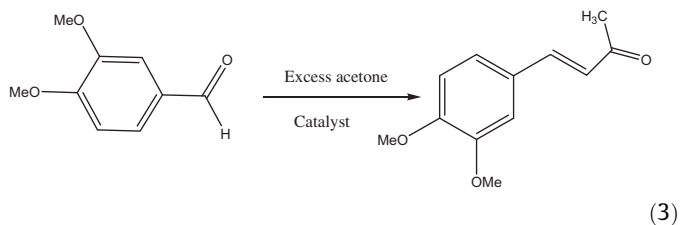
anchored to sodium ion. The sodium ions are further coordinated to three water molecules. The two coordinated water molecules are terminal ligands whereas one acts as bridging ligands. The

Table 3
Selected bond distances (Å) and bond angles (°) of complex **2**.

Bond parameter	For 2	Bond parameter	For 2
Zn(1)–O(8)	1.942(6)	<O15–Na1–O3	53.9(4)
Zn(1)–O(13)	1.951(8)	<O17–Na1–O3	175.4(4)
Zn(1)–O(11)	1.973(5)	<O14–Na1–O3	93.6(4)
Zn(1)–O(4)	1.980(6)	<O15–Na1–O12	52.6(4)
Na(1)–O(3)	2.402(7)	<O17 Na1–O12	85.7(3)
Na(1)–O(17)	2.352(9)	<O14–Na1–O12	170.9(5)
Na(1)–O(16)	2.404(10)	<O3–Na1–O12	89.9(3)
Na(2)–O(19)	2.485(13)	<O15–Na1–O16	126.4(4)
Na(1)–O(15)	1.943(18)	<O17–Na1–O16	89.6(4)
Na(2)–O(18)	2.461(17)	<O14–Na1–O16	94.6(4)
Na(1)–O(14)	2.378(11)	<O3–Na1–O16	92.1(4)
Na(1)–O(12)	2.403(7)	<O12–Na1–O16	93.7(3)
Na(2)–O(7)	2.292(8)	<O15–Na1–O8	52.0(4)
<O8–Zn1–O13	123.1(3)	<O17–Na1–O8	96.5(3)
<O8–Zn1–O11	109.1(2)	<O14–Na1–O8	82.7(4)
<O13–Zn1–O11	95.9(3)	<O3–Na1–O8	82.0(2)
<O8–Zn1–O4	112.1(3)	<O12–Na1–O8	89.5(2)
<O13–Zn1–O4	103.1(3)	<O16–Na1–O8	173.3(4)
<O15–Na1–O17	121.8(5)	<O15–Na1–O14	123.9(4)
<O17–Na1–O14	90.6(4)		

bond angles and bond distances describing the coordination environment are listed in Table 3. There are good numbers of literature of aqua bridged sodium complexes either leading to dimeric or polymeric structures [24,26]. Further to this the sodium ions can adopt six to eight coordination numbers [26]. These aqua bridges together with the carboxylate bridges make a polymeric structure, in which the sodium ions are in seven coordination geometry. Aqua bridged sodium complexes are common in literature [24–26]. However, the importance about this carboxylato complex is the observation of mixed metal as well as mixed carboxylato ligands, which is uncommon in literature.

It is interesting to note that the acetate groups act as bridge between two sodium ions along with a side-on interaction with zinc(II) ion. Each sodium ion is coordinated to three carboxylate ligands to make a network structure. In structure determination by single crystal X-ray crystallography we could not locate precisely the hydrogen atoms anchored to oxygen atoms of water molecules. The compound has tetrahedral geometry around each zinc ions and the sodium ions are hepta-coordinated. The mononuclear coordination complex of **L'** with copper(II) is recently reported [27], however the present complex is a coordination polymer.

