

**( $\mu$ -Perfluorosebacato- $\kappa^2$ O:O')bis[aquabis(1,10-phenanthroline- $\kappa^2$ N,N')]zinc(II)] perfluorosebacate bis[triaqua(perfluorosebacato- $\kappa$ O)(1,10-phenanthroline- $\kappa^2$ N,N')]zinc(II)] 3.32-hydrate****Kani Ibrahim,<sup>a</sup> Onur Şahin,<sup>b</sup>  
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Büyükgüngör<sup>b\*</sup>**<sup>a</sup>Department of Chemistry, Anadolu University, TR-26470 Eskişehir, Turkey, and <sup>b</sup>Department of Physics, Ondokuz Mayıs University, TR-55139 Samsun, Turkey

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The asymmetric unit of the title compound,  $[\text{Zn}_2\{\text{O}_2\text{C}(\text{CF}_2)_8\text{CO}_2\}(\text{C}_{12}\text{H}_8\text{N}_2)_4(\text{H}_2\text{O})_2](\text{C}_{10}\text{F}_{16}\text{O}_4) \cdot [\text{Zn}\{\text{O}_2\text{C}(\text{CF}_2)_8\text{CO}_2\}(\text{C}_{12}\text{H}_8\text{N}_2)(\text{H}_2\text{O})_3] \cdot 3.32\text{H}_2\text{O}$ , contains a neutral mononuclear  $[\text{ZnL}(\text{phen})(\text{H}_2\text{O})_3]$  complex (phen is 1,10-phenanthroline and *L* is perfluorosebacate), one half each of a centrosymmetric  $[\text{Zn}_2\text{L}(\text{phen})_4(\text{H}_2\text{O})_2]^{2+}$  binuclear complex and an uncoordinated centrosymmetric *L* ligand, and 1.66 water molecules of solvation. The  $\text{Zn}^{\text{II}}$  atoms in both the mononuclear and the binuclear complexes are six-coordinated in a distorted octahedral geometry.

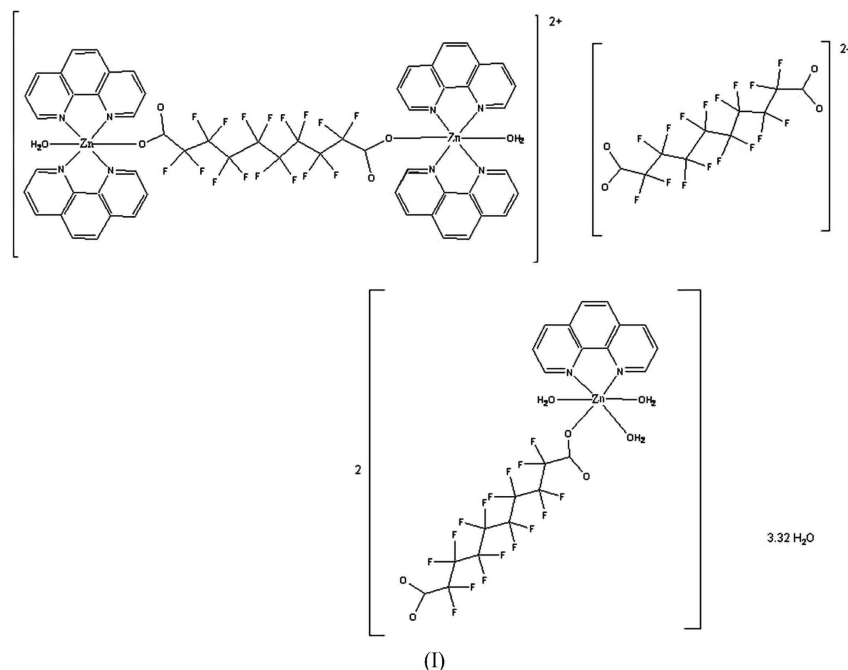
**Key indicators**

Single-crystal X-ray study  
 $T = 100\text{ K}$   
 Mean  $\sigma(\text{C}-\text{C}) = 0.004\text{ \AA}$   
 Disorder in solvent or counterion  
 $R$  factor = 0.045  
 $wR$  factor = 0.122  
 Data-to-parameter ratio = 14.7

