

The one-dimensional chain polymer of aqua(tyrosinato)zinc(II)

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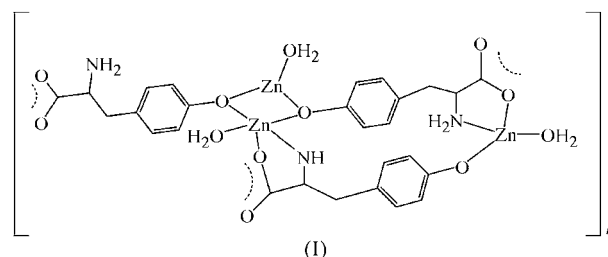
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In the title compound, *catena*-poly[[aqua(zinc(II))]- μ_3 -tyrosinato], $[\text{Zn}(\text{C}_9\text{H}_7\text{NO}_3)(\text{H}_2\text{O})]_n$, each Zn atom has a distorted square-pyramidal geometry comprised of three O atoms and one N atom from three tyrosinate (tyr) ligands, and one aqua ligand. Two inversion-related Zn^{2+} ions are bridged by two O atoms from the phenolate groups of two tyr ligands to form a centrosymmetric dimeric unit, which can be described as a planar Zn_2O_2 four-membered ring. These repeating dimeric units are arranged along the *c* axis to give a one-dimensional chain coordination polymer, in which the tyr ligand adopts an unusual chelating/bridging coordination mode.

Comment

The rational design and assembly of metal-organic coordination frameworks have received much attention in recent years, owing to their intriguing structural topologies and potential or practical applications in the areas of catalysis, magnetism, gas storage, nonlinear optics, electronics and others (Bernhard *et al.*, 2003; Lin *et al.*, 1998; Sun *et al.*, 2005; Zhu *et al.*, 2005; Wu *et al.*, 2007). A number of fascinating metal-organic coordination polymers are known to be constructed by the combination of symmetrical or asymmetrical bridging ligands as the 'spacer', and metal ions or a metal cluster as the 'node'. Carboxylate-containing ligands acting as the 'spacer' have attracted much attention because of the diversity of the binding modes of the carboxylate group (Zhu *et al.*, 2005; Shi *et al.*, 2005). The tyrosinate (tyr) ligand, with a carboxylate group, and its derivatives are good spacers because they often behave similarly to isonicotinic acid, acting as a chelating/bridging ligand *via* the N and O atoms. Diverse topologies can be achieved with the tyr ligand (Ayyappan *et al.*, 2001; Lu & Babb, 2001; Lu *et al.*, 2003). However, the reported complexes of the tyr ligand are generally mononuclear (Emseis *et al.*, 2004; Harrowfield *et al.*, 1983; Majumder *et al.*, 2002), with only two coordination polymers being described in the literature, namely $[\text{Cu}(\text{H-tyr})_2]_n$ and $\{[\text{Cu}_2(\text{H-tyr})_2(4,4'\text{-bipy})\cdot 2\text{H}_2\text{O}]\cdot 2\text{ClO}_4\}_n$ (4,4'-bipy is 4,4'-bipyridine; Weng *et al.*, 2002). Interestingly, the phenolate O atom in these

two complexes is uncoordinated. In order to learn more about the coordination mode of the tyr ligand, we have chosen the zinc(II) salts as the node. The zinc coordination polymers exhibit rich structural diversity because of the variable coordination behaviours of the d^{10} metal ion Zn^{II} . We have successfully obtained the one-dimensional zinc(II) polymer *catena*-poly[[aqua(zinc(II))]- μ_3 -tyrosinato], (I), containing the unusual coordinating phenolate O atom, *via* synthesis under solvothermal conditions.



