# Synthesis of a hierarchy of zinc oxalate structures from amine oxalates

R. Vaidhyanathan, Srinivasan Natarajan and C. N. R. Rao *

*Chemistry and Physics of Materials Unit, Jawaharlal Nehru Centre for Advanced Scientific Research, Jakkur P.O., Bangalore 560 064, India. E-mail: cnrrao@jncasr.ac.in*

A hierarchy of novel zinc oxalates including monomers and dimers has been prepared by reaction of amine oxalates with zinc ions, the amine oxalates having been characterized for the first time. In most of the amine oxalates one of the carboxyl groups transfers a proton to the amino nitrogen, leaving the other carboxyl group free to form hydrogen bonds. The zinc oxalates obtained are composed of a network of $ZnO_6$ octahedra and oxalate units, and possess zero-, one-, two- and three-dimensional structures. The monomer, dimer, and chain zinc oxalates are the first members of the hierarchy of structures. Relationships amongst these various oxalate structures are noteworthy and give indications as to the manner in which these structures are formed. Thus, the three-dimensional structure can be formed by the linking of layers, and the layer structure by condensation of linear chains. The isolation and characterization of a hierarchy of zinc oxalates of differing dimensionalities assumes significance in the light of the recent finding that low-dimensional structures transform to higher, more complex structures in the phosphate family.

## Introduction

A variety of open-framework metal phosphates possessing one-, two- and three-dimensional structures are known today.[1] There is reason to believe that the low-dimensional structures, those of zero and one dimension in particular, may act as starting building units in the formation of the more complex open-framework phosphates.[2] Among the novel open-framework materials not based on phosphates, those of phosphonates[3,4] and carboxylates[5,6] are noteworthy. Open-framework zinc and tin(II) oxalates have been synthesized hydrothermally in the presence of organic amines.[7] It has been shown recently that amine phosphates may act as intermediates in the formation of open-framework metal phosphates, and provide a convenient route for the synthesis of these materials.[8] Thus, reactions of amine phosphates with metal ions yield a variety of metal phosphates with different structures. Furthermore, this route also yields metal phosphates of different dimensionalities. It occurred to us that amine carboxylates could play a similar role in the formation of metal carboxylates with open architectures. We have, therefore, investigated the reaction of oxalates of organic amines with zinc ions. For this purpose, amine oxalates had to be synthesized and characterized for the first time, as there is hardly any report on these compounds in the literature. Interestingly, we have obtained zinc oxalates with one-, two- and three-dimensional architectures, in addition to the zero-dimensional monomeric and dimeric compounds, by the reaction of zinc ions with amine oxalates. These different structures exhibit interesting relationships, suggesting the possible presence of an *aufbau* principle in the formation of the hierarchy of oxalate structures.

## Experimental

### Synthesis of amine oxalates

In order to study the reaction of the amine oxalates with zinc ions, we first prepared the oxalates of organic amines such as propylamine (PRO), guanidine (GUO), piperazine (PIPO) and 1,4-diazabicyclo[2.2.2]octane (DABCO-O). In a typical experiment, the amine was added dropwise to an aqueous solution of oxalic acid with continuous stirring. The resulting solution was heated at 85 °C for 12 h and left at room temperature to obtain single crystals of the amine oxalates. The compositions of the amine oxalates are: $[CN_3H_6][HC_2O_4]\cdot H_2O$ (GUO), $[C_4N_2H_{12}][HC_2O_4]_2$ (PIPO), $[C_6N_2H_{14}][HC_2O_4]_2$ (DABCO-O) and $[C_3NH_{10}][HC_2O_4]\cdot H_2O$ (PRO). Elemental analysis using ICP-MS (inductively coupled plasma mass spectroscopy) of the amine oxalates confirmed the above compositions. The synthesis conditions for the amine oxalates and the analysis of the products are given in Table 1. The amine oxalates, thus obtained, were characterized using single crystal X-ray diffraction and elemental analysis.

### Synthesis of zinc oxalates

The amine oxalates were treated with zinc ions under hydrothermal conditions. In a typical experiment, 0.137 g of ZnO

**Table 1** Compositions of the amine oxalates[a]

| Starting composition | Elemental analysis[b] (%) | Product composition |
|---|---|---|
| $2\ H_2C_2O_4 : CN_3H_6 : 25\ H_2O$ | N 24.95 (25.15), C 21.17 (21.55), H 5.39 (5.39) | $[CN_3H_6][HC_2O_4]\cdot H_2O$ (GUO) |
| $2\ H_2C_2O_4 : C_4H_{10}N_2 : 25\ H_2O$ | N 10.95 (10.45), C 36.48 (36.09), H 5.56 (5.26) | $[C_4N_2H_{12}]_{0.5}[HC_2O_4]$ (PIPO) |
| $2\ H_2C_2O_4 : C_6N_2H_{12} : 25\ H_2O$ | N 9.84 (9.59), C 41.86 (41.09), H 5.41 (5.49) | $[C_6N_2H_{14}][HC_2O_4]_2$ (DABCO-O) |
| $H_2C_2O_4 : C_3H_9N : 25\ H_2O$ | N 8.58 (8.81), C 37.80 (37.74), H 7.71 (8.17) | $[C_3NH_{10}][HC_2O_4]\cdot H_2O$ (PRO) |

[a] The synthesis was carried out at 85 °C for 12 h. [b] The values in parenthesis are the calculated values based on the single crystal structure.

**Table 2** Composition and synthesis conditions for the zinc oxalates **1**–**5**

| Starting composition | $T/^\circ C$ | $t/h$ | Product composition |
|---|---|---|---|
| $ZnO:5GUO:100H_2O$ | 85 | 360 | $[CN_3H_6]_2[Zn(H_2O)_2(C_2O_4)_2]$ **1** |
| $ZnO:2PIPO:100H_2O$ | 50 | 120 | $[C_4N_2H_{12}]_3[Zn_2(C_2O_4)_5] \cdot 8H_2O$ **2** |
| $ZnO:2PIPO:100H_2O$ | 85 | 96 | **2** |
| $ZnO:5PIPO:100H_2O$ | 70 | 120 | $[C_4N_2H_{12}][Zn_2(C_2O_4)_3] \cdot 4H_2O$ **4** |
| $ZnO:5PIPO:12DMF$ | 110 | 84 | **4** |
| $ZnO:DABCO\text{-}O:200H_2O$ | 150 | 72 | $[C_6N_2H_{14}][Zn(C_2O_4)_2] \cdot 3H_2O$ **3** |
| $ZnO:5DABCO\text{-}O:100H_2O$ | 110 | 192 | **3** |
| $ZnO:5DABCO\text{-}O:100H_2O$ | 150 | 120 | **3** |
| $1.5ZnO:0.5HCl:2H_2C_2O_4:1DABCO\text{-}O:200H_2O$ | 130 | 72 | **3** |
| $ZnO:1HCl:2H_2C_2O_4:1.5DABCO\text{-}O:200H_2O$ | 130 | 156 | **3** |
| $ZnO:2.2PRO:250H_2O$ | 150 | 48 | $[C_3NH_{10}]_2[Zn_2(C_2O_4)_3] \cdot 3H_2O$ **5** + $Zn(C_2O_4) \cdot 2H_2O$ |
| $ZnO:2.2PRO:250H_2O$ | 110 | 84 | **5** + PRO |
| $ZnO:2.2PRO:250H_2O$ | 150 | 72 | **5** |