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

**Comment**

Polynuclear  $d^{10}$  metal complexes are very attractive in that they not only exhibit intriguing structures but also show photoluminescent properties. As a  $d^{10}$  metal ion,  $\text{Zn}^{\text{II}}$  in particular is studied for the construction of coordination polymers and networks (Erxleben, 2003). The spherical  $d^{10}$  configuration is associated with a flexible coordination environment, so the geometries of zinc complexes can vary from tetrahedral through trigonal-bipyramidal to octahedral, and severe distortions of the ideal polyhedron easily occur. Transition metal complexes with dicarboxylates as bridging ligands

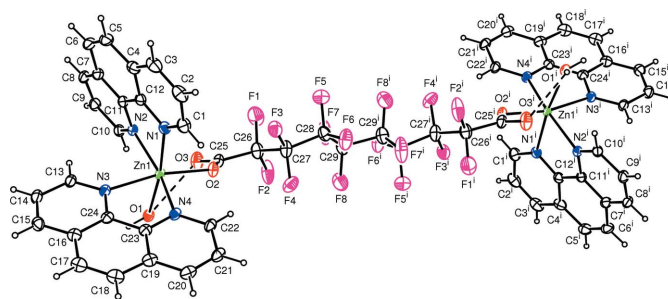


of supramolecular networks (Ye *et al.*, 2005; McCann *et al.*, 1997; Geraghty *et al.*, 1998; Zheng, Lin & Kong, 2003; Zheng, Lin & Chen, 2003; Devereux *et al.*, 1999). The coordination chemistry of saturated linear  $\alpha,\omega$ -dicarboxylate anions  $[\text{O}_2\text{C}(\text{CH}_2)_n\text{CO}_2]^{2-}$  ( $n = 1-8$ ) has not been developed and, indeed, structural information for this class of complex is relatively scarce, since it involves the formation of insoluble polymeric materials, which can be difficult to characterize and almost impossible to crystallize. Devereux *et al.* (1999, 2000) showed that the introduction of a second competing ligand, such as 1,10-phenanthroline (phen) or 2,2 bipyridine, lowers the dimensionality of the structures, since their chelation to the metal ion leaves fewer sites for dicarboxylic acid coordination. Mixed phen and long-chain  $\alpha,\omega$ -dicarboxylate ligand complexes are very rare and no published data have been found in the literature on the X-ray analysis of multinuclear  $\text{Zn}^{\text{II}}$  complexes with perfluorosebacic acid. We report here the crystal structure of the title compound, (I).

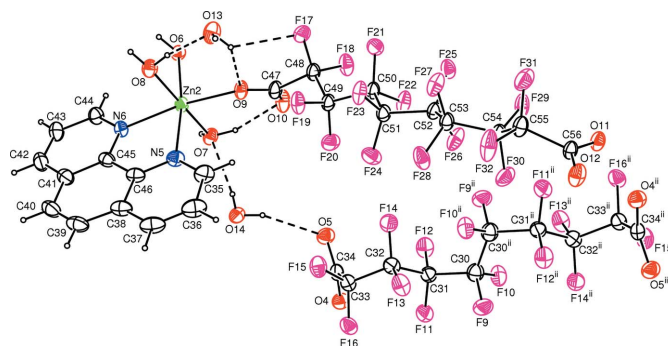
The asymmetric unit of (I) contains one half of a centrosymmetric  $[\text{Zn}_2\text{L}(\text{phen})_4(\text{H}_2\text{O})_2]^{2+}$  binuclear complex cation (Fig. 1), a neutral mononuclear  $[\text{ZnL}(\text{phen})(\text{H}_2\text{O})_3]$  complex (Fig. 2), one half of an uncoordinated centrosymmetric perfluorosebacate ligand and 1.66 water molecules of solvation (Fig. 2), where  $\text{H}_2\text{L}$  is  $\text{HO}_2\text{C}(\text{CF}_2)_8\text{CO}_2\text{H}$  and phen is 1,10-phenanthroline. Selected bond lengths and angles are listed in Table 1.