The crystal structure of (I) consists of neutral *catena*-poly[[aqua(zinc(II))]- μ_3 -tyrosinato] one-dimensional chains (see Fig. 1). Two Zn^{2+} ions are linked by two O atoms of the phenolate groups giving rise to a dimeric unit, which displays an inversion centre located in the middle of the Zn_2O_2 cores. The $\text{Zn1}-\text{Zn1}^{\text{ii}}$ intramolecular separation is 3.1981 (9) Å [symmetry code: (ii) $-x, -y, -z + 2$]. Each zinc(II) centre in the dimeric unit is coordinated to three O atoms and one N atom from three tyr ligands, and one aqua ligand in a distorted square-pyramidal coordination geometry. These dimeric units are connected by tyr ligands to form a one-dimensional chain coordination polymer propagating along the crystallographic *c* axis. The Zn–O bonds, varying from 2.006 (3) to 2.075 (3) Å,

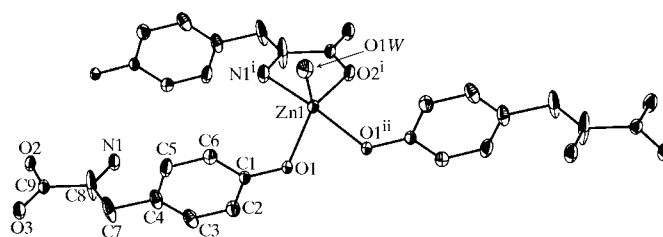


Figure 1

The coordination environment of the Zn^{II} ion. The ellipsoids are shown at the 30% probability level and all H atoms have been omitted for clarity. [Symmetry codes: (i) $-x + 1, -y, -z + 1$; (ii) $-x, -y, -z + 2$.]

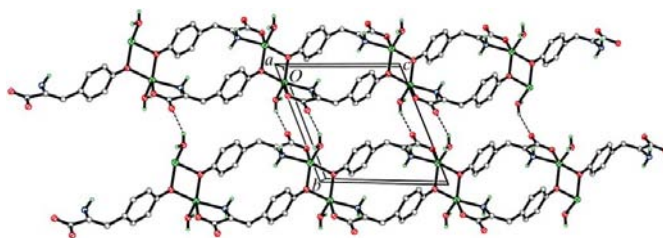
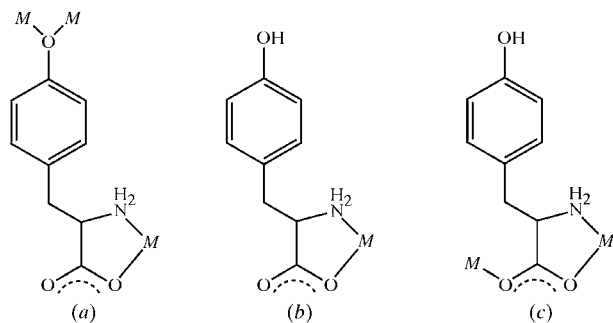


Figure 2

Part of the crystal structure of (I), showing the formation of a (100) sheet constructed from O–H...O hydrogen bonds. H atoms bonded to C atoms have been omitted for clarity.

are in good agreement with the corresponding bond lengths in $[\text{Zn}_2(\text{Rসালা})_2(\text{H}_2\text{O})_2]\cdot 2\text{H}_2\text{O}$ [Rসালা is *N*-(2-hydroxy-5-*R*-benzyl)-*L*-alanine; Vittal & Yang, 2002], $[\text{Zn}(\text{BTZ})_2]_2$ [BTZ is 2-(2-hydroxyphenyl)benzothiazolate; Yu *et al.*, 2003], $\text{Zn}_2(\text{H}_2\text{SB})_2\cdot 3\text{H}_2\text{O}\cdot \text{Me}_2\text{CO}$ [H_2SB is *N,N'*-bis(2,5-dihydroxybenzylidene)-1,4-diaminobutane; Matalobos *et al.*, 2004] and $[\text{Zn}_2(\text{C}_{22}\text{H}_{20}\text{N}_4\text{O}_2)(\text{H}_2\text{O})_2](\text{ClO}_4)_2$ (Huang *et al.*, 2001). The $\text{Zn1}-\text{N1}^{\text{i}}$ bond length is 2.154 (4) Å [symmetry code: (i) $-x + 1, -y, -z + 1$], comparable with those reported for $[\text{M}(\text{en})_3]_2\text{Sn}_2\text{S}_6$ [en is ethylenediamine; 2.14 (3)–2.23 (1) Å; Jia *et al.*, 2004] and $[\text{Zn}(\text{en})_3]_4\text{In}_{16}(\text{Te}_2)_4(\text{Te}_3)\text{Te}_{22}$ [2.12 (3)–2.32 (3) Å; Chen *et al.*, 2001]. The hydrogen bonds between the O atoms of the carboxylate groups and the H atoms of the water molecules $[\text{O1W}-\text{H}\cdots\text{O3}^{\text{iv}}$, hydrogen bonds, symmetry code: (iv) $x - 1, y - 1, z + 1$] link the adjacent chains to form a two-dimensional sheet within the (100) plane (Fig. 2); the chains further interact *via* the formation of $\text{N1}-\text{H}\cdots\text{O3}^{\text{iii}}$ and $\text{O1W}-\text{H}\cdots\text{O2}^{\text{v}}$ hydrogen bonds [symmetry code: (iii) $x - 1, y, z$; (v) $-x + 2, -y, -z + 1$] resulting in a three-dimensional hydrogen-bonding network structure.