**Table 3** Crystal data and structure refinement parameters for the amine oxalates

|  | GUO | PIPO | DABCO-O | PRO |
|---|---|---|---|---|
| Chemical formula | $C_3H_9N_3O_5$ | $C_8H_{14}N_2O_8$ | $C_{10}H_{16}N_2O_8$ | $C_{10}H_{24}N_2O_9$ |
| Formula mass | 167.13 | 266.21 | 292.25 | 316.31 |
| Crystal symmetry | Monoclinic | Monoclinic | Triclinic | Monoclinic |
| Space group | $P2_1/c$ (no. 14) | $C2/c$ (no. 15) | $P\bar{1}$ (no. 2) | $C2/c$ (no. 15) |
| $T/K$ | 293(2) | 293(2) | 293(2) | 293(2) |
| $a/\text{Å}$ | 6.699(1) | 15.963(11) | 6.971(11) | 18.004(11) |
| $b/\text{Å}$ | 10.552(6) | 5.716(2) | 9.607(2) | 5.679(2) |
| $c/\text{Å}$ | 10.224(4) | 12.354(4) | 10.633(4) | 13.986(4) |
| $\alpha/^\circ$ |  |  | 91.25(7) |  |
| $\beta/^\circ$ | 103.77(3) | 108.07(3) | 107.5(3) | 126.85(3) |
| $\gamma/^\circ$ |  |  | 109.3(6) |  |
| $V/\text{Å}^3$ | 702.0(9) | 1071.5(9) | 634.8(9) | 1144.4(9) |
| $Z$ | 4 | 4 | 2 | 4 |
| $\mu/\text{mm}^{-1}$ | 0.149 | 0.49 | 0.134 | 0.117 |
| No. of measured/observed reflections | 1012/663 | 760/686 | 1781/1436 | 1134/970 |
| $R1$, $wR2$ [$I > 2\sigma(I)$] | 0.08, 0.21 | 0.029, 0.076 | 0.049, 0.139 | 0.043, 0.12 |

**Table 4** Crystal data and structure refinement parameters for the zinc oxalates **1**–**4**

|  | **1** | **2** | **3** | **4** |
|---|---|---|---|---|
| Chemical formula | $C_6H_{16}N_6O_{10}Zn$ | $C_{11}H_{18}N_3O_{14}Zn$ | $C_{10}H_{20}N_2O_{11}Zn$ | $C_{10}H_{20}N_2O_{16}Zn_2$ |
| Formula mass | 397.62 | 481.65 | 409.65 | 555.1 |
| Crystal symmetry | Monoclinic | Monoclinic | Monoclinic | Monoclinic |
| Space group | $C2/c$ (no. 15) | $C2/c$ (no. 15) | $P2_1/n$ (no. 14) | $C2/c$ (no. 15) |
| $T/K$ | 293(2) | 293(2) | 293(2) | 293(2) |
| $a/\text{Å}$ | 14.170(2) | 13.799(1) | 9.433(1) | 16.725(3) |
| $b/\text{Å}$ | 10.129(1) | 11.524(2) | 16.860(2) | 9.254(1) |
| $c/\text{Å}$ | 11.324(3) | 25.412(2) | 9.788(1) | 31.298(2) |
| $\beta/^\circ$ | 115.4(2) | 105.2(1) | 91.4(1) | 98.59(1) |
| $V/\text{Å}^3$ | 1468.2(3) | 3897.2(2) | 1556.1(2) | 4789.9(3) |
| $Z$ | 4 | 8 | 4 | 4 |
| $\mu//\text{mm}^{-1}$ | 1.739 | 1.337 | 1.641 | 2.086 |
| No. of measured/observed reflections | 1053/916 | 2758/2421 | 2246/1366 | 3439/2403 |
| $R1$, $wR2$ [$I > 2\sigma(I)$] | 0.044, 0.098 | 0.042, 0.116 | 0.048, 0.104 | 0.054, 0.135 |

*a* For structural details for compound **5**, please see ref. 12.

was dispersed in 3 ml of water and 2 g of GUO added with continuous stirring. The contents were homogenized, transferred to a PTFE-lined stainless steel acid digestion bomb (Parr, USA) and heated at 85 °C for 15 days. The final composition of the mixture was $ZnO:5GUO:100H_2O$. The above reaction resulted in the formation of colorless rod-shaped crystals of composition $[CN_3H_6]_2[Zn(H_2O)_2(C_2O_4)_2]$ **1**. A similar procedure was adopted for the preparation of compounds **2**–**5** by employing different amine oxalates. In the majority of cases good quality single crystals, stable under laboratory conditions, were obtained. The single crystals were employed for all subsequent characterization purposes. Powder X-ray diffraction (XRD) patterns on the powdered crystals indicated that the products were consistent with the structure determined by

single crystal X-ray diffraction. A summary of all the synthesis conditions and compositions of the products obtained is presented in Table 2.

**Single crystal structure determination**

A suitable single crystal of each compound including the amine oxalates was carefully selected under a polarizing microscope and glued to a thin glass fiber with cyanoacrylate (super glue) adhesive. Single crystal structure determination by X-ray diffraction was performed on a Siemens Smart-CCD diffractometer (Mo-Kα radiation, $\lambda = 0.71073$ Å). A hemisphere of intensity data was collected at room temperature. Pertinent experimental details for the amine oxalates and zinc oxalates are presented in Tables 3 and 4.

**Table 5** Important hydrogen bond distances and angles for the amine oxalates

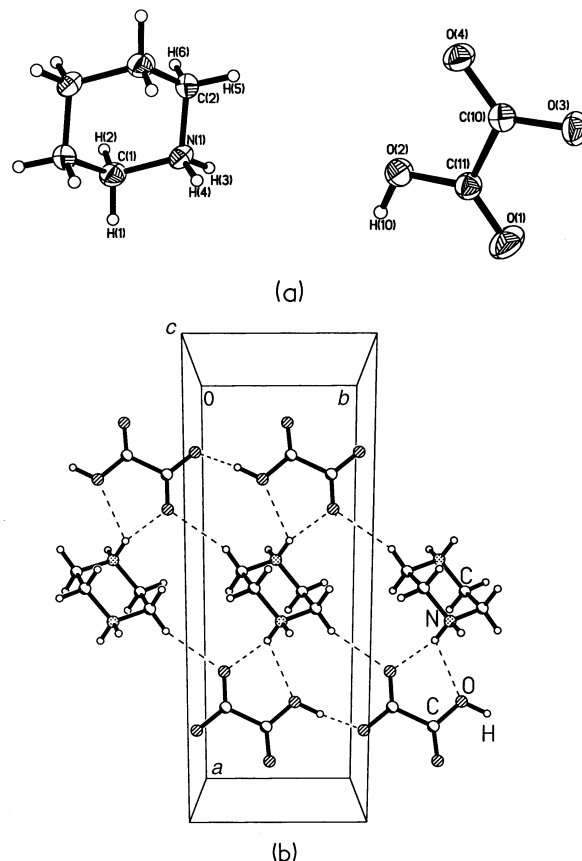| Compound | N···O/Å | N–H···O/° | O···O/Å | O–H···O/° | C···O/Å | C–H···O/° |
|---|---|---|---|---|---|---|
| GUO[a] | 2.881(5) | 177.0(4) | — | — | — | — |
| | 2.923(5) | 171.0(4) | — | — | — | — |
| PIPO[b] | 2.816(19) | 150.0(2) | 2.563(16) | 172.0(2) | 3.431(2) | 163.0(17) |
| | 2.784(2) | 158.0(2) | — | — | 3.328(2) | 159.0(18) |
| | — | — | — | — | 3.373(2) | 158.0(19) |
| DABCO-O[c] | 2.619(3) | 152.0(2) | 2.619(3) | 158.0(3) | 3.393(3) | 165.0(2) |
| | 2.619(3) | 148.8(19) | 2.741(3) | 157.0(3) | 3.359(3) | 141.0(18) |
| | — | — | — | — | 3.419(3) | 153.1(18) |
| PRO[b] | 2.868(4) | 142 | 2.580(2) | 176 | 3.427(8) | 147 |
| | 2.862(6) | 172 | — | — | — | — |