Each  $\text{Zn}^{\text{II}}$  atom of the binuclear complex cation has a distorted octahedral coordination geometry, defined by four N atoms from two chelating phen ligands and an O atom from the carboxylate group of a bridging perfluorosebacate ligand and the O atom of a water molecule. The observed distortion from octahedral geometry is caused by the small bite angles of the chelating phen ligands (Table 1). Around the central  $\text{Zn}^{\text{II}}$  atom, both chelating phen planes are oriented nearly perpendicular to each other [dihedral angle  $85.38(10)^\circ$ ]. The  $\text{N1}-\text{Zn1}-\text{O1}$  angle exhibits less deviation from linearity compared with the other *trans* angles. The  $\text{Zn1}-\text{O1}$  distance is slightly longer than the  $\text{Zn1}-\text{O2}$  distance. All  $\text{Zn}-\text{N}$  bond distances are comparable with those observed in similar compounds (Zhang *et al.*, 2003; Yin *et al.*, 2004; Guo *et al.*, 2004; Viossat *et al.*, 2005). An intramolecular  $\text{C}-\text{H}\cdots\pi$  interaction and an  $\text{OW}-\text{H}\cdots\text{O}$  hydrogen bond (Table 2) are observed in the complex cation.

In the neutral mononuclear  $[\text{ZnL}(\text{phen})(\text{H}_2\text{O})_3]$  complex, the  $\text{Zn}^{\text{II}}$  atom is six-coordinated in a distorted octahedral geometry by two N atoms from a chelating phen ligand, three O atoms from three water molecules and one O atom from a deprotonated perfluorosebacate ligand. The perfluorosebacate ligand is coordinated to the metal atom in monodentate fashion. The bite angle of the phen ligand is  $77.75(9)^\circ$  and the *cis* angles lie in the range  $86.88(9)-96.25(9)^\circ$ . The  $\text{N6}-\text{Zn2}-\text{O9}$  *trans* angle exhibits the largest deviation from linearity.  $\text{Zn}-\text{O}$  distances lie in the range  $2.0587(18)-2.144(2)$  Å. Intramolecular  $\text{O}-\text{H}\cdots\text{O}$  hydrogen bonds involving the coordinated water molecules are observed in the mononuclear complex (Table 2).



**Figure 1**  
The structure of the  $[\text{Zn}_2\text{L}(\text{phen})_4(\text{H}_2\text{O})_2]^{2+}$  complex, showing 50% probability displacement ellipsoids and the atomic numbering. Hydrogen bonds are shown as dashed lines. [Symmetry code: (i)  $1-x, 2-y, 1-z$ .]



**Figure 2**  
The structures of the  $[\text{ZnL}(\text{phen})(\text{H}_2\text{O})_3]$  and  $\text{C}_{10}\text{F}_{16}\text{O}_4^{2-}$  units, showing 50% probability displacement ellipsoids and the atomic numbering. Hydrogen bonds are shown as dashed lines. [Symmetry code: (ii)  $1-x, 1-y, 1-z$ .]

The free perfluorosebacate anion lies between the two zinc(II) complexes and it is linked to them *via* strong  $\text{O}-\text{H}\cdots\text{O}$  hydrogen bonds involving the coordinated water molecules (Table 2).