The possible coordination modes of tyr^{2-} and H-tyr^- are shown in the scheme below. The usual chelating mode is (b), as exemplified by $[\text{Co}(\text{en})(2\text{-N-eth-en})(\text{H-tyr})](\text{ClO}_4)_2\cdot 2\text{H}_2\text{O}$ (2-*N-eth-en* is 2-acetaldimino-1-ethanamine; Harrowfield *et al.*, 1983), $[\text{Cu}(\text{hista})(\text{H-tyr})(\text{ClO}_4)]$ (hista is histamine; Yamachi *et al.*, 1989), $[\text{Ru}(2,2'\text{-bpy})_2(\text{H-tyr})]\text{ClO}_4$ (Majumder *et al.*, 2002), $[\text{Cu}(\text{H-tyr})(\text{phen})\text{ClO}_4]\cdot 2.5\text{H}_2\text{O}$ (phen is 1,10-phenanthroline; Sugimori *et al.*, 1997) and $[\text{Co}(\text{picchxn})(\text{H-tyr})]\text{Br}_2\cdot 3.5\text{H}_2\text{O}$ (picchxn is *N,N'*-di-2-picolyl-1,2-diaminocyclohexane; Emseis *et al.*, 2004). The bridging mode (c) is less common, with only two examples found, $[\text{Cu}(\text{H-tyr})_2]_n$ and $\{[\text{Cu}_2(\text{H-tyr})_2(4,4\text{-bipy})(\text{H}_2\text{O})_2](\text{ClO}_4)_2\}_n$ (Weng *et al.*, 2002). The most remarkable feature of (I) is the unusual coordination mode (a) of the tyr^{2-} ligand. The tyr ligand adopts a chelating/bridging coordination mode, in which its amino and carboxylate groups bind a Zn^{2+} ion to form a chelating five-membered ring. In addition, the phenol OH group bridges another two Zn^{2+} ions, resulting in the formation of a planar Zn_2O_2 four-membered ring which contributes to the distortion of the square-pyramidal geometry around the metal ion.



Experimental

Single crystals of the title complex suitable for X-ray crystallographic analysis were obtained by solvothermal treatment of $\text{Zn}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ (0.2 mmol), $\text{H}_2\text{-tyr}$ (0.1 mmol), CH_3OH (5 ml) and NH_3 (0.2 ml). The

reagents were placed in a thick Pyrex tube (*ca* 20 cm long). The tube was cooled with liquid N_2 and the air evacuated. The sealed tube was heated at 413 K for 10 d to yield yellow block-shaped crystals in about 25% yield.