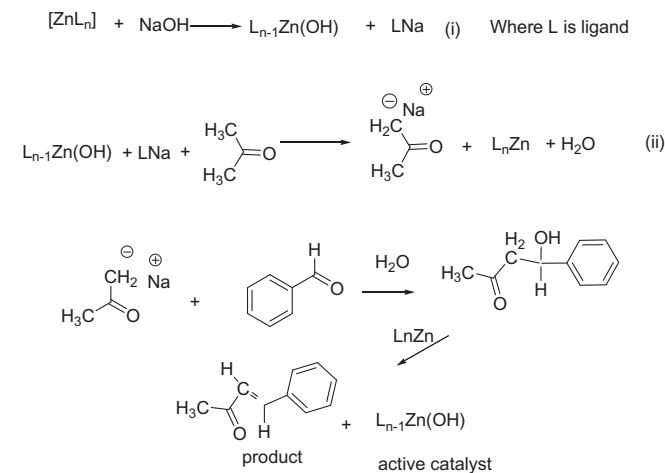


Selective catalytic reactions by proline [15–18] and its zinc complexes [19] are well studied. Since the zinc complexes that catalyses such aldol type reactions have heteroatom on a cyclic counterpart with a carboxylate functional group, we investigated the possibility of catalytic aldol reactions by complex **1** and **2**. It is found that the sodium salt of **HL'** as well as **1**, **2** is suitable catalyst for aldol reactions. The complexes **1** and **2** independently catalyse the reaction between aromatic aldehydes and acetone in mild basic medium. The reactions led to unsaturated carbonyl derivatives as illustrated in Eq. (3). One such reaction is mentioned here but the reaction is also applicable to condensation reaction between acetone and other electron rich aromatic aldehydes like

Table 4
Catalytic C–C bond formation reactions between 3,4-dimethoxybenzaldehyde with acetone.

Sl. No.	Catalyst ^a	Isolated yield (%)	Time (h)
2	NaL'	98	3
3	1	92	5
4	2	94	3
6	zinc-oxide	96	4

^a In all cases 1 mol% of catalyst is taken with 5 mol% sodiumhydroxide in acetone (15 ml) at room temperature.



Scheme 1. Proposed mechanism for zinc catalysed reactions.

4-methoxybenzaldehyde. The reaction time and reaction condition for different catalysts are listed in Table 4. Based on the results obtained from control experiments, a mechanism is proposed in Scheme 1. In the absence of these catalysts, the reaction does not take place. Further to this sodium hydroxide is also required in each case to cause the catalytic reactions, or in other word the metal complexes alone do not catalyse the reactions. The reactivity of the reactions are similar to zinc oxide in sodium hydroxide or similar to sodium salt of the ligand. No homo-coupling reaction between acetones is observed. This is due to the ease at which the cross coupling takes place, that dominates. The homo-coupling is also not observed in acetone earlier [19]. Thus, the role of sodium hydroxide is to generate zinc hydroxide derivatives in situ to act as catalyst. Since chiral induction was not possible and unsaturated carbonyl compounds were formed as the final product in these reactions, obvious interpretation is that the zinc complexes helps in dehydration and leads to active catalyst in the final step, so that the catalytic reactions continues. The zinc proline complex catalysed reaction do not eliminate water [19] but we have obtained exclusively the unsaturated carbonyl compounds which are formed by elimination of water from their corresponding alcohols. The coordination polymer **2** is made up of dinuclear sodium units holding tetrahedral zinc centers, this complex can be easily decompose by sodium hydroxide and the original polymeric complex can not be obtained after dissolution in dilute sodium hydroxide. This also suggests the role of zinc hydroxyl species as active catalyst in these reactions.

In conclusion we have synthesized and characterized two zinc carboxylate complexes that have the carboxylate ligands attached to heterocyclic rings. The catalytic activities of these two complexes are tested and it is found that in combination with sodium hydroxide these complexes catalyses condensation cum elimination reactions of acetone with aromatic aldehydes.

Acknowledgements

The authors thank Department Science and Technology, India, for financial support and one of the author W.M.S thanks Council of Scientific and Industrial Research, India, for a Senior Research Fellowship.

