DALTON

Synthesis and characterization of zinc(II) oxydiacetate (oda) complexes. Crystal structures of [{Zn(oda)·0.3H_2O}$_n$], [Zn(oda)(bipy)(H_2O)]·2.5H_2O and [Zn(oda)(phen)(H_2O)]·1.5H_2O (bipy = 2,2′-bipyridine, phen = 1,10-phenanthroline)

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Three novel zinc(II) oxydiacetate (oda) compounds [{Zn(oda)·0.3H_2O}$_n$] **1**, [Zn(oda)(bipy)(H_2O)]·2.5H_2O **2** (bipy = 2,2′-bipyridine) and [Zn(oda)(phen)(H_2O)]·1.5H_2O **3** (phen = 1,10-phenanthroline) have been synthesized and their structures determined by single-crystal X-ray diffraction methods. Compound **1** consists of polymeric sheets formed by ZnO_5 units bridged by carboxylate groups in *anti-syn* conformation along the *z* axis; **2** and **3** are mononuclear with the zinc atoms in distorted octahedral ZnN_2O_4 co-ordination geometries. Thermal decomposition of the compounds under an oxygen atmosphere affords ZnO at *ca.* 500 °C.

The study of the co-ordination chemistry of zinc(II) with carboxylate ligands to give complexes of different nuclearities is being actively pursued, prompted by the relevance of such complexes as structural and spectroscopic models in biological systems[1–6] and solid-state materials.[7,8]

Oxydiacetate (oda = $^{-}O_2CCH_2OCH_2CO_2^{-}$) is a versatile complexing agent having five potential oxygen-donor atoms. Crystallographic studies of oda complexes with cadmium(II),[9–11] calcium(II),[12] copper(II),[13–15] iron(III),[16] lanthanide[17] and actinide[18] metal ions have previously been reported and different types of structures with the ligand bonded in mono-, bi- and tri-dentate fashion have been observed. Our recent work on its complexing properties towards zirconium(IV)[19] and lanthanum(III)[20] has further highlighted its versatility for co-ordination to one or more metal centres in a variety of ways.

In this paper we report the synthesis, characterization and crystal structures of the novel polymeric zinc complex [{Zn(oda)·0.3H_2O}$_n$] **1** and of two mononuclear mixed-ligand complexes with bidentate nitrogen ligands [Zn(oda)(bipy)(H_2O)]·2.5H_2O **2** (bipy = 2,2′-bipyridine) and [Zn(oda)(phen)(H_2O)]·1.5H_2O **3** (phen = 1,10-phenanthroline).

Experimental

General

All commercially available reagents and chemicals were of analytical or reagent-grade purity and used as received. Water was purified by a Millipore Milli-Q system yielding 18 MΩ cm water. Elemental analyses (C, H, N, O) were performed at the Instituto de Quimica Fisica de los Materiales, Medio Ambiente y Energia with a Carlo Erba EA 1108 analyser. Zinc was analysed at the Analytical Division of the Department of Inorganic Chemistry on a Varian Pectron AA-5 spectrophotometer. Infrared spectra were recorded as KBr pellets or as mulls in Nujol supported between CsI discs with a Nicolet 510P FT-IR spectrophotometer, Raman spectra of single crystals on a Jarrel Ash 25-300 spectrophotometer equipped with a Coherent Radiation 52 G argon-ion laser. Thermogravimetric analyses were performed on a Mettler TG-50 thermal analyser under an oxygen atmosphere at a heating rate of 10 °C min^{-1}. Powder X-ray diffraction (XRD) data were collected using monochromated Cu-Kα radiation on a Phillips X'Pert diffractometer.

Syntheses

[{Zn(oda)·0.3H_2O}$_n$] 1. To a hot solution of oxydiacetic acid (2.0 g, 15 mmol) in water (200 cm^3) was added zinc acetate dihydrate (2.0 g, 10 mmol) in portions of 25 mg. The reaction mixture was stirred at 80 °C for 10 h. Colourless crystals of the product formed and were filtered off from the hot solution and dried in air. The product was recrystallized by dissolving in a very small portion in boiling water and allowing the solution to cool slowly. Colourless prismatic crystals suitable for X-ray analysis were filtered off and dried *in vacuo*. Yield: 1.7 g, 85% (Found: C, 23.55; H, 2.30; O, 42.15; Zn, 32.50. $C_4H_4O_5Zn$·0.3H_2O requires C, 23.65; H, 2.25; O, 41.80; Zn, 32.20%). IR (KBr disc, $\tilde{\nu}_{max}$/cm^{-1}): 3607m, 3441m, 2994w, 2959w, 2932w, 1670s, 1597vs, 1477m, 1447s, 1422s, 1358w, 1308s, 1244w, 1144s, 1046s, 937m, 745w, 718w, 625s, 606s and 540w. All Raman lines coincide with infrared bands within ± 10 cm^{-1}, and are not included. Compound **1** was similarly obtained when zinc carbonate hydroxide hydrate or zinc oxide was used in the preparation.

