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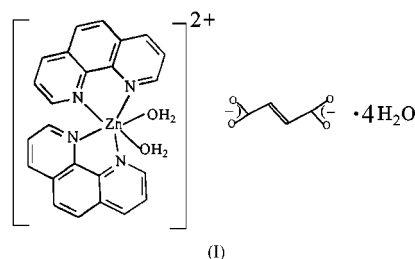
## Key indicators

Single-crystal X-ray study  
 $T = 293$  K  
Mean  $\sigma(\text{C}-\text{C}) = 0.003$  Å  
 $R$  factor = 0.026  
 $wR$  factor = 0.082  
Data-to-parameter ratio = 14.9For details of how these key indicators were  
automatically derived from the article, see  
<http://journals.iucr.org/e>.An aquazinc(II) complex of 1,10-phenanthroline  
with fumarate counter-ions

In the title compound, diaquabis(1,10-phenanthroline- $\kappa^2N,N'$ )zinc(II) fumarate tetrahydrate,  $[\text{Zn}(\text{phen})_2(\text{H}_2\text{O})_2]L \cdot 4\text{H}_2\text{O}$ , where phen is 1,10-phenanthroline ( $\text{C}_{12}\text{H}_8\text{N}_2$ ) and  $L^{2-} = \text{fumarate}$  ( $\text{C}_4\text{H}_2\text{O}_4$ ), the zinc(II) cation is six-coordinated by two water molecules and four N atoms from two phen molecules. Each of the two independent  $L^{2-}$  anions is located about an inversion centre and does not coordinate to zinc(II) cations, acting rather as a counter-ion. The water molecules and  $L^{2-}$  anions are linked through a complicated hydrogen-bonding network to form a three-dimensional structure.

## Comment

Interest in the synthesis and characterization of complexes with mixed ligands (Cariati *et al.*, 1983) arises from the advantage that their structural and chemical properties may be significantly varied depending on the choice of ligands (Robl, 1992). On the basis of reported X-ray structures, the anion derived from fumaric acid has been found to be a versatile ligand, and the coordination mode can be tailored by introducing different neutral ligands to the complex (Young *et al.*, 1998). In this paper, we present the preparation and crystal structure of an aquazinc complex of 1,10-phenanthroline containing fumarate as a non-coordinating species, (I).



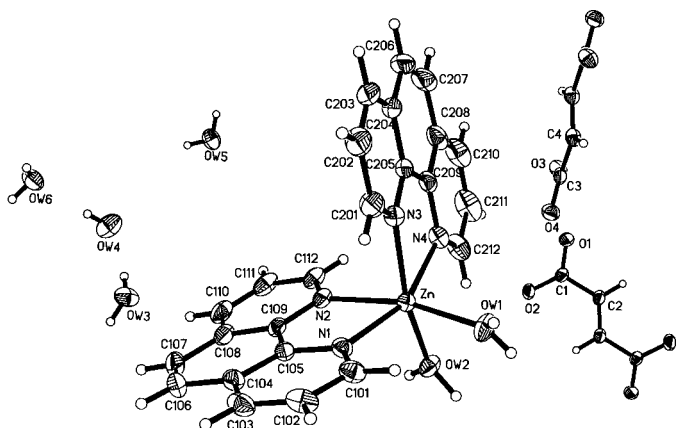
The structure determination of (I) shows the coordination environment of the zinc(II) cation to be defined by two water molecules and four N atoms, derived from two phen molecules (Fig. 1 and Table 1). Charge balance is provided by two independent fumarate anions, each located about a centre of inversion. Finally, there are four non-coordinating water molecules in the asymmetric unit.

The presence of an uncoordinated carboxylate group for the  $L^{2-}$  anion is somewhat unexpected, because the carboxylate group is generally thought of as being a better coordinating group than water for zinc(II). In the related compound  $[\text{Cu}_2(\text{C}_4\text{H}_2\text{O}_4)(\text{C}_{14}\text{H}_{33}\text{N}_3)_2](\text{ClO}_4)_2$  (Charpin *et al.*, 1987), the carboxylate O atoms coordinate to copper(II) to form a dimer. The average Zn—N distance of 2.1866 (16) Å is

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**Figure 1**

View of the extended asymmetric unit of (I), with the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level (Sheldrick, 1990).

near to that of  $[\text{Zn}L'_{1.5}(\text{H}_2\text{O})_2](\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ , where  $L'$  is 1,1'-(1,4-butanediyl)bis(imidazole) (Ma *et al.*, 2000).

In (I), the  $L^{2-}$  anions and water molecules are linked through hydrogen bonds to form a complicated three-dimensional structure (Table 2). It is noted that there are 12 H atoms available for hydrogen bonding in the asymmetric unit and each of these participates in such interactions. The water molecules play a role as both acceptors and donors, while the carboxylate O atoms act only as acceptors.

## Experimental

A mixture of fumaric acid (0.116 g, 1 mmol) and ZnO (0.081 g, 1 mmol) in water (10 ml) was stirred at room temperature. Then 1,10-phenanthroline (0.198 g, 1 mmol) was added to the solution. Colourless crystals of (I) were obtained after several days; yield: 68% (based on Zn). Analysis calculated for  $\text{C}_{28}\text{H}_{30}\text{N}_4\text{O}_{10}\text{Zn}$ : C 51.86, H 4.63, N 8.64%; found: C 51.79, H 4.44, N 8.77%.