Crystal data

$[\text{Zn}(\text{C}_9\text{H}_7\text{NO}_3)(\text{H}_2\text{O})]$	$\gamma = 78.440 (3)^\circ$
$M_r = 260.54$	$V = 484.81 (17) \text{ \AA}^3$
Triclinic, $P\bar{1}$	$Z = 2$
$a = 5.8633 (12) \text{ \AA}$	Mo $K\alpha$ radiation
$b = 9.681 (2) \text{ \AA}$	$\mu = 2.52 \text{ mm}^{-1}$
$c = 9.772 (2) \text{ \AA}$	$T = 273 (2) \text{ K}$
$\alpha = 65.336 (3)^\circ$	$0.14 \times 0.10 \times 0.06 \text{ mm}$
$\beta = 75.334 (3)^\circ$	

Data collection

Rigaku Mercury diffractometer	3474 measured reflections
Absorption correction: multi-scan (Jacobson, 1998)	1841 independent reflections
$T_{\text{min}} = 0.719, T_{\text{max}} = 0.863$	1645 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.020$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.044$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.109$	$\Delta\rho_{\text{max}} = 0.61 \text{ e \AA}^{-3}$
$S = 1.06$	$\Delta\rho_{\text{min}} = -0.51 \text{ e \AA}^{-3}$
1841 reflections	
144 parameters	
2 restraints	

Table 1

Selected geometric parameters (Å, °).

$\text{Zn1}-\text{O1}$	2.006 (3)	$\text{Zn1}-\text{O1}^{\text{ii}}$	2.075 (3)
$\text{Zn1}-\text{O2}^{\text{i}}$	2.032 (3)	$\text{Zn1}-\text{N1}^{\text{i}}$	2.154 (4)
$\text{Zn1}-\text{O1W}$	2.041 (4)		
$\text{O1}-\text{Zn1}-\text{O2}^{\text{i}}$	128.61 (13)	$\text{O1W}-\text{Zn1}-\text{O1}^{\text{ii}}$	103.19 (14)
$\text{O1}-\text{Zn1}-\text{O1W}$	121.18 (15)	$\text{O1}-\text{Zn1}-\text{N1}^{\text{i}}$	95.71 (14)
$\text{O2}^{\text{i}}-\text{Zn1}-\text{O1W}$	110.19 (15)	$\text{O2}^{\text{i}}-\text{Zn1}-\text{N1}^{\text{i}}$	79.16 (13)
$\text{O1}-\text{Zn1}-\text{O1}^{\text{ii}}$	76.84 (12)	$\text{O1W}-\text{Zn1}-\text{N1}^{\text{i}}$	96.35 (16)
$\text{O2}^{\text{i}}-\text{Zn1}-\text{O1}^{\text{ii}}$	91.12 (12)	$\text{O1}^{\text{ii}}-\text{Zn1}-\text{N1}^{\text{i}}$	160.22 (15)

Symmetry codes: (i) $-x + 1, -y, -z + 1$; (ii) $-x, -y, -z + 2$.

Table 2

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{N1}-\text{H1B}\cdots\text{O3}^{\text{iii}}$	0.90	2.18	3.056 (6)	165
$\text{O1W}-\text{H1W1}\cdots\text{O3}^{\text{iv}}$	0.86 (5)	2.15 (5)	2.950 (6)	156 (6)
$\text{O1W}-\text{H1W2}\cdots\text{O2}^{\text{v}}$	0.85 (5)	2.21 (5)	3.051 (6)	175 (9)

Symmetry codes: (iii) $x - 1, y, z$; (iv) $x - 1, y - 1, z + 1$; (v) $-x + 2, -y, -z + 1$.

H atoms on C and N atoms were positioned geometrically and were allowed to ride on their parent atoms, with $\text{C}-\text{H} = 0.93 \text{ \AA}$ and $\text{N}-\text{H} = 0.90 \text{ \AA}$, and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ or $1.2U_{\text{eq}}(\text{N})$. H atoms on O atoms were located in a difference map and refined. High displacement parameters suggest some disorder in the C8 atom of the tyr ligand, but this could not be resolved.

Data collection: *CrystalClear* (Molecular Structure Corporation & Rigaku, 2001); cell refinement: *CrystalClear*; data reduction: *CrystalStructure* (Rigaku/MS, 2004); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SF3044). Services for accessing these data are described at the back of the journal.

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