[Zn(oda)(bipy)(H_2O)]·2.5H_2O 2. To a solution of oxydiacetic acid (1.5 g, 11.25 mmol) and 2,2′-bipyridine (1.8 g, 11.25 mmol) in water (100 cm^3) was added zinc acetate dihydrate (1.0 g, 7.5 mmol) in portions of 25 mg. After being stirred for 6 h at 80 °C the resultant solution was cooled to room temperature, passed through a glass filter and concentrated to *ca.* 50 cm^3 on a rotary evaporator. After 24 h a white solid was collected, washed with small amounts of cold water and dried in air. It was recrystallized by dissolving a small portion in warm water and allowing the solution to cool slowly. After 2 d colourless prismatic crystals of compound **2** suitable for X-ray analysis were filtered off and dried *in vacuo*. Yield: 1.45 g, 75% (Found:

C, 40.15; H, 4.55; N, 6.70; Zn, 15.50. $C_{14}H_{14}N_2O_6Zn{\cdot}2.5H_2O$ requires C, 40.35; H, 4.55; N, 6.70; Zn, 15.70%). IR (KBr disc, $\tilde{\nu}_{max}/cm^{-1}$): 3382m, 3256m, 3115m, 2920m, 1655s, 1613vs, 1476m, 1462m, 1443m, 1423s, 1318m, 1306m, 1161m, 1146m, 1024m, 770s, 737m, 654m, 631m and 569w. Compound **2** was also obtained when zinc carbonate hydroxide hydrate or zinc oxide was used in the preparation.

[Zn(oda)(phen)(H_2O)]·1.5H_2O 3. 1,10-Phenanthroline (1.35 g, 7.5 mmol) was dissolved in water-ethanol (1 : 1, 100 cm^3) to which [{Zn(oda)]·0.3H_2O}$_n$] (1 g, 5 mmol) was added. The reaction mixture was stirred at room temperature for 4 h, concentrated to *ca.* 50 cm^3 on a rotary evaporator and passed through a glass filter. The filtrate was stored for a few days whereupon colourless prismatic crystals of compound **3** suitable for X-ray analysis were filtered off and dried *in vacuo.* Yield: 1.20 g, 55% (Found C, 45.55; H, 4.00; N, 6.65; Zn, 15.65. $C_{16}H_{14}N_2O_6Zn{\cdot}1.5H_2O$ requires C, 45.50; H, 4.00; N, 6.60; Zn, 15.50%). IR (KBr disc, $\tilde{\nu}_{max}/cm^{-1}$): 3493s, 3059s, 1613vs, 1518s, 1495w, 1428vs, 1356m, 1310m, 1302m, 1130vs, 1028m, 920w, 868m, 853s, 789w, 729vs, 644m, 608m and 567m.

Crystallography

Crystal data and details of measurements for compounds **1–3** are summarized in Table 1. All data were collected at 298 K on a Siemens R3m diffractometer equipped with a graphite monochromator and Mo-Kα (λ = 0.710 73 Å) radiation. The unit-cell parameters were determined by least-squares refinement of 25 reflections. Two standard reflections were monitored every 98, and showed no systematic changes. Intensities were corrected for Lorentz-polarization effects, and semiempirical absorption corrections (ψ scan) were also applied. The structures were solved by a combination of direct methods and Fourier difference syntheses. Refinement was done by full-matrix least squares on F^2, with anisotropic thermal parameters for the non-hydrogen atoms. The four methylene hydrogen atoms of the oda ligands were placed at calculated positions [*d*(C–H) = 0.95 Å]. All water hydrogen atoms that were located in Fourier difference maps were included in the last stages of refinement with a restrained geometry [*d*(O–H) = 0.85(3) and *d*(H–H) = 1.37(3) Å]. All the hydrogen atoms were allowed to ride with an isotropic thermal parameter 1.3 times the isotropic equivalent of the atom to which they were attached. Computer programs used in this study were SHELXTL PC[21a] and SHELXL 93.[21b]

The resolution of the structure of compound **1** showed a disordered water molecule split into two partially occupied sites. The best refinement was achieved with a fixed thermal parameter of 0.05 $Å^{-2}$ and a combined occupancy of 0.3. This is in accordance with the chemical analysis and TGA results.

The structure of **2** could not be solved in any of the space groups suggested by the symmetry of the intensity data, *viz.* orthorhombic *Cmma* and *Abm*2, the latter in two possible different orientations. However, with allowance for violations of systematic extinctions, the structure could easily be solved and satisfactorily refined in *Fdd*2. This suggested that the correct space group ought to be a subgroup of the latter, a situation only compatible with monoclinic *C*2 or *Cc* or triclinic *P*1. Attempts to refine in these lower-symmetry variants resulted in larger standard deviations and *R* factors, probably due to the expected very high correlations, as well as a very unfavourable data : parameters ratio. In view of these facts it was decided to report the final results in the reference frame of the super group *Fdd*2, where the best refinement was achieved. It must be considered, however, that they represent average values over at least four (or even perhaps eight) nearly equivalent moieties, and the fairness of the approximation can be ascertained by inspection of the rather low values obtained both for the *R* index as well as for the standard deviations for derived parameters.

Complex **3** belongs to the space group *P*2$_1$/*c* and each unit cell is composed of two very similar but crystallographically independent molecules (denoted a and b in Table 4). These appear to be related by a set of quasi-symmetry operations. When referred to a system given by the transformed axis (*A*, *B*, *C*) = (0 0 1, 1 0 0, 0 1 0) (*a*, *b*, *c*) they are compatible with a *Pbcn* symmetry. However, main departures from a regular orthorhombic *Pbcn* symmetry are the β value of 94.62(1)° and the translation component of the pseudo-screw axis parallel to *c* of 0.28 (0.72) instead of the required 0.50. The existence of this pseudo-symmetry does not impair the quality of the structural model refined in the space group *P*2$_1$/*c*, since no correlation coefficients larger than 0.50 were found.

Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/64.

