Triclinic
$P\bar{1}$
$a = 11.9557\,(7)$ Å
$b = 12.1110\,(7)$ Å
$c = 17.931\,(1)$ Å
$\alpha = 99.790\,(1)^\circ$
$\beta = 98.943\,(1)^\circ$
$\gamma = 114.365\,(1)^\circ$
$V = 2255.9\,(2)$ Å^3
$Z = 2$
$D_x = 1.325$ Mg m^{-3}
D_m not measured

Cell parameters from 5599 reflections
$\theta = 2.6$–28.3°
$\mu = 0.396$ mm^{-1}
$T = 188\,(2)$ K
Block
0.4 × 0.3 × 0.3 mm
Purple

Data collection

Siemens SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1997*a*)
$T_{\min} = 0.873$, $T_{\max} = 0.976$
14 640 measured reflections
10 520 independent reflections

9504 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.016$
$\theta_{\max} = 28.33^\circ$
$h = -15 \rightarrow 15$
$k = -13 \rightarrow 16$
$l = -23 \rightarrow 23$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.032$
$wR(F^2) = 0.081$
$S = 1.104$
10 520 reflections
532 parameters
H atoms constrained
$w = 1/[\sigma^2(F_o^2) + (0.0227P)^2 + 1.9648P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.04$
$\Delta\rho_{\max} = 0.40$ e Å^{-3}
$\Delta\rho_{\min} = -0.47$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Zr—Cl	2.5112 (5)	Zr—N3	2.2631 (15)
Zr—N1	2.2465 (14)	Zr—N4	2.2608 (15)
Zr—N2	2.2948 (15)	Zr—N5	2.1009 (15)
Cl—Zr—N1	135.15 (4)	N2—Zr—N3	79.25 (5)
Cl—Zr—N2	79.27 (4)	N2—Zr—N4	125.85 (5)
Cl—Zr—N3	84.21 (4)	N2—Zr—N5	140.12 (6)
Cl—Zr—N4	143.71 (4)	N3—Zr—N4	76.87 (5)
Cl—Zr—N5	81.33 (4)	N3—Zr—N5	132.77 (6)
N1—Zr—N2	76.37 (5)	N4—Zr—N5	89.13 (6)
N1—Zr—N3	126.41 (5)	Si1—N5—Si2	114.59 (9)
N1—Zr—N4	80.15 (5)	Si1—N5—Zr	122.04 (8)
N1—Zr—N5	94.06 (6)	Si2—N5—Zr	119.65 (8)

The crystal showed no significant decay and thus no correction was applied for decay. The structure was solved by direct methods. H atoms were added at calculated positions and refined using a riding model with $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}({\rm C})$.

Data collection: *SMART* (Siemens, 1996). Cell refinement: *SAINT* (Siemens, 1996). Data reduction: *SAINT*. Program(s) used to solve structure: *SHELXTL* (Sheldrick, 1997*b*). Program(s) used to refine structure: *SHELXTL*. Molecular graphics: *SHELXTL*. Software used to prepare material for publication: *SHELXTL*.

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Tetraaqua(1,10-phenanthroline)zinc(II) sulfate dihydrate

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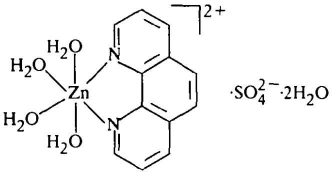
Abstract

A novel monomeric phenanthroline (phen) zinc complex, $[{\rm Zn}({\rm C}_{12}{\rm H}_8{\rm N}_2)({\rm H}_2{\rm O})_4]{\rm SO}_4{\cdot}2{\rm H}_2{\rm O}$, has been characterized by X-ray analysis. The Zn atom is coordinated in a slightly distorted octahedral geometry by two N atoms from 1,10-phenanthroline and four O atoms from water ligands. The Zn—N bond lengths are in the range 2.136 (3)–2.156 (2) Å and the Zn—O bond lengths are in the range 2.083 (2)–2.130 (2) Å. Hydrogen bonds stabilize the structure.