The crystal packing of (I) is stabilized by a complicated network of  $\text{O}-\text{H}\cdots\text{O}$  and  $\text{O}-\text{H}\cdots\text{F}$  hydrogen bonds. In addition, a  $\pi-\pi$  stacking interaction is observed between adjacent phen ligands. The  $\text{Cg}2\cdots\text{Cg}3^{\text{iii}}$  and  $\text{Cg}3\cdots\text{Cg}3^{\text{iv}}$  distances are  $3.459(2)$  and  $3.411(2)$  Å, respectively, where  $\text{Cg}2$  and  $\text{Cg}3$  are centroids of the central  $\text{C}4-\text{C}7/\text{C}11/\text{C}12$  and  $\text{C}39-\text{C}41/\text{C}45/\text{C}46$  benzene rings [symmetry codes: (iii)  $x, y, -1+z$ ; (iv)  $1-x, 2-y, 2-z$ ]. The  $\pi-\pi$  interactions are similar to those in the known analogues of Mn, Cu, Zn and Co complexes, with characteristic interplanar distances between the rings of  $\sim 3.6$  Å (Geraghty *et al.*, 1999; Zheng & Kong, 2004; Zheng & Ying, 2005).

## Experimental

$\text{Na}_2\text{CO}_3$  (0.5 ml, 1 mol) was added to a stirred solution of  $\text{Zn}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$  (121.4 mg, 0.408 mmol) in  $\text{H}_2\text{O}$  (10 ml). The resultant precipitate was separated by filtration, washed several times with distilled water and finally added to a stirred solution of phenanthroline monohydrate (80.78 mg, 0.408 mmol) and perfluorosebacic acid (200 mg, 0.408 mmol) dissolved in EtOH and  $\text{H}_2\text{O}$  (1:1 *v/v*, 20 ml). The mixture was stirred for *ca* 2 h and the solution was allowed to stand at room temperature for 2 d to obtain colourless crystals of (I) (m.p. 500 K).

Crystal data

[Zn<sub>2</sub>(C<sub>10</sub>F<sub>16</sub>O<sub>4</sub>)(C<sub>12</sub>H<sub>8</sub>N<sub>2</sub>)<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>]-  
(C<sub>10</sub>F<sub>16</sub>O<sub>4</sub>)-[Zn(C<sub>10</sub>F<sub>16</sub>O<sub>4</sub>)-  
(C<sub>12</sub>H<sub>8</sub>N<sub>2</sub>)(H<sub>2</sub>O)<sub>3</sub>].3.32H<sub>2</sub>O  
M<sub>r</sub> = 3499.05  
Triclinic, P1̄  
a = 13.505 (2) Å  
b = 15.271 (2) Å  
c = 17.332 (3) Å  
α = 70.556 (12)°  
β = 81.673 (13)°  
γ = 70.530 (11)°  
V = 3175.6 (9) Å<sup>3</sup>  
Z = 1  
D<sub>x</sub> = 1.830 Mg m<sup>-3</sup>  
Mo Kα radiation  
μ = 0.92 mm<sup>-1</sup>  
T = 100 K  
Prism, colourless  
0.54 × 0.35 × 0.23 mm

Data collection

Stoe IPDS II diffractometer  
ω scans  
Absorption correction: integration  
(X-RED32; Stoe & Cie, 2002)  
T<sub>min</sub> = 0.686, T<sub>max</sub> = 0.809  
46049 measured reflections  
15080 independent reflections  
12163 reflections with I > 2σ(I)  
R<sub>int</sub> = 0.061  
θ<sub>max</sub> = 27.9°

Refinement

Refinement on F<sup>2</sup>  
R[F<sup>2</sup> > 2σ(F<sup>2</sup>)] = 0.045  
wR(F<sup>2</sup>) = 0.122  
S = 0.99  
15080 reflections  
1028 parameters  
H atoms treated by a mixture of  
independent and constrained  
refinement  
w = 1/[σ<sup>2</sup>(F<sub>o</sub><sup>2</sup>) + (0.0623P)<sup>2</sup>  
+ 3.9061P]  
where P = (F<sub>o</sub><sup>2</sup> + 2F<sub>c</sub><sup>2</sup>)/3  
(Δ/σ)<sub>max</sub> = 0.003  
Δρ<sub>max</sub> = 1.40 e Å<sup>-3</sup>  
Δρ<sub>min</sub> = -0.78 e Å<sup>-3</sup>

Table 1

Selected geometric parameters (Å, °).