[a] Amine and oxalate units alternate in the layer resulting in only N–H···O type hydrogen bonds. [b] Linear chains are formed by oxalate moieties. [c] Dimer units are formed by oxalate moieties as in oxalic acid.
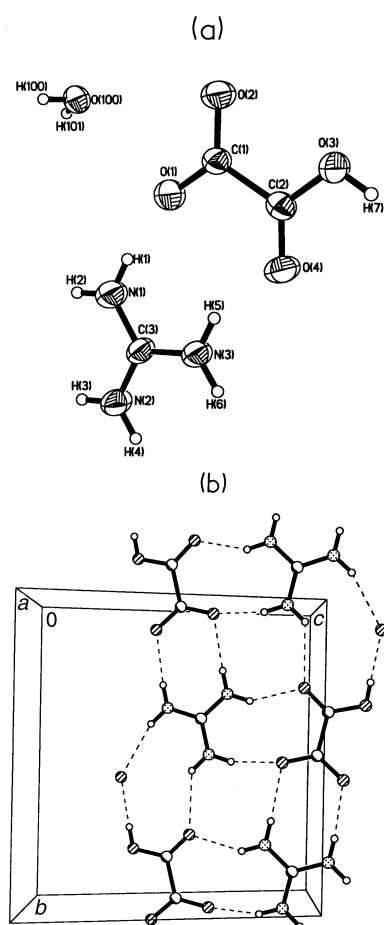


**Fig. 1** (a) An ORTEP[12] plot of guanidinium oxalate, $[CN_3H_6]$-$[HC_2O_4] \cdot H_2O$ (GUO). Thermal ellipsoids (in all the structures) are given at 50% probability. (b) Packing diagram of GUO along the $bc$ plane showing the hydrogen bond interactions (dashed lines).



**Fig. 2** (a) ORTEP plot of piperazinium oxalate, $[C_4N_2H_{12}][HC_2O_4]_2$ (PIPO). Asymmetric unit is labeled. (b) Packing diagram of PIPO along the $ab$ plane showing the arrangement of the oxalate and the amine. Note that the oxalate units form a chain-like arrangement with the amine in between.

An empirical absorption correction based on symmetry equivalent reflections was applied for all five compounds using the SADABS[9] program and the structures of the amine oxalates as well as of the zinc oxalates were solved by direct methods using SHELXS 86[10] and Fourier difference syntheses. All the hydrogen positions for the amine oxalates and compounds **1**–**4** were initially located in the Fourier difference maps, and for the final refinement the hydrogen atoms were placed geometrically and held in the riding mode. The last cycles of refinement included positions for all the atoms, anisotropic thermal parameters for all non-hydrogen atoms and isotropic thermal parameters for all the hydrogen atoms. Full-matrix least-squares structure refinement against $|F^2|$ was carried out using the SHELXTL PLUS[11] package of programs. Important bond distances and angles related to the hydrogen bonds in the amine oxalates are listed in Table 5, selected bond distances and angles of **1**, **2** and **3** in Tables 6, 7 and 8 and for **4** in Tables 9 and 10 respectively.

CCDC reference numbers 151822–151825, 151827–151830.

See http://www.rsc.org/suppdata/dt/b0/b008571p/ for crystallographic data in CIF or other electronic format.

## Results

### Amine oxalates

The structures of the amine oxalates synthesized and characterized in the present study are given in Figs. 1–4. They show strong hydrogen bond interactions typical of non-covalent solids involving the oxalate and amine moieties. The structurally significant hydrogen bonds arise mainly from N–H···O and O–H···O interactions. In most of the amine oxalates one
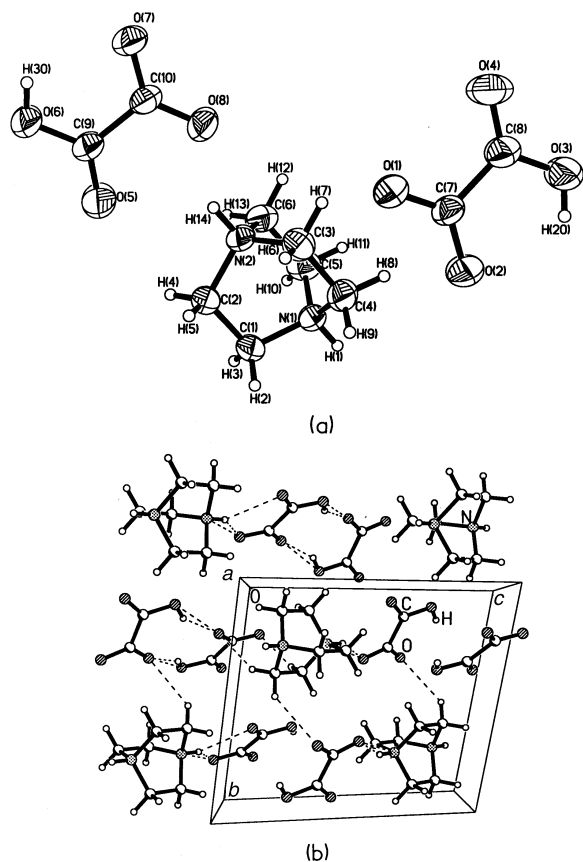
Fig. 3 (a) ORTEP plot of DABCO oxalate, $[C_6N_2H_{14}][HC_2O_4]_2$ (DABCO-O). (b) Structure of DABCO-O along the *bc* direction. Note the formation of oxalic acid dimers.
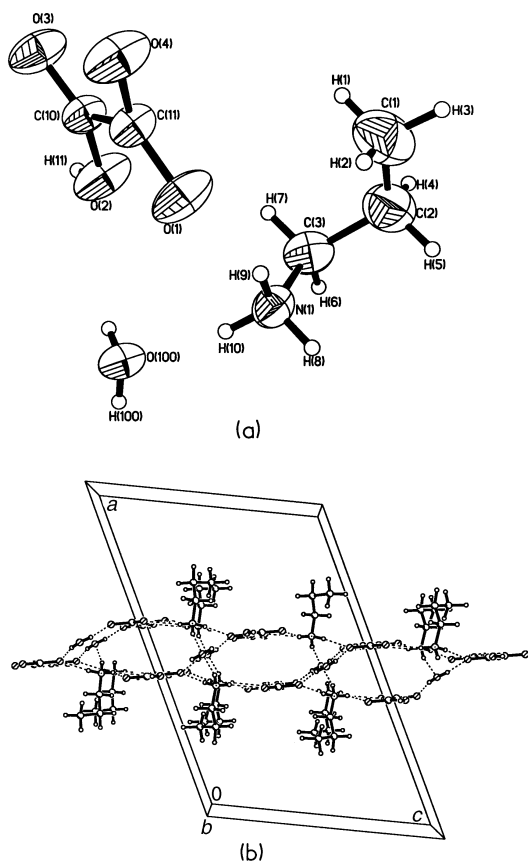