Results and Discussion

The reaction of zinc(II) acetate, basic carbonate or oxide with oxydiacetic acid in water and subsequent work-up led to the isolation of polymeric [{Zn(oda)·0.3H_2O}$_n$] **1**. When the medium contained 2,2′-bipyridine the reaction under similar conditions afforded mononuclear [Zn(oda)(bipy)(H_2O)]·2.5H_2O **2**. Reaction of **1** with an excess of 1,10-phenanthroline (1 : 1.5) in water–ethanol (1 : 1) gave mononuclear [Zn(oda)-(phen)(H_2O)]·1.5H_2O **3**. Single-crystal X-ray analysis have been carried out on complexes **1–3**. The solid compounds are stable when kept in a dry atmosphere at room temperature.

Structure of [{Zn(oda)·0.3H_2O)}$_n$] 1

The crystal structure of compound **1** consists of two-dimensional polymer sheets perpendicular to the *z* axis. The extended sheets are built up by ZnO_5 units linked by the carboxylate groups of the oda ligands in *anti-syn* bridging form, Fig. 1. The closest Zn · · · Zn separation within the layers is 4.86 Å and the corresponding distance between neighbouring sheets is 5.20 Å. No water molecule is bound to the metal. They occupy isolated positions in the lattice and are not involved in hydrogen-bonding interactions between layers. The latter are only weakly linked by other hydrogen bonds involving the oda ligands [C(3)–H(3B) · · · O(2)].

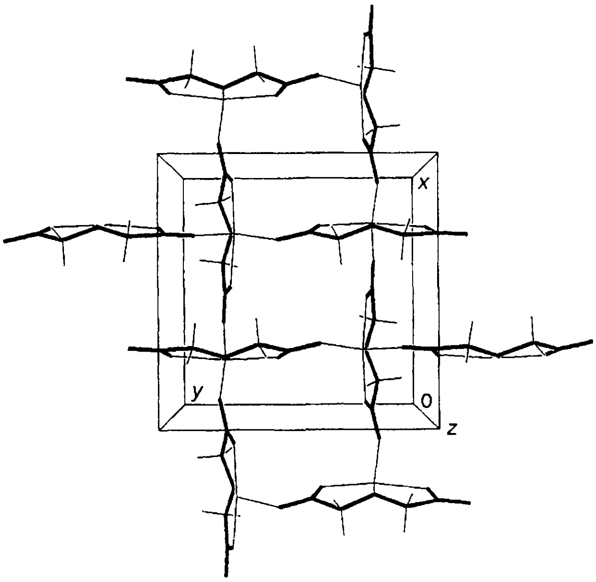

Fig. 1 Packing diagram of [{Zn(oda)·0.3H_2O}$_n$] **1** showing polymeric sheets perpendicular to the *z* axis. The water of crystallization is not shown

Table 1 Crystal data for [{Zn(oda)•0.3H$_2$O}$_n$] **1**, [Zn(oda)(bipy)(H$_2$O)]•2.5H$_2$O **2** and [Zn(oda)(phen)(H$_2$O)]•1.5H$_2$O **3***

	1	2	3
Formula	$(C_4H_{4.6}O_{5.3}Zn)_n$	$C_{14}H_{19}N_2O_{8.5}Zn$	$C_{16}H_{17}N_2O_{7.5}Zn$
M	202.85	416.68	422.68
Crystal system	Tetragonal	Orthorhombic	Monoclinic
Space group (number)	$I\bar{4}$ (no. 82)	$Fdd2$ (no. 43)	$P2_1/c$ (no. 14)
Crystal size/mm	0.55 × 0.35 × 0.12	0.40 × 0.38 × 0.35	0.48 × 0.26 × 0.18
a/Å	9.903(1)	13.686(2)	10.472(2)
b/Å		47.901(7)	24.009(4)
c/Å	13.520(2)	10.758(1)	14.060(3)
β/°			94.62(1)
U/Å^3	1325.9(3)	7052.7(16)	3523.5(12)
Z	4	16	8
D_c/g cm^{-3}	2.03	1.57	1.59
F(000)	808	3440	1736
μ/mm^{-1}	3.67	1.44	1.44
Maximum, minimum transmission	0.989, 0.667	0.770, 0.736	0.98, 0.653
θ Range/°	2.55–22.52	1.70–22.49	1.68–22.55
hkl Ranges	0–10, 0–10, −1 to 14	0–14, 0–51, 0–11	0–11, −1 to 25, −15 to 15
Reflections: total, independent, observed [$I > 2\sigma(I)$]	573, 558, 547	1251, 1231, 1001	5218, 4630, 3194
Data, restraints, parameters	558, 7, 96	1231, 13, 231	4608, 6, 479
Goodness of fit on F^2	1.230	1.000	1.054
$R1$, $wR2$ [$I > 2\sigma(I)$]	0.055, 0.134	0.036, 0.062	0.046, 0.098
(all data)	0.056, 0.135	0.058, 0.070	0.085, 0.257
Parameters a, b in weighting scheme	0.0231, 49.0377	0.0223, 0.0000	0.0476, 5.8036
Maximum difference peak, hole/e Å^{-3}	0.56, −0.48	0.33, −0.27	0.43, −0.44

* Details in common: $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; colourless prisms: $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{\frac{1}{2}}$; $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, $P = (F_o^2 + 2F_o^2)/3$.