Comment

Phenanthroline, which has an excellent planar π system, has often been involved in model compounds to mimic non-covalent interactions in biological processes. Transition metal complexes of phenanthroline and its substituted derivatives have been found to be useful probes for examining distinctive conformations along the DNA helix (Barton, 1989). Zinc complexes with N- and O-donor ligands are also of considerable interest since such systems are known to exist at the active site of some zinc-containing enzymes, such as phospholipase C (Huogh *et al.*, 1989) and bovine lens leucine aminopeptidase (Burley *et al.*, 1992). Several 1,10-phenanthroline- or 2,2′-bipyridine-containing zinc complexes have been synthesized and characterized structurally by X-ray diffraction (Uhlenbrock & Krebs, 1992; Chen *et al.*, 1994). We report here the crystal structure of a mononuclear zinc complex with only one phen ligand as a chelate, (I).



(I)

The title compound, (I), consists of a discrete $[Zn(phen)(H_2O)_4]^{2+}$ cation, a sulfate anion and two water molecules. The $[Zn(phen)(H_2O)_4]^{2+}$ cation displays distorted octahedral coordination, with phen acting as a bidentate ligand through both N atoms. Four water molecules complete the environment around the metal atom. The phen molecule in (I) has bond distances and angles that are in good agreement with those reported for the free base (Nishigaki *et al.*, 1978) and also in many zinc complexes (Bencini *et al.*, 1989). In the octahedral moiety, the mean Zn—N distance [2.150 (3) Å] is in good accord with those reported in other six-coordinate Zn–phen complexes, *e.g.* $[Zn(phen)_2(H_2O)_2]^{2+}$ [2.17 (1) Å; Hu & Liu, 1991], but apparently longer than those found in $[Zn(phen)Cl_2]$ [2.061 (7) Å; Khan & Tuck, 1984] due to the change in coordination number from four to six. The bite angle of 77.4 (1)° is similar to those found in $[Zn(phen)_2(H_2O)_2]^{2+}$ [average 76.8 (1)°; Hu & Liu, 1991], but slightly smaller than that reported in $[Zn(phen)Cl_2]$ [80.4 (3)°; Khan & Tuck, 1984]. The distances and angles for the sulfate ion are normal.

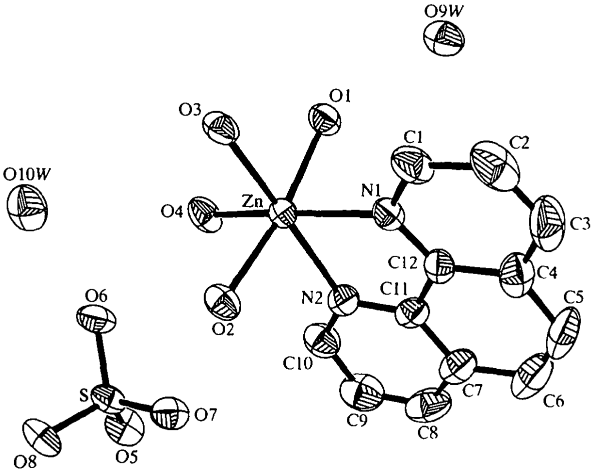


Fig. 1. The molecular structure of (I) showing 50% probability displacement ellipsoids. H atoms have been omitted for clarity.

Experimental

To an aqueous solution of zinc sulfate (10 mmol, 20 ml) was added an aqueous solution of 1,10-phenanthroline (10 mmol, 20 ml) with stirring for 30 min. Good shaped crystals suitable for X-ray diffraction analysis were obtained by slow evaporation of the filtrate of the above solution.

Crystal data

$[Zn(C_{12}H_8N_2)(H_2O)_4]SO_4{\cdot}2H_2O$
M_r = 449.73
Orthorhombic
Pbca
a = 8.906 (1) Å
b = 18.295 (2) Å
c = 21.855 (3) Å
V = 3560.9 (7) Å^3
Z = 8
D_x = 1.678 Mg m^{-3}
D_m = 1.68 Mg m^{-3}
D_m measured by flotation in 1,2-dibromoethane and cyclohexane

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 32 reflections
θ = 2.90–15.92°
μ = 1.552 mm^{-1}
T = 291 (2) K
Prism
0.40 × 0.40 × 0.20 mm
Colourless