Fig. 4 (a) ORTEP plot of propylammonium oxalate, $[C_3NH_{10}]-[HC_2O_4] \cdot H_2O$ (PRO). (b) Structure of PRO along the *ac* plane. Note the strong hydrogen bond interaction between the oxalate and water molecule.
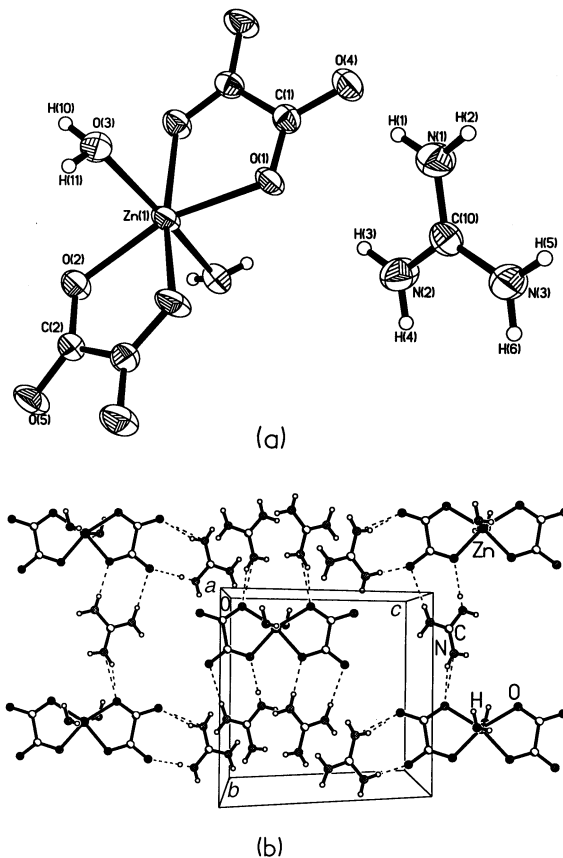
Fig. 5 (a) ORTEP plot of the zinc oxalate monomer, $[CN_3H_6]_2[Zn-(H_2O)_2(C_2O_4)_2]$ **1**. Asymmetric unit is labeled. (b) Structure of the monomer along the [100] direction. Dashed lines represent hydrogen bond interactions.
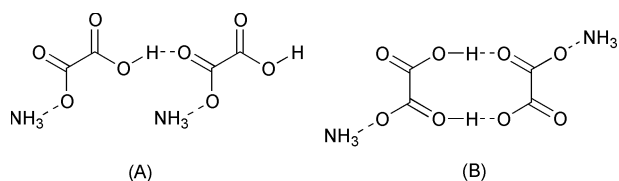


of the carboxyl groups transfers a proton to the amino nitrogen, leaving the other carboxyl group free to form a linear hydrogen bonded chain as shown schematically in structure **A**. In DABCO-O the amine forms two N–H $\cdots$ O bonds giving a distorted cyclic carboxylic dimer in the *anti* conformation as shown in structure **B**. The N $\cdots$ O and O $\cdots$ O distances in the amine oxalates are all around 2.5 Å and the N–H $\cdots$ O and O–H $\cdots$ O bond angles are larger than 150° (Table 5).

### Zinc oxalates

**Zero-dimensional $[CN_3H_6]_2[Zn(H_2O)_2(C_2O_4)_2]$ 1 and $[C_4N_2H_{12}]_3[Zn_2(C_2O_4)_5] \cdot 8H_2O$ 2.** The asymmetric unit of compound **1**, presented in Fig. 5a, contains 12 non-hydrogen atoms. The structure of **I** is that of a monomer consisting of two oxalate units directly linked to Zn atoms, which are also bonded to two water molecules. The monomeric zinc oxalate units are held by strong hydrogen bonds with the monoprotonated amine (Fig. 5b). The Zn atoms are octahedrally coordinated with respect to oxygen atoms with Zn–O distances in the range 2.082(3)–2.154(4) Å (av. 2.113 Å) and C–O bond distances in the range 1.238(5)–1.265(5) Å (av. 1.254 Å) (Table 6). The O–Zn–O angles are in the range 83.08(14)–171.0(2)° (av. 108.6°) and the O–C–O bond angles have an average value of 125.7°. These values are typical for this type of bonding and similar bond distances and angles have been observed earlier in similar compounds.[13,14]

**Table 6** Selected bond distances (Å) and angles (°) for [CN$_3$H$_6$]$_2$[Zn-(H$_2$O)$_2$(C$_2$O$_4$)$_2$] **1**

| | | | |
|---|---|---|---|
| Zn(1)–O(1) | 2.082(3) | O(1)–C(1) | 1.256(5) |
| Zn(1)–O(1)$^{\#1}$ | 2.082(3) | O(2)–C(2) | 1.265(5) |
| Zn(1)–O(2)$^{\#1}$ | 2.102(3) | O(4)–C(1) | 1.257(5) |
| Zn(1)–O(2) | 2.102(3) | O(5)–C(2) | 1.238(5) |
| Zn(1)–O(3) | 2.154(4) | C(1)–C(2)$^{\#1}$ | 1.563(6) |
| Zn(1)–O(3)$^{\#1}$ | 2.154(4) | | |
| | | | |
| O(1)–Zn(1)–O(1)$^{\#1}$ | 85.9(2) | O(1)$^{\#1}$–Zn(1)–O(3) | 90.2(2) |
| O(1)–Zn(1)–O(2)$^{\#1}$ | 79.28(11) | O(2)–Zn(1)–O(3) | 92.19(13) |
| O(1)–Zn(1)–O(2) | 162.87(12) | O(2)$^{\#1}$–Zn(1)–O(3) | 83.08(14) |
| O(2)$^{\#1}$–Zn(1)–O(2) | 116.6(2) | O(3)–Zn(1)–O(3)$^{\#1}$ | 171.0(2) |
| O(1)–Zn(1)–O(3) | 96.39(14) | O(4)–C(1)–C(2)$^{\#1}$ | 119.2(4) |
| C(1)–O(1)–Zn(1) | 114.3(3) | O(5)–C(2)–C(1)$^{\#1}$ | 117.6(4) |
| C(2)–O(2)–Zn(1) | 113.5(3) | O(1)–C(1)–O(4) | 124.3(4) |
| O(1)–C(1)–C(2)$^{\#1}$ | 116.5(4) | O(5)–C(2)–O(2) | 127.0(4) |
| O(2)–C(2)–C(1)$^{\#1}$ | 115.4(4) | | |

Symmetry transformation used to generate equivalent atoms: #1 $-x + 1$, $y$, $-z + \frac{3}{2}$.

**Table 7** Selected bond distances (Å) and angles (°) in [C$_4$N$_2$H$_{12}$]$_3$[Zn$_2$-(C$_2$O$_4$)$_5$]·8H$_2$O **2**

| | | | |
|---|---|---|---|
| Zn(1)–O(1) | 2.042(3) | O(1)–C(1) | 1.279(5) |
| Zn(1)–O(2) | 2.069(3) | O(7)–C(1) | 1.233(5) |
| Zn(1)–O(4) | 2.093(3) | O(2)–C(2) | 1.257(5) |
| Zn(1)–O(5) | 2.097(3) | O(3)–C(2) | 1.242(6) |
| Zn(1)–O(9) | 2.160(3) | O(4)–C(3) | 1.268(5) |
| Zn(1)–O(10) | 2.164(3) | O(6)–C(3) | 1.242(5) |
| C(1)–C(3) | 1.555(6) | O(5)–C(4) | 1.269(5) |
| C(2)–C(4) | 1.569(6) | O(8)–C(4) | 1.226(6) |
| C(5)–C(5)$^{\#1}$ | 1.544(8) | O(9)–C(5) | 1.268(5) |
| | | O(10)–C(5)$^{\#1}$ | 1.252(5) |
| | | | |
| O(1)–Zn(1)–O(2) | 171.33(13) | O(5)–Zn(1)–O(10) | 91.35(12) |
| O(1)–Zn(1)–O(4) | 79.98(11) | O(9)–Zn(1)–O(10) | 77.14(10) |
| O(2)–Zn(1)–O(4) | 96.35(12) | C(1)–O(1)–Zn(1) | 114.9(3) |
| O(1)–Zn(1)–O(5) | 93.59(12) | C(2)–O(2)–Zn(1) | 114.5(3) |
| O(2)–Zn(1)–O(5) | 79.64(13) | C(3)–O(4)–Zn(1) | 112.9(3) |
| O(4)–Zn(1)–O(5) | 104.41(12) | C(4)–O(5)–Zn(1) | 114.0(3) |
| O(1)–Zn(1)–O(9) | 101.35(13) | C(5)–O(9)–Zn(1) | 111.6(2) |
| O(2)–Zn(1)–O(9) | 86.41(12) | C(5)$^{\#1}$–O(10)–Zn(1) | 111.3(3) |
| O(4)–Zn(1)–O(9) | 89.57(12) | O(7)–C(1)–O(1) | 125.9(4) |
| O(5)–Zn(1)–O(9) | 161.16(11) | O(3)–C(2)–O(2) | 125.2(4) |
| O(1)–Zn(1)–O(10) | 90.85(12) | O(6)–C(3)–O(4) | 126.2(4) |
| O(2)–Zn(1)–O(10) | 94.69(13) | O(8)–C(4)–O(5) | 126.0(4) |
| O(4)–Zn(1)–O(10) | 162.13(12) | O(10)$^{\#1}$–C(5)–O(9) | 125.5(4) |

Symmetry transformation used to generate equivalent atoms: #1 $-x$, $y$, $-z + \frac{3}{2}$.