Table 2 Selected bond distances (Å) and angles (°) with estimated standard deviations (e.s.d.s) for [{Zn(oda)•0.3H$_2$O}$_n$] **1***

Zn–O(4^{I})	1.962(11)	Zn–O(2^{II})	2.013(13)
Zn–O(5)	2.029(13)	Zn–O(1)	2.085(13)
Zn–O(3)	2.116(10)		
O(4^{I})–Zn–O(2^{II})	98.0(5)	O(4^{I})–Zn–O(5)	106.5(6)
O(2^{II})–Zn–O(5)	99.4(6)	O(4^{I})–Zn–O(1)	95.4(6)
O(2^{II})–Zn–O(1)	95.2(6)	O(5)–Zn–O(1)	151.5(5)
O(4^{I})–Zn–O(3)	130.1(7)	O(2^{II})–Zn–O(3)	131.3(7)
O(5)–Zn–O(3)	76.7(5)	O(1)–Zn–O(3)	75.3(5)

* Symmetry operations: I $-y + \frac{3}{2}, x + \frac{1}{2}; -z + \frac{1}{2}$; II $-y + \frac{1}{2}, x + \frac{1}{2}, -z + \frac{1}{2}$.

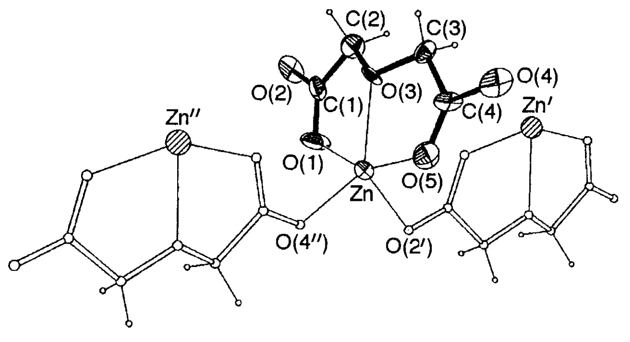

Fig. 2 Local environment for Zn in compound **1**

Each zinc atom is associated with an O$_5$ donor set; Fig. 2 shows the central co-ordination unit together with the atomic labelling system. Selected interatomic distances and angles are collected in Table 2. Each zinc atom has trigonal-bipyramidal geometry to a reasonably good approximation, comprising the two carboxylate oxygen atoms and the ether oxygen atom of the tridentate oda ligand [Zn–O(1) 2.085(13), Zn–O(5) 2.029(13), Zn–O(3) 2.116(10) Å], and two outer carboxylate oxygen atoms from two adjacent zinc polyhedra [Zn–O(2) 2.013(13), Zn–O(4) 1.962(11) Å]. Atoms O(1) and O(5) occupy the axial sites with respect to the triangular plane [O(5)–Zn–O(1) 151.5(5)°]. The ligand is completely deprotonated forming two five-membered chelate rings so that the resulting species is neutral. The two five-membered chelate rings with a common Zn–O bond for the oda ligand, Zn, O(1), C(1), C(2), O(3) and Zn, O(5), C(4), C(3), O(3), are planar, the dihedral angle being 10°. It appears that the shape of the Zn(oda) unit allows an efficient interlocking between neighbouring molecules. The distortions of the ZnO$_5$ core may be considered as the result of the geometrical constraints of the tridentate ligand. Other distances and angles within the ligand molecule are consistent with values reported for other metal oxydiacetato compounds. The mean Zn–O (carboxylate) bond length [2.057(28) Å] in **1** is comparable with values found in the literature [2.018(59) Å] for eight five-co-ordinate zinc carboxylates.[22] The Zn–O (ether) bond [2.116(10) Å] is slightly longer than the former, and demonstrates its comparative weakness. The co-ordination of a nearly planar oda ligand is also observed in the cadmium [10,11] and calcium [12] complexes [{[Cd(oda)]$_2$(H$_2$O)$_5$•2H$_2$O}$_n$], [{Cd(oda)}$_2$(H$_2$O)$_6$] and [Ca(oda)(H$_2$O)$_5$]•H$_2$O. The ligand adopts a *cis* co-ordination in related cadmium [9] and copper [13] complexes, [{Cd(oda)(H$_2$O)$_2$•H$_2$O}$_n$] and [{Cu(oda)•0.5H$_2$O}$_n$] with dihedral angles of 84 and 101.9°, respectively.

Compound **1** is the first example of a structurally characterized zinc oxydiacetate complex. Its structure differs substantially from those found in the cadmium oda complexes of different nuclearities with metal to ligand ratio 1 : 1. In these the cadmium atoms are surrounded by seven oxygen atoms forming pentagonal bipyramids with the apices occupied by water oxygen atoms. The ligands exhibit mono-, bi- and tridentate co-ordination modes. The different co-ordination environments in the zinc and cadmium complexes may be attributed to the increase in the metal-ion size; Zn^{2+} and Cd^{2+} differ in size by 0.21 Å (six-co-ordinate ionic radii)[23] which may have relevance to their different biological activities.

Structures of [Zn(oda)(bipy)(H$_2$O)]•2.5H$_2$O 2 and [Zn(oda)(phen)(H$_2$O)]•1.5H$_2$O 3

The structure of compound **2** is composed of discrete neutral units of [Zn(oda)(bipy)(H$_2$O)] and water molecules of crystallization. Fig. 3 shows the co-ordination environment of the zinc atom together with the atomic labelling scheme.