Data collection

Siemens *P*4 diffractometer
ω scans
Absorption correction: empirical ψ scan (North *et al.*, 1968)
T_{min} = 0.725, T_{max} = 0.996
4750 measured reflections
3868 independent reflections
2342 reflections with $I > 2\sigma(I)$

R_{int} = 0.020
θ_{max} = 27°
$h = 0 \rightarrow 11$
$k = 0 \rightarrow 23$
$l = -1 \rightarrow 27$
3 standard reflections every 97 reflections intensity decay: 14.14%

Refinement

Refinement on F^2
$R(F)$ = 0.035
$wR(F^2)$ = 0.070

$(\Delta/\sigma)_{max} = -0.001$
$\Delta\rho_{max}$ = 0.339 e Å^{-3}
$\Delta\rho_{min}$ = −0.282 e Å^{-3}

$S = 1.008$
3868 reflections
276 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0355P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

Extinction correction: *SHELXL*93
Extinction coefficient: 0.0028 (2)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Zn—O4	2.083 (2)	Zn—N2	2.156 (3)
Zn—O2	2.096 (2)	S—O8	1.465 (2)
Zn—O3	2.128 (2)	S—O7	1.466 (2)
Zn—O1	2.130 (2)	S—O5	1.468 (2)
Zn—N1	2.136 (3)	S—O6	1.478 (2)
O4—Zn—O2	89.0 (1)	O1—Zn—N2	100.5 (1)
O4—Zn—O3	93.0 (1)	N1—Zn—N2	77.4 (1)
O2—Zn—O3	87.4 (1)	O8—S—O7	109.3 (1)
O4—Zn—O1	86.1 (1)	O8—S—O5	109.6 (1)
O2—Zn—O1	171.2 (1)	O7—S—O5	109.8 (1)
O3—Zn—O1	85.5 (1)	O8—S—O6	109.5 (2)
O4—Zn—N1	167.1 (1)	O7—S—O6	109.7 (1)
O2—Zn—N1	98.89 (9)	O5—S—O6	108.9 (1)
O3—Zn—N1	97.6 (1)	C1—N1—Zn	127.6 (2)
O1—Zn—N1	87.3 (1)	C12—N1—Zn	113.9 (2)
O4—Zn—N2	92.9 (1)	C10—N2—Zn	128.3 (2)
O2—Zn—N2	87.0 (1)	C11—N2—Zn	113.6 (2)
O3—Zn—N2	171.8 (1)		

The phen H atoms were placed using a riding model. Water H atoms were found from a difference Fourier synthesis, except for those on O10, which could not be modelled.

Data collection: *XSCANS* (Siemens, 1991). Cell refinement: *XSCANS*. Data reduction: *SHELXTL-Plus* (Sheldrick, 1990*a*). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990*b*). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *XP* (Siemens, 1990). Software used to prepare material for publication: *SHELXTL-Plus* (Sheldrick, 1990*a*).

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Chloro(*meso*-tetrapropylporphyrinato)-iron(III)

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Abstract

In the chloroiron(III) complex of *meso*-tetrapropylporphyrin, [Fe($C_{32}H_{36}N_4$)Cl], the Fe^{III} atom has slightly distorted square-pyramidal coordination. The porphyrin ring shows a typical S_4-ruffled structure in addition to a normally observed domed core; the deviations of the *meso*-C and Fe atoms from the least-squares plane of the $C_{20}N_4$ core are 0.366 (4) (maximum) and 0.578 (1) Å, respectively. The average Fe—N_p bond distance is 2.063 (4) Å.

Comment

Non-planar distortions of porphyrin macrocycles are found frequently in haemoproteins and are expected to play important roles in biological functions (Finzel *et al.*, 1984; Hobbs & Shelnutt, 1995). Through extensive studies using non-planar haem model complexes, it is now clear that non-planarity of the porphyrin influences various physicochemical properties (Barkigia *et al.*, 1990; Jentzen *et al.*, 1995; Nakamura *et al.*, 1996; Senge *et al.*, 1995). Recent X-ray crystallographic analyses, as well as molecular-mechanics calculations, have revealed the existence of several deformation modes in porphyrin rings such as waving, doming, saddling and ruffling. In order to understand the effects of the deformation mode on the physicochemical properties,

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