N1–Zn1	2.197 (2)	O1–Zn1	2.1532 (19)
N2–Zn1	2.126 (2)	O2–Zn1	2.040 (2)
N3–Zn1	2.206 (2)	O6–Zn2	2.0587 (18)
N4–Zn1	2.138 (2)	O7–Zn2	2.144 (2)
N5–Zn2	2.136 (2)	O8–Zn2	2.113 (2)
N6–Zn2	2.168 (2)	O9–Zn2	2.0980 (18)
O2–Zn1–N2	103.70 (8)	O6–Zn2–O9	95.59 (8)
O2–Zn1–N4	92.33 (9)	O6–Zn2–O8	87.90 (8)
N2–Zn1–N4	160.24 (9)	O9–Zn2–O8	91.13 (8)
O2–Zn1–O1	91.47 (8)	O6–Zn2–N5	171.75 (9)
N2–Zn1–O1	97.71 (8)	O9–Zn2–N5	90.90 (8)
N4–Zn1–O1	93.28 (8)	O8–Zn2–N5	86.88 (9)
O2–Zn1–N1	94.92 (9)	O6–Zn2–O7	88.76 (8)
N2–Zn1–N1	77.40 (8)	O9–Zn2–O7	90.83 (8)
N4–Zn1–N1	89.95 (8)	O8–Zn2–O7	176.28 (7)
O1–Zn1–N1	172.71 (8)	N5–Zn2–O7	96.25 (9)
O2–Zn1–N3	167.92 (8)	O6–Zn2–N6	95.67 (8)
N2–Zn1–N3	88.03 (8)	O9–Zn2–N6	168.64 (8)
N4–Zn1–N3	76.81 (8)	O8–Zn2–N6	87.75 (8)
O1–Zn1–N3	84.00 (8)	N5–Zn2–N6	77.75 (9)
N1–Zn1–N3	90.39 (8)	O7–Zn2–N6	90.95 (8)

Table 2

Hydrogen-bond geometry (Å, °).

Cg1 is the centroid of the N1/C7–C11 ring.

D–H...A	D–H	H...A	D...A	D–H...A
O1–H1A...O11 <sup>i</sup>	0.82 (2)	2.13 (3)	2.833 (3)	143 (3)
O1–H1A...O3	0.82 (2)	2.55 (3)	3.003 (3)	116 (3)
O1–H1A...F29 <sup>i</sup>	0.82 (2)	2.54 (3)	3.133 (2)	130 (3)
O1–H1B...O4 <sup>ii</sup>	0.83 (2)	2.01 (2)	2.834 (3)	168 (4)
O6–H6A...O4 <sup>iii</sup>	0.82 (2)	1.87 (2)	2.661 (3)	162 (4)
O6–H6B...O11 <sup>iv</sup>	0.82 (2)	1.90 (2)	2.706 (3)	168 (4)
O7–H7A...O10	0.84 (2)	1.96 (3)	2.706 (3)	148 (4)
O7–H7B...O5 <sup>iii</sup>	0.83 (2)	1.95 (2)	2.776 (3)	176 (4)

D–H...A	D–H	H...A	D...A	D–H...A
O8–H8A...O13	0.83 (2)	1.88 (2)	2.698 (3)	171 (4)
O8–H8B...O12 <sup>iv</sup>	0.82 (2)	1.93 (2)	2.724 (3)	163 (4)
O13–H13A...O3 <sup>v</sup>	0.82 (2)	1.99 (2)	2.806 (3)	170 (4)
O13–H13B...O9	0.82 (2)	2.29 (3)	2.991 (3)	143 (4)
O13–H13B...F17	0.82 (2)	2.50 (3)	3.151 (3)	137 (4)
O14–H14A...O7	0.83 (2)	2.12 (3)	2.930 (4)	163 (6)
O14–H14B...O5	0.82 (2)	2.17 (3)	2.955 (4)	159 (6)
C13–H13...Cg1	0.93	2.84	3.613 (3)	142