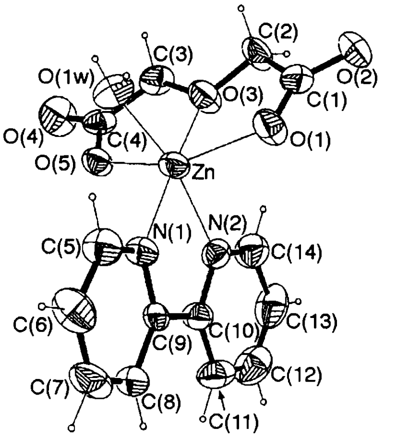

Fig. 3 Perspective view of [Zn(oda)(bipy)(H_2O)] with thermal ellipsoids at the 50% probability level

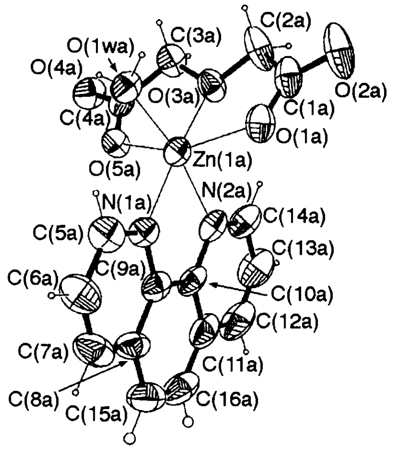

Fig. 4 Perspective view of [Zn(oda)(phen)(H_2O)] (molecule a) with thermal ellipsoids at the 50% probability level

Table 3 Selected bond distances (Å) and angles (°) with e.s.d.s for [Zn(oda)(bipy)(H_2O)]·2.5H_2O **2**

Zn–O(1)	2.054(6)	Zn–O(5)	2.084(5)
Zn–O(1w)	2.095(5)	Zn–N(1)	2.102(5)
Zn–N(2)	2.145(6)	Zn–O(3)	2.160(5)
O(1)–Zn–O(5)	149.0(2)	O(1)–Zn–O(1w)	94.8(2)
O(5)–Zn–O(1w)	85.3(2)	O(1)–Zn–N(1)	109.6(2)
O(5)–Zn–N(1)	101.3(2)	O(1w)–Zn–N(1)	90.8(2)
O(1)–Zn–N(2)	94.5(2)	O(5)–Zn–N(2)	91.5(2)
O(1w)–Zn–N(2)	166.8(2)	N(1)–Zn–N(2)	77.2(2)
O(1)–Zn–O(3)	74.7(2)	O(5)–Zn–O(3)	74.5(2)
O(1w)–Zn–O(3)	96.4(2)	N(1)–Zn–O(3)	171.3(2)
N(2)–Zn–O(3)	95.1(2)		

Table 4 Selected bond distances (Å) and angles (°) with e.s.d.s for [Zn(oda)(phen)(H_2O)]·1.5H_2O **3**

Zn(1a)–O(1a)	2.064(4)	Zn(1b)–O(1b)	2.089(4)
Zn(1a)–O(1wa)	2.080(4)	Zn(1b)–O(1wb)	2.071(4)
Zn(1a)–O(5a)	2.089(4)	Zn(1b)–O(5b)	2.094(4)
Zn(1a)–N(1a)	2.102(5)	Zn(1b)–N(1b)	2.128(5)
Zn(1a)–N(2a)	2.146(5)	Zn(1b)–N(2b)	2.146(5)
Zn(1a)–O(3a)	2.145(4)	Zn(1b)–O(3b)	2.149(4)
O(1a)–Zn(1a)–O(1wa)	91.4(2)	O(1b)–Zn(1b)–O(1wb)	89.5(2)
O(1a)–Zn(1a)–O(5a)	50.2(2)	O(1b)–Zn(1b)–O(5b)	149.4(2)
O(1wa)–Zn(1a)–O(5a)	90.2(2)	O(1wb)–Zn(1b)–O(5b)	93.8(2)
O(1a)–Zn(1a)–N(1a)	107.6(2)	O(1b)–Zn(1b)–N(1b)	118.2(2)
O(1wa)–Zn(1a)–N(1a)	92.2(2)	O(1wb)–Zn(1b)–N(1b)	90.3(2)
O(5a)–Zn(1a)–N(1a)	102.0(2)	O(5b)–Zn(1b)–N(1b)	92.2(2)
O(1wa)–Zn(1a)–O(3a)	96.4(2)	O(1wb)–Zn(1b)–O(3b)	96.5(2)
O(1a)–Zn(1a)–O(3a)	75.7(2)	O(1b)–Zn(1b)–O(3b)	75.3(2)
O(5a)–Zn(1a)–O(3a)	74.6(2)	O(5b)–Zn(1b)–O(3b)	74.12(14)
O(1a)–Zn(1a)–N(2a)	96.4(2)	O(1b)–Zn(1b)–N(2b)	89.1(2)
O(1wa)–Zn(1a)–N(2a)	169.0(2)	O(1wb)–Zn(1b)–N(2b)	165.8(2)
O(5a)–Zn(1a)–N(2a)	86.9(2)	O(5b)–Zn(1b)–N(2b)	94.5(2)
N(1a)–Zn(1a)–O(3a)	170.7(2)	N(1b)–Zn(1b)–O(3b)	165.1(2)
N(1a)–Zn(1a)–N(2a)	78.1(2)	N(1b)–Zn(1b)–N(2b)	78.0(2)
O(3a)–Zn(1a)–N(2a)	93.0(2)	N(2b)–Zn(1b)–O(3b)	96.8(2)