**Fig. 6** (a) ORTEP plot of the zinc oxalate, dimer [C$_4$N$_2$H$_{12}$]$_3$-[Zn$_2$(C$_2$O$_4$)$_5$]·8H$_2$O **2**. (b) Structure of the dimer, along the [010] direction. The dimer and the amine alternate in a plane. Water molecules are omitted for clarity. Dashed lines are hydrogen bond interactions.

The asymmetric unit of compound **2** contains 29 non-hydrogen atoms (Fig. 6a). Unlike in **1**, in **2** there are two Zn atoms, which are connected by one oxalate unit. The Zn atoms also possess two terminal oxalates forming a dimeric unit. Just as in **1**, the dimeric zinc oxalate is strongly hydrogen bonded to the diprotonated amine and water molecules (Fig. 6b). The octahedrally coordinated Zn atoms have Zn–O distances in the range 2.042(3)–2.164(3) Å (av. 2.104 Å). Of the six oxygens bound to zinc, three are associated with Zn–O distances in the range 2.042(3)–2.093(3) Å and the remaining three have distances in the range 2.097(3)–2.164(5) (Table 7). Formally these correspond to singly and doubly bonded oxygens bound to the carbon atoms respectively. The C–O bond distances are

in the range 1.226(6)–1.279(5) Å (av. 1.255 Å) and the variations in them are also reflected in this bonding as well. The O–Zn–O angles are in the range 77.14(10)–171.33(13)° (av. 105.33°). The O–C–O bond angles are in the range 125.2(4)–126.0(4)° (av. 125.8°). The observed geometric parameters are as expected.
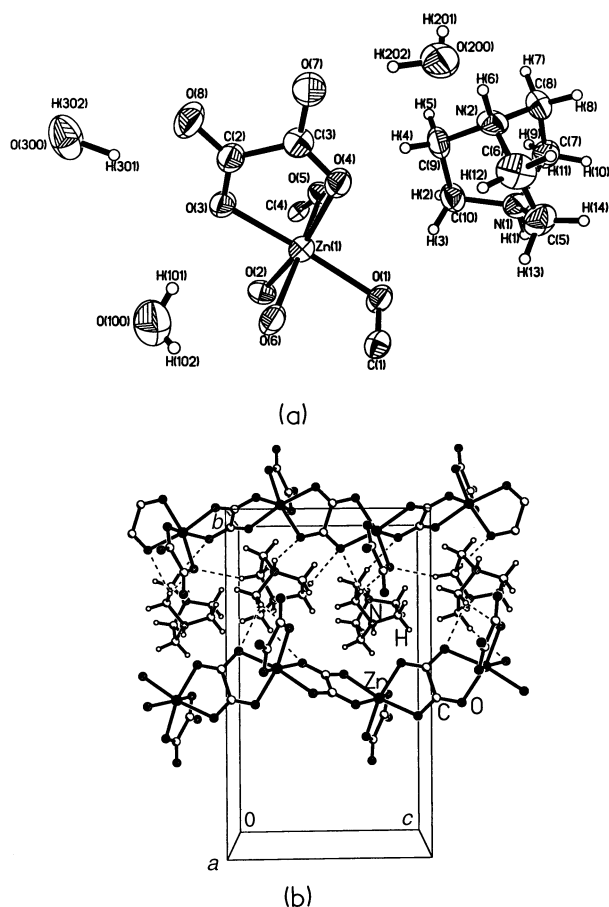
**One-dimensional [C$_6$N$_2$H$_{14}$][Zn(C$_2$O$_4$)$_2$]·3H$_2$O 3.** The asymmetric unit of compound **3** contains 24 non-hydrogen atoms, of which 13 belong to the framework (Fig. 7a). Of the remaining 11 atoms, 3 belong to the water molecules and 8 to the amine. The Zn atoms are six-coordinated with respect to the oxygens with Zn–O distances in the range 2.074(4)–2.134(4) Å (av. 2.099 Å). Of the six oxygens bound to zinc, three are associated with Zn–O distances in the range 2.074(4)–2.089(4) Å and the remaining three have distances in the range 2.103(4)–2.134(4) Å (Table 8). These correspond to the singly and doubly bonded oxygens bound to the carbon atoms respectively. The C–O bond distances are in the range 1.238(7)–1.257(7) Å (av. 1.249 Å). The O–Zn–O angles are in the range 79.2(2)–169.9(2)° (av. 105.33°) and the O–C–O bond angles are in the range 125.6(6)–126.2(6)° (av. 125.9°). These geometric parameters are in agreement with those reported earlier for similar compounds. Unlike the zero-dimensional monomeric and dimeric zinc oxalates, in **3**, the Zn atoms and the oxalate units are so connected as to form a one-dimensional chain with each Zn possessing a terminal oxalate unit. The diprotonated amine is situated in between these chains and interacts with the terminal oxalate *via* hydrogen bonds (Fig. 7b). Zinc oxalate dihydrate, [Zn(C$_2$O$_4$)(H$_2$O)$_2$], with a chain architecture is known,[14] but **3** is the first example of a chain zinc oxalate synthesized in the presence of an organic amine.

**Two-dimensional [C$_4$N$_2$H$_{12}$]$_2$[Zn$_2$(C$_2$O$_4$)$_3$]$_2$·4H$_2$O 4.** The asymmetric unit of compound **4** contains 36 non-hydrogen atoms (Fig. 8a). It consists of macroanionic sheets of formula [Zn$_2$(C$_2$O$_4$)$_3$]$^{2-}$ with interlamellar [C$_4$N$_2$H$_{12}$]$^{2+}$ ions. The asymmetric unit contains two crystallographically independent Zn atoms. The Zn atoms are octahedrally coordinated with respect to oxygen atoms with Zn–O distances in the range 2.074(5)–2.126(5) Å (av. Zn(1)–O 2.1007; Zn(2)–O 2.1007). Of the six oxygens bound to zinc, three are associated with Zn–O distances in the range 2.079(5)–2.100(5) Å for Zn(1) and 2.074(5)–