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

One of the uncoordinated water molecules is disordered, with a partial occupancy factor of 0.658 (9). The water H atoms were located in a difference map and refined with an O–H distance restraint of 0.83 (2) Å and with U<sub>iso</sub>(H) = 1.5U<sub>eq</sub>(O). C-bound H atoms were refined using the riding-model approximation, with C–H = 0.93 Å and U<sub>iso</sub>(H) = 1.2U<sub>eq</sub>(C). The structure contains a solvent-accessible void of volume 45 Å<sup>3</sup> around (0 0.5 0), but there is no evidence of any solvent molecule, as the modelling of the electron density using PLATON (Spek, 2003) showed no electron density in the void space. The highest peak in the final difference map is located 1.20 Å from atom F6 and the deepest hole 0.59 Å from F1.

Data collection: X-AREA (Stoe & Cie, 2002); cell refinement: X-AREA; data reduction: X-RED32 (Stoe & Cie, 2002); program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: ORTEP-3 for Windows (Farrugia, 1997); software used to prepare material for publication: WinGX (Farrugia, 1999).

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References

- Devereux, M., McCann, M., Cronin, J. F., Ferguson, V. & McKee, V. (1999). *Polyhedron*, **18**, 2141–2148.  
Devereux, M., McCann, M., Leon, V., Geraghty, M., McKee, V. & Wikaria, J. (2000). *Polyhedron*, **19**, 1205–1211.  
Erxleben, A. (2003). *Coord. Chem. Rev.* **246**, 203–228.  
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.  
Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.  
Geraghty, M., McCann, M., Casey, M. T., Curran, M., Devereux, M., McKee, V. & McCreagh, J. (1998). *Inorg. Chim. Acta*, **277**, 257–262.  
Geraghty, M., McCann, M., Devereux, M. & McKee, V. (1999). *Inorg. Chim. Acta*, **293**, 160–166.  
Guo, W., Peng, Z., Li, D. & Zhou, Y. (2004). *Polyhedron*, **23**, 1707–1707.  
McCann, S., McCann, M., Casey, M. T., Devereux, M., McKee, V., McMichael, P. & McCreagh, J. G. (1997). *Polyhedron*, **16**, 4247–4252.  
Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.  
Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.  
Stoe & Cie (2002). *X-RED32* and *X-AREA*. Stoe & Cie, Darmstadt, Germany.  
Viossat, V., Lemoine, P., Dayan, E. & Viossat, B. (2005). *J. Mol. Struct.* **741**, 45–52.  
Ye, B. H., Tong, M. L. & Chen, X. M. (2005). *Coord. Chem. Rev.* **249**, 545–565.  
Yin, M.-C., Yuan, L.-J., Ai, C.-C., Wang, C.-W., Yuan, E.-T. & Sun, J.-T. (2004). *Polyhedron*, **23**, 529–536.  
Zhang, L.-Y., Liu, G.-F., Zheng, S.-L., Ye, B.-H., Zhang, X.-M. & Chen, X.-M. (2003). *Eur. J. Org. Chem.* pp. 2965–2971.  
Zheng, Y. Q. & Kong, Z. P. (2004). *J. Solid State Chem.* **177**, 1352–1358.  
Zheng, Y. Q., Lin, J. L. & Chen, B. Y. (2003). *J. Mol. Struct.* **646**, 151–159.  
Zheng, Y. Q., Lin, J. L. & Kong, Z. P. (2003). *Polyhedron*, **22**, 2699–2708.  
Zheng, Y. Q. & Ying, E. B. (2005). *Polyhedron*, **24**, 397–406.