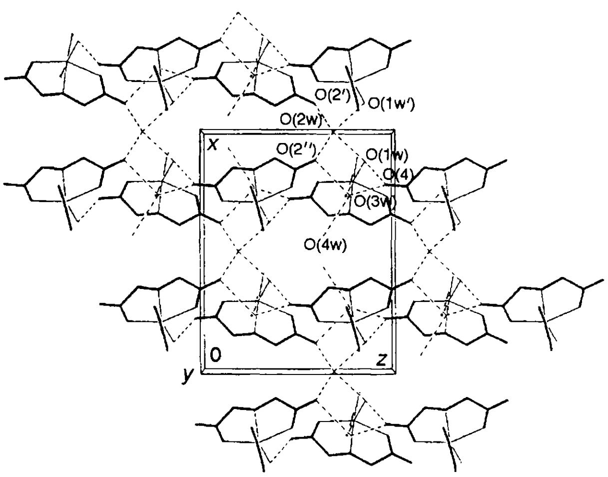

Fig. 5 Packing diagram for [Zn(oda)(bipy)(H_2O)]·2.5H_2O **2** along the *b* axis (bipy is represented schematically)

Selected interatomic distances and angles are given in Table 3. Complex **3** contains two neutral crystallographically independent molecules of [Zn(oda)(phen)(H_2O)] (denoted a and b) which differ only slightly in bond distances and angles and water molecules of crystallization. A perspective view of molecule a is shown in Fig. 4 together with the atomic labelling scheme. Selected bond lengths and angles for the two independent molecules are given in Table 4. Both compounds contain six-co-ordinated zinc atoms bonded to a tridentate oda, a bipy or phen and an aqua ligand in a similarly distorted octahedral arrangement. The ZnN_2O_4 co-ordination sphere is best described by two interpenetrating squares [O(1), O(3), O(5), N(1) and O(1w), O(3), N(2), N(1)] sharing the O(3)–N(1) diagonal and including the metal atom at the centre. The square planes are nearly perpendicular with dihedral angles in the fairly narrow range 87.8–89.7°. Atoms O(3) and N(1) occupy the axial positions, while O(1), O(1w), O(5), N(2) and Zn define a basal plane with large deviations from the least-squares planes (mean value 0.32; maximum 0.44 Å). The major source of distortion may be ascribed to the steric constraints of the oda and bipy or phen ligands. The five-membered chelate rings of the oda ligands are planar, with dihedral angles of 7.7° in **2** and 7.3 (molecule a) and 6.5° (b) in **3**. This situation is similar to that found in the copper[15] and iron[16] adducts [Cu(oda)(terpy)]·2H_2O (terpy = 2,2′:6′,2″-terpyridine) and [Fe(oda)(H_2O)$_2$X] (X = Cl or Br). In contrast, in the related copper[14] complex [Cu(oda)(bipy)(H_2O)]·4H_2O the oda ligand is in the *cis* conformation with a dihedral angle of 103.2°.

The Zn–O (carboxylate), Zn–O (aqua) and Zn–N (bipy) distances are comparable with literature values for octahedral geometry,[22] but the mean Zn–N (phen) in **3** [2.131(10) Å] is somewhat shorter than that reported for six-co-ordinate [Zn(S_2CNBu_2)$_2$(phen)] [2.218(1) Å].[24] The Zn–O (ether) bonds of 2.160(5) Å in **2** and 2.145(4) and 2.149(4) Å in **3** are slightly longer than the corresponding value in the five-co-ordinate complex **1** [2.116(10) Å]. The Zn–O (ether) distance

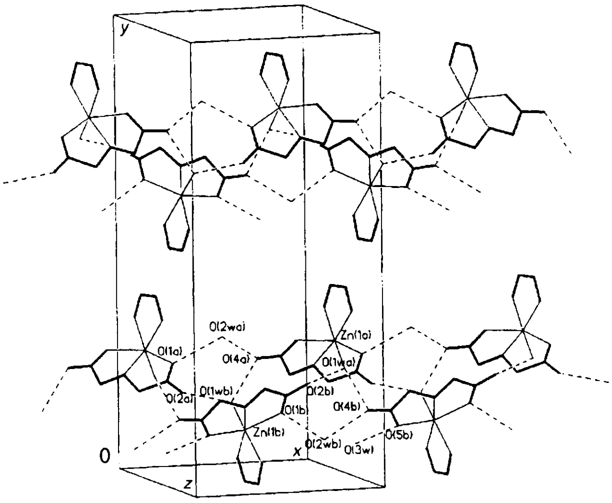

Fig. 6 Packing diagram for [Zn(oda)(phen)(H_2O)]·1.5H_2O **3** showing the chains running along the *a* axis (phen is represented schematically)

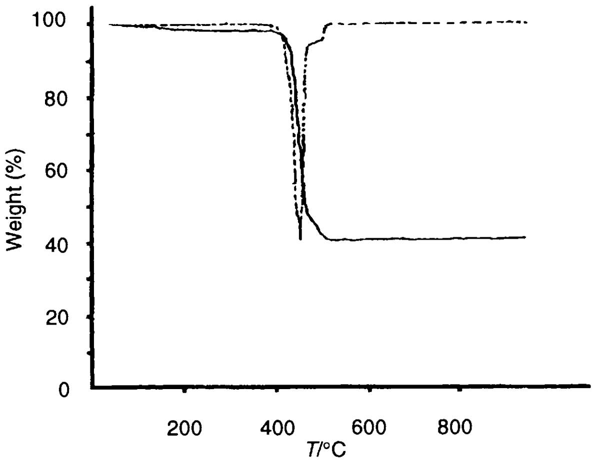

Fig. 7 The TGA diagram for [{Zn(oda)·0.3H_2O}$_n$] **1**. Theoretical values for weight percentages: 97%, **1** – 0.3H_2O; 41%, ZnO/**1**

reported for a four-co-ordinate species is 2.093(5) Å.[25] These results suggest that the Zn–O (ether) bond lengths should be shortened with decrease in co-ordination number. So far, very few crystal structures of zinc complexes with co-ordinating ether oxygen atoms have been reported to permit further comparison.