**Table 8** Selected bond distances (Å) and angles (°) for [C$_6$N$_2$H$_{14}$][Zn-(C$_2$O$_4$)$_2$]·3H$_2$O **3**

| | | | |
|---|---|---|---|
| Zn(1)–O(1) | 2.074(4) | O(1)–C(1) | 1.253(7) |
| Zn(1)–O(2) | 2.085(4) | O(2)–C(4)$^{#1}$ | 1.245(6) |
| Zn(1)–O(3) | 2.089(4) | O(3)–C(2) | 1.238(7) |
| Zn(1)–O(4) | 2.103(4) | O(4)–C(3) | 1.252(6) |
| Zn(1)–O(5) | 2.112(4) | O(5)–C(4) | 1.252(7) |
| Zn(1)–O(6) | 2.134(4) | O(6)–C(1)$^{#2}$ | 1.257(7) |
| C(1)–C(1)$^{#2}$ | 1.546(11) | O(7)–C(3) | 1.248(7) |
| C(2)–C(3) | 1.549(9) | O(8)–C(2) | 1.248(7) |
| C(4)–C(4)$^{#1}$ | 1.550(12) | | |
| | | | |
| O(1)–Zn(1)–O(2) | 100.1(2) | O(4)–Zn(1)–O(6) | 100.6(2) |
| O(1)–Zn(1)–O(3) | 159.9(2) | O(5)–Zn(1)–O(6) | 169.9(2) |
| O(2)–Zn(1)–O(3) | 93.1(2) | C(1)–O(1)–Zn(1) | 114.2(4) |
| O(1)–Zn(1)–O(4) | 90.1(2) | C(4)$^{#1}$–O(2)–Zn(1) | 113.4(4) |
| O(2)–Zn(1)–O(4) | 166.3(2) | C(2)–O(3)–Zn(1) | 112.9(4) |
| O(3)–Zn(1)–O(4) | 79.7(2) | C(3)–O(4)–Zn(1) | 112.3(4) |
| O(1)–Zn(1)–O(5) | 102.2(2) | C(4)–O(5)–Zn(1) | 112.7(3) |
| O(2)–Zn(1)–O(5) | 79.6(2) | C(1)$^{#2}$–O(6)–Zn(1) | 112.6(4) |
| O(3)–Zn(1)–O(5) | 94.9(2) | O(1)–C(1)–O(6)$^{#2}$ | 126.1(5) |
| O(4)–Zn(1)–O(5) | 89.4(2) | O(3)–C(2)–O(8) | 125.6(6) |
| O(1)–Zn(1)–O(6) | 79.2(2) | O(7)–C(3)–O(4) | 126.2(6) |
| O(2)–Zn(1)–O(6) | 90.3(2) | O(2)$^{#1}$–C(4)–O(5) | 125.9(5) |
| O(3)–Zn(1)–O(6) | 85.7(2) | | |

Symmetry transformations used to generate equivalent atoms: #1 $-x$, $-y + 1$, $-z$; #2 $-x$, $-y + 1$, $-z + 1$.

**Table 9** Selected bond distances (Å) for [C$_4$N$_2$H$_{12}$][Zn$_2$(C$_2$O$_4$)$_3$]·4H$_2$O **4**

| | | | |
|---|---|---|---|
| Zn(1)–O(1) | 2.079(5) | Zn(2)–O(7) | 2.074(5) |
| Zn(1)–O(2) | 2.092(5) | Zn(2)–O(8) | 2.082(5) |
| Zn(1)–O(3) | 2.100(5) | Zn(2)–O(9) | 2.098(5) |
| Zn(1)–O(4) | 2.103(5) | Zn(2)–O(10) | 2.101(5) |
| Zn(1)–O(5) | 2.107(5) | Zn(2)–O(11) | 2.123(5) |
| Zn(1)–O(6) | 2.123(5) | Zn(2)–O(12) | 2.126(5) |
| O(1)–C(1)$^{#1}$ | 1.257(8) | O(7)–C(3) | 1.248(9) |
| O(2)–C(2)$^{#1}$ | 1.264(8) | O(8)–C(1) | 1.257(8) |
| O(3)–C(3) | 1.256(9) | O(9)–C(5)$^{#2}$ | 1.250(9) |
| O(4)–C(4) | 1.244(8) | O(10)–C(2) | 1.251(8) |
| O(5)–C(5) | 1.259(9) | O(11)–C(6) | 1.260(8) |
| O(6)–C(6) | 1.251(8) | O(12)–C(4)$^{#2}$ | 1.253(8) |
| C(1)–C(2) | 1.540(11) | C(3)–C(6) | 1.554(10) |
| C(4)–C(5) | 1.548(10) | | |

Symmetry transformations used to generate equivalent atoms: #1 $x - \frac{1}{2}$, $y + \frac{1}{2}$, $z$; #2 $x$, $y - 1$, $z$.

O–Zn–O angles are in the range 78.9(2)–169.7(2)° (av. O–Zn(1)–O 105.7; O–Zn(2)–O 105.8°) (Table 10). The O–C–O bond angles are in the range 125.4(7)–126.9(7)° (av. 126.0°). The geometrical parameters associated with the Zn and oxalate units are as expected.

The individual layers in compound **4** involve a network of ZnO$_6$ octahedra and C$_2$O$_4$ units. Each Zn is cross-linked to six oxalate oxygens, forming a two-dimensional layer structure involving the honeycomb motif as in many of the divalent metal oxalates (Fig. 8b). The honeycomb layers stack one over the other, along the $c$ axis. Such perforated sheets have been observed in layered aluminophosphates[15] and the recently discovered iron oxalate phosphates.[16] The diprotonated amine sits in the middle of a 12-membered ring (6 Zn and 6 oxalate units) as shown in Fig. 8(b). The four water molecules, present in **4**, are present in between the layers. The amine and water molecules participate in extensive hydrogen bonding, lending structural stability.

**Three-dimensional [C$_3$NH$_{10}$]$_2$[Zn$_2$(C$_2$O$_4$)$_3$]·3H$_2$O 5.** The asymmetric unit of compound **5** contains 19 non-hydrogen atoms and is shown in Fig. 9(a). The structure also consists of a network of ZnO$_6$ octahedra and oxalate units and three oxalate units connect with the Zn atoms. Of the three oxalate units, two connect *via* an in-plane linkage and the third is cross-linked to the Zn atom in an out-of-plane manner as shown in Fig. 9(b). The connectivity between Zn and the oxalates units gives rise to a 20-membered aperture, which on projection forms 12-membered square channels. The amine sits in the middle of the channels. **5** was recently synthesized by employing the conventional hydrothermal procedure and the structure reported.[13] We will not, therefore, discuss its structure in detail.
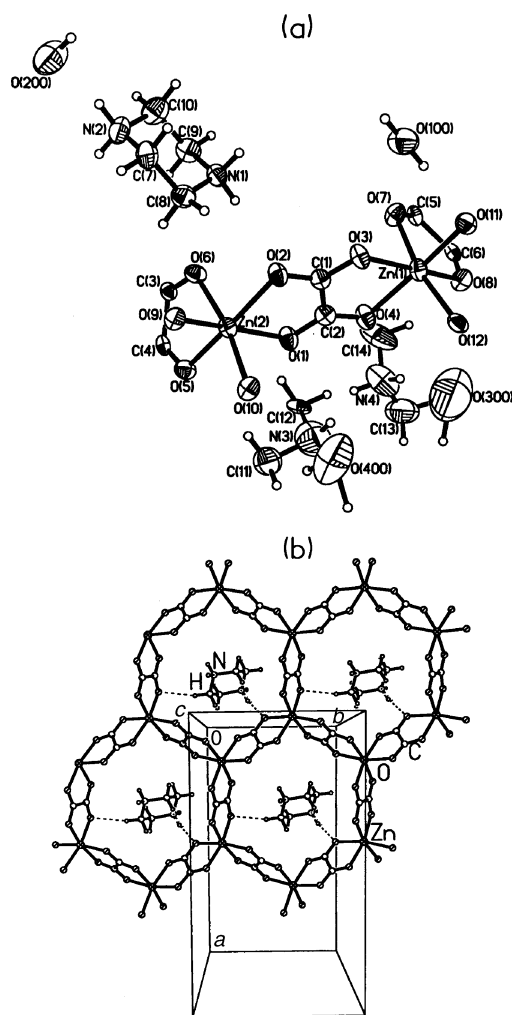
## Discussion

Five zinc oxalates, [CN$_3$H$_6$]$_2$[Zn(H$_2$O)$_2$(C$_2$O$_4$)$_2$] **1**, [C$_4$N$_2$H$_{12}$]$_3$-[Zn$_2$(C$_2$O$_4$)$_5$]·8H$_2$O **2**, [C$_6$N$_2$H$_{14}$][Zn(C$_2$O$_4$)$_2$]·3H$_2$O **3**, [C$_4$N$_2$H$_{12}$]-[Zn$_2$(C$_2$O$_4$)$_3$]·4H$_2$O **4** and [C$_3$NH$_{10}$]$_2$[Zn$_2$(C$_2$O$_4$)$_3$]·3H$_2$O **5**, possessing novel structures have been synthesized by the reaction of amine oxalates with zinc ions, the amine oxalates themselves having been synthesized and characterized for the first time. The amine oxalates exhibit strong hydrogen bond interactions *via* O–H···O and N–H···O bonding. While there is no simple relation between the starting amine oxalate and the product zinc oxalates, what is significant is that zinc oxalates with one-, two- and three-dimensional architectures, in addition to the monomeric and dimeric oxalates, could be synthesized by using amine oxalates under mild conditions.