### Crystal data

$[\text{Zn}(\text{C}_{12}\text{H}_8\text{N}_2)_2(\text{H}_2\text{O})_2] \cdot (\text{C}_4\text{H}_2\text{O}_4) \cdot 4\text{H}_2\text{O}$   
 $M_r = 647.93$   
 Triclinic,  $P\bar{1}$   
 $a = 10.481(2) \text{ \AA}$   
 $b = 10.597(2) \text{ \AA}$   
 $c = 13.568(3) \text{ \AA}$   
 $\alpha = 97.12(3)^\circ$   
 $\beta = 93.55(3)^\circ$   
 $\gamma = 105.38(3)^\circ$   
 $V = 1434.7(6) \text{ \AA}^3$

$Z = 2$   
 $D_x = 1.500 \text{ Mg m}^{-3}$   
 Mo  $K\alpha$  radiation  
 Cell parameters from 7123 reflections  
 $\theta = 1.5\text{--}27.5^\circ$   
 $\mu = 0.92 \text{ mm}^{-1}$   
 $T = 293(2) \text{ K}$   
 Block, colourless  
 $0.50 \times 0.32 \times 0.10 \text{ mm}$

### Data collection

Rigaku R-AXIS-RAPID diffractometer  
 $\omega$  scans  
 Absorption correction: multi-scan (ABSCOR; Higashi, 1995)  
 $T_{\min} = 0.767$ ,  $T_{\max} = 0.912$   
 13836 measured reflections

6500 independent reflections  
 5423 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.021$   
 $\theta_{\text{max}} = 27.5^\circ$   
 $h = -13 \rightarrow 13$   
 $k = -13 \rightarrow 13$   
 $l = -17 \rightarrow 17$

### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.026$   
 $wR(F^2) = 0.082$   
 $S = 1.06$   
 6500 reflections  
 436 parameters

H atoms treated by a mixture of independent and constrained refinement  
 $w = 1/[\sigma^2(F_o^2) + (0.052P)^2]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} = 0.001$   
 $\Delta\rho_{\text{max}} = 0.51 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\text{min}} = -0.36 \text{ e \AA}^{-3}$

**Table 1**

Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ).

Zn—OW1	2.0742 (14)	Zn—N2	2.2323 (15)
Zn—OW2	2.0493 (13)	Zn—N3	2.2065 (15)
Zn—N1	2.1522 (16)	Zn—N4	2.1554 (17)
OW1—Zn—OW2	85.59 (6)	OW2—Zn—N4	91.16 (6)
OW1—Zn—N1	95.04 (6)	N1—Zn—N2	76.09 (6)
OW1—Zn—N2	166.71 (5)	N1—Zn—N3	89.43 (6)
OW1—Zn—N3	93.27 (6)	N1—Zn—N4	157.97 (6)
OW1—Zn—N4	102.31 (6)	N2—Zn—N3	96.48 (6)
OW2—Zn—N1	103.74 (6)	N2—Zn—N4	88.81 (6)
OW2—Zn—N2	86.94 (6)	N3—Zn—N4	76.23 (6)
OW2—Zn—N3	166.82 (5)		

**Table 2**

Hydrogen-bonding geometry ( $\text{\AA}$ ,  $^\circ$ ).

$D\text{--}H\cdots A$	$D\text{--}H$	$H\cdots A$	$D\cdots A$	$D\text{--}H\cdots A$
OW1—H11 $\cdots$ OW3 <sup>i</sup>	0.92 (2)	1.79 (2)	2.702 (2)	174 (2)
OW3—H32 $\cdots$ O2 <sup>ii</sup>	0.90 (2)	1.84 (2)	2.736 (2)	178 (2)
OW5—H51 $\cdots$ OW6 <sup>iii</sup>	0.88 (2)	2.04 (2)	2.898 (2)	165 (2)
OW4—H41 $\cdots$ O4 <sup>iv</sup>	0.85 (3)	1.93 (3)	2.770 (2)	172 (3)
OW5—H52 $\cdots$ O3 <sup>v</sup>	0.84 (3)	1.99 (3)	2.817 (2)	170 (2)
OW6—H61 $\cdots$ O1 <sup>v</sup>	0.89 (3)	1.92 (3)	2.796 (2)	169 (3)
OW1—H12 $\cdots$ O2	0.87 (3)	1.87 (3)	2.7399 (19)	177 (3)
OW2—H22 $\cdots$ O1	0.92 (2)	1.78 (2)	2.6877 (18)	172 (2)
OW2—H21 $\cdots$ O3	0.86 (2)	1.76 (2)	2.6202 (19)	175 (2)
OW3—H31 $\cdots$ OW4	0.85 (2)	1.90 (2)	2.739 (3)	166 (2)
OW4—H42 $\cdots$ OW6	0.80 (3)	2.02 (3)	2.826 (3)	177 (3)
OW6—H62 $\cdots$ OW5 <sup>vi</sup>	0.90 (3)	1.92 (3)	2.810 (2)	171 (3)

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

All H atoms on C atoms were generated geometrically and refined in the riding-model approximation, with  $C\text{--}H = 0.93 \text{ \AA}$  and  $U_{\text{iso}}(H) = 1.2U_{\text{eq}}(C)$ . The H atoms of water molecules were located from difference Fourier map and were refined with restrained O—H distances of 0.90 (1)  $\text{\AA}$ .

Data collection: *PROCESS-AUTO* (Rigaku, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *PROCESS-AUTO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL-Plus* (Sheldrick, 1990); software used to prepare material for publication: *SHELXTL-Plus*.

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