Appendix A. Supplementary material

CCDC 769587 and 747667 contain the supplementary crystallographic data for complexes 1 and 2, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2010.08.045.

References

- [1] T. Darbre, M. Machuqueiro, *Chem. Commun.* 15 (2003) 1090–1091.
- [2] D.J. Darensbourg, J.R. Wildeson, J.C. Yarbrough, *Inorg. Chem.* 41 (2002) 973.
- [3] T. Tsuruta, Y. Kawakami, *Tetrahedron* 29 (1973) 1179.
- [4] K. Soga, E. Imai, I. Hattori, *Polym. J. (Japan)* 13 (1981) 407.
- [5] M. Super, E. Berluce, C. Costello, E. Beckman, *Macromolecules* 30 (1997) 368.
- [6] D.J. Darensbourg, M.S. Zimmer, *Macromolecules* 32 (1999) 2137.
- [7] B.-H. Ye, X.-Y. Li, *Inorg. Chem.* 41 (2002) 6426.
- [8] B. Singh, J.R. Long, *J. Am. Chem. Soc.* 119 (1997) 7030.
- [9] W.M. Singh, J.B. Baruah, *Dalton Trans.* (2009) 2352.
- [10] W.M. Singh, J. Das, A. Karmakar, J.B. Baruah, *Inorg. Chim. Acta* 362 (2009) 2071.
- [11] G.M. Sheldrick, *Acta Crystallogr., Sect. A* 64 (2008) 112.
- [12] A.M. Baruah, A. Karmakar, J.B. Baruah, *Polyhedron* 26 (2007) 4518.
- [13] B.O. Patrick, C.L. Stevens, A. Storr, R.C. Thompson, *Polyhedron* 22 (2003) 3025.
- [14] F. Manteghi, M. Ghadermazi, H. Aghabozorg, *Acta Crystallogr., Sect. E* 63 (2007) o2809.
- [15] B. List, R.A. Lerner, C.F. Barbas III., *J. Am. Chem. Soc.* 122 (2000) 2395.
- [16] A.B. Northrup, D.W.C. MacMillan, *J. Am. Chem. Soc.* 124 (2002) 6798.
- [17] K. Sakthivel, W. Notz, T. Bui, C.F. Barbas III., *J. Am. Chem. Soc.* 123 (2001) 5260.
- [18] T. Darbre, M. Machuqueiro, *Chem. Commun.* (2003) 1090.
- [19] L. Chen, X.-M. Lin, Y. Ying, Q.-G. Zhan, Z.-H. Hong, J.-Y. Li, N.S. Weng, Y.-P. Cai, *Inorg. Chem. Commun.* 12 (2009) 761.
- [20] G.-H. Wang, Z.-G. Li, H.-Q. Jia, N.-H. Hu, J.-W. Xu, *CrystEngComm* 11 (2009) 292.
- [21] H. Yin, S.-X. Liu, *J. Mol. Struct.* 918 (2009) 165.
- [22] H. Aghabozorg, E. Sadr-khanlou, J. Soleimannejad, H. Adams, *Acta Crystallogr., Sect. E* 63 (2007) m1769.
- [23] S.O.H. Gutschke, A.M.Z. Zlawin, P.T. Wood, *J. Chem. Soc. Chem. Commun.* (1995) 2197.
- [24] A. Karmakar, J.B. Baruah, *Inorg. Chem. Commun.* 12 (2009) 140.
- [25] T. Chattopadhyay, K.S. Banu, S. Chattopadhyay, A. Banerjee, S. Mondal, E. Suresh, D. Das, *Inorg. Chem. Commun.* 12 (2009) 26.
- [26] L. Shen, Z.M. Jing, *Acta Crystallogr., Sect. C* 58 (2002) m591.
- [27] W.M. Singh, J. Das, A. Karmakar, J.B. Baruah, *Inorg. Chim. Acta* 362 (2009) 2071.