Compounds **1**–**3** are new members of the zinc oxalate family. Monomeric **1** and dimeric **2** can be considered to be zero-dimensional oxalate structures, in contrast to **3** which has a



**Fig. 7** (a) ORTEP plot of the zinc oxalate chain [C$_6$N$_2$H$_{14}$][Zn-(C$_2$O$_4$)$_2$]·3H$_2$O **3**. (b) Structure of the linear chain along the [100] direction. The oxalate chains are separated by the amine.

2.098(5) Å for Zn(2), and the remaining three have distances in the range 2.103(5)–2.123(5) for Zn(1) and 2.110(5)–2.126(5) Å for Zn(2) (Table 9). These distances formally correspond to the singly and doubly bonded oxygens bound to the carbon atoms respectively. The C–O bond distances are in the range 1.244(8)–1.264(8) Å (av. 1.254 Å) and the variations in their distances are also reflected in this bonding as well. The

**Table 10** Selected bond angles (°) for $[C_4N_2H_{12}][Zn_2(C_2O_4)_3]\cdot 4H_2O$ **4**

| | | | |
|---|---|---|---|
| O(1)–Zn(1)–O(2) | 79.8(2) | O(7)–Zn(2)–O(8) | 92.6(2) |
| O(1)–Zn(1)–O(3) | 95.1(2) | O(7)–Zn(2)–O(9) | 165.8(2) |
| O(2)–Zn(1)–O(3) | 166.5(2) | O(8)–Zn(2)–O(9) | 97.9(2) |
| O(1)–Zn(1)–O(4) | 92.0(2) | O(7)–Zn(2)–O(10) | 98.5(2) |
| O(2)–Zn(1)–O(4) | 99.5(2) | O(8)–Zn(2)–O(10) | 80.1(2) |
| O(3)–Zn(1)–O(4) | 93.1(2) | O(9)–Zn(2)–O(10) | 92.8(2) |
| O(1)–Zn(1)–O(5) | 167.8(2) | O(7)–Zn(2)–O(11) | 79.6(2) |
| O(2)–Zn(1)–O(5) | 93.2(2) | O(8)–Zn(2)–O(11) | 167.4(2) |
| O(3)–Zn(1)–O(5) | 93.8(2) | O(9)–Zn(2)–O(11) | 91.6(2) |
| O(4)–Zn(1)–O(5) | 79.1(2) | O(10)–Zn(2)–O(11) | 91.3(2) |
| O(1)–Zn(1)–O(6) | 97.8(2) | O(7)–Zn(2)–O(12) | 90.6(2) |
| O(2)–Zn(1)–O(6) | 88.9(2) | O(8)–Zn(2)–O(12) | 94.9(2) |
| O(3)–Zn(1)–O(6) | 79.4(2) | O(9)–Zn(2)–O(12) | 78.9(2) |
| O(4)–Zn(1)–O(6) | 168.1(2) | O(10)–Zn(2)–O(12) | 169.7(2) |
| O(5)–Zn(1)–O(6) | 92.1(2) | O(11)–Zn(2)–O(12) | 94.9(2) |
| C(1)[#1]–O(1)–Zn(1) | 113.3(5) | C(3)–O(7)–Zn(2) | 114.3(5) |
| C(2)[#1]–O(2)–Zn(1) | 113.1(4) | C(1)–O(8)–Zn(2) | 113.1(4) |
| C(3)–O(3)–Zn(1) | 113.4(5) | C(5)[#2]–O(9)–Zn(2) | 113.6(5) |
| C(4)–O(4)–Zn(1) | 113.8(5) | C(2)–O(10)–Zn(2) | 112.2(4) |
| C(5)–O(5)–Zn(1) | 113.2(5) | C(6)–O(11)–Zn(2) | 111.9(4) |
| C(6)–O(6)–Zn(1) | 112.5(4) | C(4)[#2]–O(12)–Zn(2) | 113.6(5) |
| O(1)[#3]–C(1)–O(8) | 126.0(7) | O(4)–C(4)–O(12)[#4] | 126.9(7) |
| O(10)–C(2)–O(2)[#3] | 125.8(7) | O(9)[#4]–C(5)–O(5) | 125.4(7) |
| O(7)–C(3)–O(3) | 126.4(7) | O(6)–C(6)–O(11) | 125.7(7) |

Symmetry transformations used to generate equivalent atoms: #1 $x - \frac{1}{2}$, $y + \frac{1}{2}$, $z$; #2 $x$, $y - 1$, $z$; #3 $x + \frac{1}{2}$, $y - \frac{1}{2}$, $z$; #4 $x$, $y + 1$, $z$.



**Fig. 9** (a) ORTEP plot of the zinc oxalate $[C_3NH_{10}]_2[Zn_2(C_2O_4)_3]\cdot 3H_2O$ **5** possessing three-dimensional structure. (b) Three-dimensional structure along the [010] direction showing 12-membered square channels. Dashed lines represent the various hydrogen bond interactions.



**Fig. 8** (a) ORTEP plot of the zinc oxalate layer $[C_4N_2H_{12}][Zn_2-(C_2O_4)_3]\cdot 4H_2O$ **4**. (b) The layer structure along the [001] direction showing the honeycomb architecture. The amine molecules sit in the middle of the 12-membered aperture. The water molecules are not shown for clarity.
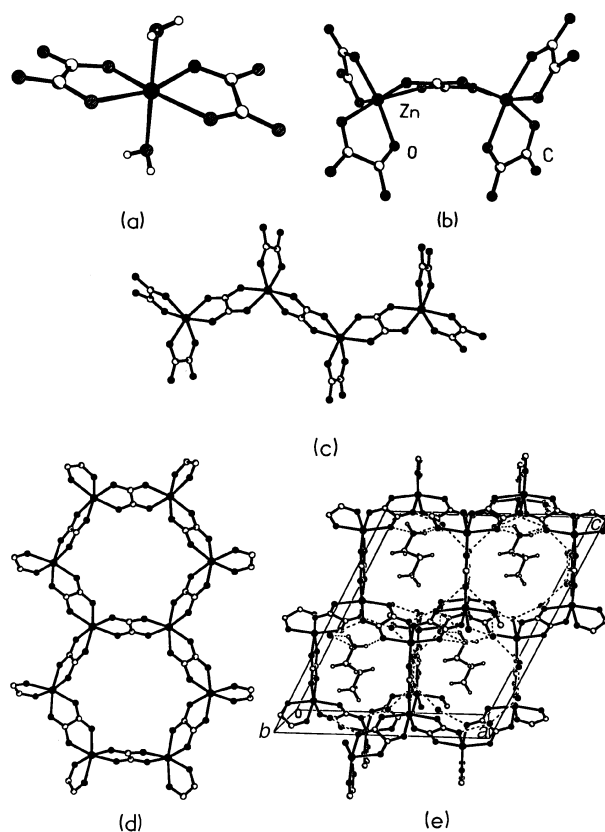