Hydrogen-bonding interactions by water molecules are very important in determining the packing of complexes **2** and **3** in the crystals and are illustrated for clarity in Figs. 5 and 6. In **2** the hydrogen bonds involving the co-ordinated and lattice water molecules and the oxygen atoms of the oda ligands give rise to layers parallel to the (010) planes. In complex **3** these hydrogen bonds give chains running along the crystallographic *a* axis. In addition, the layers in **2** and the chains in **3** are weakly interlinked by other hydrogen bonds involving the bipy and the phen ligands. A summary of bond distances and angles involving hydrogen bonding in complexes **1**–**3** is given in Table 5.

Vibrational properties

As a result of complex formation the strong IR absorption of oxydiacetic acid at 1734 cm^{-1} indicative of the acid carbonyl groups disappears and is replaced by very strong and broad bands centred at *ca.* 1600 cm^{-1} and strong and well defined bands at 1430 ± 10 cm^{-1}. The former correspond to the asymmetric vibrations of the RCO_2^- groups and the latter may be assigned to the symmetric vibrations of the RCO_2^- groups. The spectra of the complexes show many absorptions in the 3600–3200 and 1640–1610 cm^{-1} regions, assignable to co-ordinated and lattice water modes.[27] Besides these bands, the mixed-ligand complexes **2** and **3** show bands typical of co-ordinated 2,2′-bipyridine (770s and 737m cm^{-1})[28] and 1,10-phenanthroline (1518vs, 853s and 729vs cm^{-1}).[28,29]

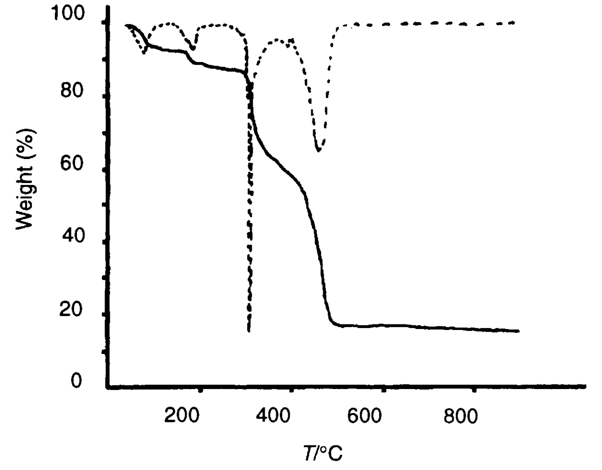

Fig. 8 The TGA diagram for [Zn(oda)(bipy)(H_2O)]·2.5H_2O **2**. Theoretical values for weight percentages: 89%, **2** – 2.5H_2O; 19%, ZnO/**2**

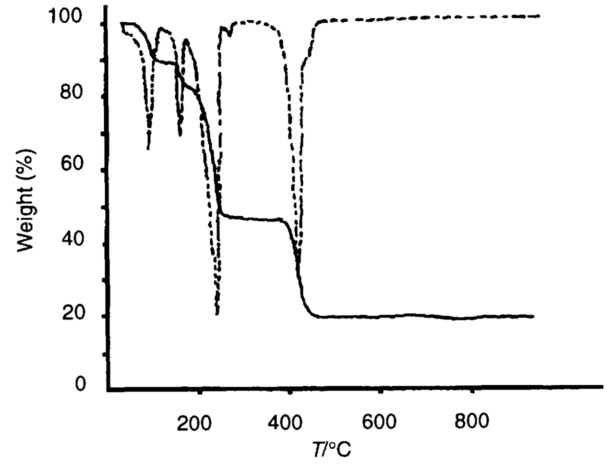

Fig. 9 The TGA diagram for [Zn(oda)(phen)(H_2O)]·1.5H_2O **3**. Theoretical values for weight percentages: 89%, **3** – 2.5H_2O; 47%, **3** – (2.5H_2O + phen); 19%, ZnO/**3**

The Δ values [$\nu_{asym}(CO_2^-) - \nu_{sym}(CO_2^-)$] in the range 200–150 cm^{-1} suggest that the co-ordinated carboxylate groups in the three compounds studied are probably bridging.[30] This is clearly the case for **1** whereas the carboxylate bridging in **2** and **3** may be regarded as 'pseudo-bridging' arrangements. Here the carboxylate oxygens not bonded to a metal centre are hydrogen bonded to the water ligands.

Further evidence for complex formation was obtained from the low-frequency spectra (400–200 cm^{-1}) where the metal-to-ligand sensitive modes are expected. Comparison of the spectra of the reactants with those of the complexes may provide an effective criterion for metal–ligand bonding. Complex **1** shows new broad and poorly structured bands at 255 and 233 cm^{-1} and complexes **2** and **3** at 243 and 213 cm^{-1}, respectively. Owing to their positions and intensity they may be broadly attributed to the prevailing contribution of the Zn–O modes in **1**, and of the Zn–O and Zn–N mixed modes in **2** and **3**, respectively.