**Fig. 10** Various types of zinc oxalate structures obtained in the present study: (a) monomer, (b) dimer, (c) one-dimensional chain, (d) two-dimensional layer and (e) three-dimensional structure. Note the close relationships amongst them.
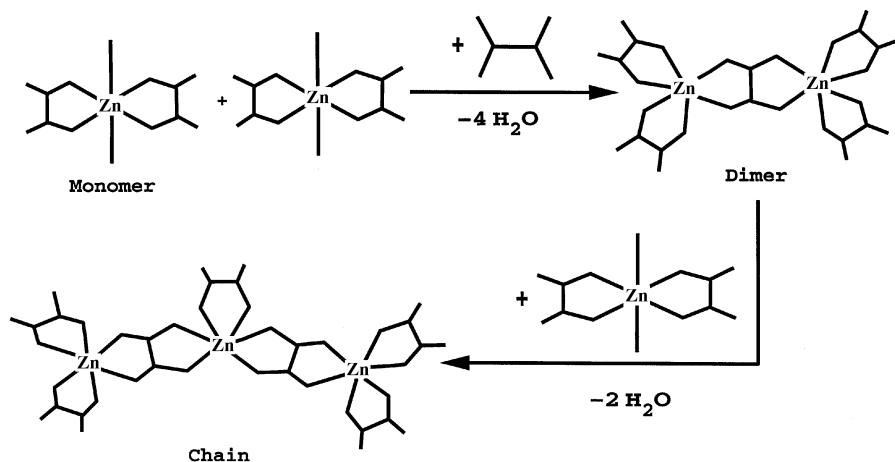
**Fig. 11** Schematic showing the formation of chain architecture from the monomer *via* hydrolysis and, condensation.

one-dimensional chain structure. In **1**, the connectivity between the Zn and the oxalate moieties forms a monomer, *i.e.* the Zn atoms have two free oxalate units and possess two terminal water molecules, and in **2** one oxalate joins two zinc centers with two free oxalates. In the case of **3** the connectivity forms a one-dimensional zinc oxalate chain and the Zn has one free oxalate group. These lower dimensional structures are stabilized by extensive hydrogen bonding. Unlike in **3**, the oxalates link up with Zn to form a honeycomb-like layer in **4**. The Zn atoms do not have any free oxalate groups in the layer structure. The number of free oxalate groups attached to the Zn probably governs the reactivity of the zinc oxalates. Thus, the monomer must be most reactive followed by the dimer, chain and the layer.

In Fig. 10 we present the various types of structures obtained by us to demonstrate the similarities and relationships. We can derive the structure of the dimer from that of the monomer, the chain from the dimer, and the layer from the chain. It is easy to see how the layers in **4** get connected by the oxalate units to form the three-dimensional structure of **5**. Just as the four-membered ring monomeric phosphate unit plays a crucial role in the building of framework phosphates,[2,17] it is possible that the monomeric and dimeric oxalates are involved in the construction of the extended oxalate framework structures.

## Conclusion

The present study shows that new types of zinc oxalates can be obtained under relatively mild conditions by the reaction of amine oxalates with zinc ions. Open-framework zinc phosphates are known to occur in four structure classes: monomers, chains, sheets and 3-D structures. We have obtained the oxalate analogues of all these four structures by the amine oxalate route, along with a dimer structure, which is unique to oxalates. Hydrothermal synthesis of the metal oxalates in the presence of amines is known to yield both two- and three-dimensional structures.[13] While it is possible that the zero- and one-dimensional structures are also formed under hydrothermal conditions, their isolation might be rendered difficult. This is because once the zero-dimensional structures are formed they may readily transform to higher dimensional structures. Such transformations from the zero-dimensional monomer to the linear chain structure are shown schematically in Fig. 11. The chains can readily condense to give the two-dimensional honeycomb structures. The reaction of amine oxalates with metal ions is likely to provide a better control of the reactant concentrations and the kinetics of the reaction, thereby enabling isolation of the initial building units such as the zero- and one-dimensional structures. The variety of structures obtained by us by the amine oxalate route suggests that it would be most worthwhile to investigate the reactions of various amine dicarb-

oxylates with metal ions. The hierarchy of oxalate structures formed here also suggests that there is likely to be a building up principle in the formation of open-framework oxalates just as in the phosphates,[2a] wherein low-dimensional structures transform to higher dimensional ones.

## References

1 A. K. Cheetham, G. Ferey and T. Loiseau, *Angew. Chem.*, *Int. Ed.*, 1999, **38**, 3268.
2 (*a*) C. N. R. Rao, S. Natarajan, A. Choudhury, S. Neeraj and A. A. Ayi, *Acc. Chem. Res.*, 2000, **34**, 80; (*b*) S. Neeraj, S. Natarajan and C. N. R. Rao, *J. Solid State Chem.*, 2000, **150**, 417; (*c*) R. I. Walton, F. Millange, A. Le Bail, T. Loiseau, C. Serre, D. O'Hare and G. Ferey, *Chem. Commun.*, 2000, 203.
3 Q. Gao, N. Guillou, M. Nogues, A. K. Cheetham and G. Ferey, *Chem. Mater.*, 1999, **11**, 2937; D. Riou and G. Ferey, *J. Mater. Chem.*, 1998, **8**, 2733; D. Riou, C. Serre and G. Ferey, *Microporous Mesoporous Mater.*, 1998, **23**, 23.
4 G. B. Hix, D. S. Wragg, I. Bull, R. E. Morris and P. A. Wright, *Chem. Commun.*, 1999, 2421; B. Zhang, D. M. Poojary and A. Clearfield, *Inorg. Chem.*, 1998, **37**, 1844; A. Clearfield, *Chem. Mater.*, 1998, **10**, 2733 and references therein.
5 F. Serpaggi and G. Ferey, *J. Mater. Chem.*, 1998, **8**, 2737; F. Serpaggi and G. Ferey, *J. Mater. Chem.*, 1998, **8**, 2749; C. Livage, C. Egger, M. Nogues and G. Ferey, *J. Mater. Chem.*, 1998, **8**, 2743; C. Livage, C. Egger and G. Ferey, *Chem. Mater.*, 1999, **11**, 1546 and references therein.
6 T. M. Reineke, M. Eddaoudi, M. O'Keeffe and O. M. Yaghi, *Angew. Chem.*, *Int. Ed.*, 1999, **38**, 2590; H. Li, M. Eddaoudi, T. L. Groy and O. M. Yaghi, *J. Am. Chem. Soc.*, 1998, **120**, 8571.
7 S. Ayyappan, A. K. Cheetham, S. Natarajan and C. N. R. Rao, *Chem. Mater.*, 1998, **10**, 3746; S. Natarajan, R. Vaidhyanathan, C. N. R. Rao, S. Ayyappan and A. K. Cheetham, *Chem. Mater.*, 1999, **11**, 1633.
8 S. Neeraj, S. Natarajan and C. N. R. Rao, *Angew. Chem.*, *Int. Ed.*, 1999, **38**, 3480; C. N. R. Rao, S. Natarajan and S. Neeraj, *J. Am. Chem. Soc.*, 2000, **122**, 2810.
9 G. M. Sheldrick, SADABS, Siemens Area Detector Absorption Correction Program, University of Göttingen, 1994.
10 SHELXS 86, Program for Crystal Structure Determination, University of Göttingen, 1986; G. M. Sheldrick, *Acta Crystallogr.*, *Sect. A*, 1990, **35**, 467.
11 G. M. Sheldrick, SHELXTL-PLUS, Program for Crystal Structure Solution and Refinement, University of Göttingen, 1993.
12 C. K. Johnson, ORTEP II, Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN, 1976.
13 R. Vaidhyanathan, S. Natarajan, A. K. Cheetham and C. N. R. Rao, *Chem. Mater.*, 1999, **11**, 3636.
14 R. Deyrieux, C. Bero and A. Penelous, *Bull. Soc. Chim. Fr.*, 1973, 25.
15 J. M. Thomas, R. H. Jones, J. Chen, R. Xu, A. M. Chippindale, S. Natarajan and A. K. Cheetham, *J. Chem. Soc.*, *Chem. Commun.*, 1992, 929.
16 A. Choudhury, S. Natarajan and C. N. R. Rao, *Chem. Mater.*, 1999, **11**, 2316.
17 S. Oliver, A. Kuperman and G. A. Ozin, *Angew. Chem.*, *Int. Ed.*, 1998, **37**, 46; S. Oliver, A. Kuperman, A. Lough and G. A. Ozin, *Chem. Mater.*, 1996, **8**, 2391.