Table 5 Hydrogen-bond distances (Å) and angles (°) related to compounds **1–3**[a]

Compound	X–H · · · Y	X–H	X · · · Y	H · · · Y	X–H · · · Y
1	C(3)–H(3b) · · · O(2^{I})	1.080	3.329(23)	2.429	139.97
2	O(1w)–H(1wb) · · · O(2w^{III})	0.938	2.660(8)	1.731	170.04
	O(1w)–H(1wb) · · · O(2w^{IV})	0.938	2.660(8)	1.731	170.04
	O(1w)–H(1wa) · · · O(2^{II})	0.938	2.688(8)	1.755	172.74
	O(2w)–H(2wa) · · · O(4^{V})	0.938	2.662(7)	1.765	159.15
	O(3w)–H(3wa) · · · O(2^{VI})	0.938	2.759(11)	1.863	159.08
	O(4w)–H(4wa) · · · O(3w)	0.938	2.773(10)	1.880	158.31
	O(3w)–H(3wb) · · · O(4^{VII})	0.938	2.911(11)	1.973	177.76
	C(8)–H(8a) · · · O(1^{VII})	1.080	3.283(9)	2.402	137.74
	C(12)–H(12a) · · · O(5^{VIII})	1.080	3.362(12)	2.457	140.57
3	O(1wb)–H(1wd) · · · O(2a^{XIV})	0.938	2.629(6)	1.704	167.98
	O(1wb)–H(1wc) · · · O(4a^{XII})	0.938	2.671(6)	1.740	171.84
	O(1wa)–H(1wb) · · · O(4b^{X})	0.938	2.691(6)	1.766	167.86
	O(1wa)–H(1wa) · · · O(2b^{IX})	0.938	2.668(6)	1.777	157.54
	C(3b)–H(3ba) · · · O(2a^{XV})	1.080	3.292(7)	2.221	170.93
	C(12a)–H(12a) · · · O(2wb^{XII})	1.080	3.335(10)	2.266	169.96
	C(7a)–H(7aa) · · · O(5a^{XI})	1.080	3.167(8)	2.296	136.40
	C(12b)–H(12b) · · · O(2wa^{X})	1.080	3.401(10)	2.358	161.85
	O(2wa) · · · O(1a^{XIV})	—[b]	2.924(6)	—	—
	O(2wa) · · · O(4a^{XIII})	—[b]	2.872(7)	—	—
	O(2wb) · · · O(1b^{XVI})	—[b]	2.844(7)	—	—
	O(2wb) · · · O(4b^{XVII})	—[b]	2.816(7)	—	—
	O(3w) · · · O(5b^{XVII})	—[b]	2.845(8)	—	—

[a] Values involving H atoms normalized following Ref. 26. Symmetry operations: I $y, -x+1, -z+1$; II $-x+\frac{1}{2}, -y, z+\frac{1}{2}$; III $x+\frac{1}{4}, -y+\frac{1}{4}, z-\frac{3}{4}$; IV $-x-\frac{1}{4}, y-\frac{1}{4}, z-\frac{3}{4}$; V $x-\frac{3}{4}, -y+\frac{1}{4}, z+\frac{1}{4}$; VI $x-\frac{1}{4}, -y+\frac{1}{4}, z+\frac{3}{4}$; VII $x-\frac{1}{4}, -y+\frac{1}{4}, z-\frac{1}{4}$; VIII $x+\frac{1}{4}, -y+\frac{1}{4}, z+\frac{1}{4}$; IX $-x+1, y+\frac{1}{2}, -z+\frac{3}{2}$; X $-x, y+\frac{1}{2}, -z+\frac{3}{2}$; XI $-x+1, -y+1, -z+1$; XII $x, -y+\frac{1}{2}, z+\frac{1}{2}$; XIII $-x+1, y-\frac{1}{2}, -z+\frac{3}{2}$; XIV $-x, y-\frac{1}{2}, -z+\frac{3}{2}$; XV $-x, -y+1, -z+2$; XVI $x, -y+\frac{1}{2}, z-\frac{1}{2}$; XVII $x+1, -y+\frac{1}{2}, z-\frac{1}{2}$. [b] Hydrogen atom could not be found.

Thermal properties

The thermal properties of compounds **1–3** were investigated by thermal gravimetric analysis (TGA) carried out under an oxygen atmosphere. The TGA diagrams are given in Figs. 7–9, where the dashed lines are the first derivatives of the weight-loss curves. The final products of these degradations were identified by XRD.[31] No attempts were made to identify the intermediate products during these thermolyses.

Compound **1** lost about 2.7% weight at 150 °C which corresponds to the removal of the water molecules in the lattice. The final weight loss occurring in the temperature range 400–500 °C corresponds to complete combustion to ZnO. The thermogravimetric curve of **2** contains four steps. The first two steps from 50 to 200 °C may be attributed to loss of the water molecules of crystallization. Further degradation of the intermediate product to ZnO occurs in two overlapping steps involving removal of aqua and bipy ligands and combustion reactions and is finished at about 500 °C. Compound **3** also decomposes in four steps. The first weight loss corresponds to simultaneous loss of the water of crystallization and co-ordination. Subsequent degradation occurs in two overlapping steps at 140–280 °C approximately and corresponds to removal of the phen molecule. The residual mass at 280 °C is consistent with the empirical formula Zn(oda). The fourth step consists of complete combustion of the latter leading to the final residue ZnO at about 460 °C.

Conclusion

The oda anion is an effective bridging unit between the hard zinc(II) metal ions creating polymeric $[Zn(oda)]_n$ layers containing ZnO_5 cores. The use of bipy or phen as blocking ligands prevents such polymerization by co-ordinatively saturating the zinc(II) centres, resulting in the formation of mononuclear ZnN_2O_4 cores. In addition we have established that compounds **1–3** are stable inorganic precursors to zinc oxide.

Acknowledgements

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