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Key indicators

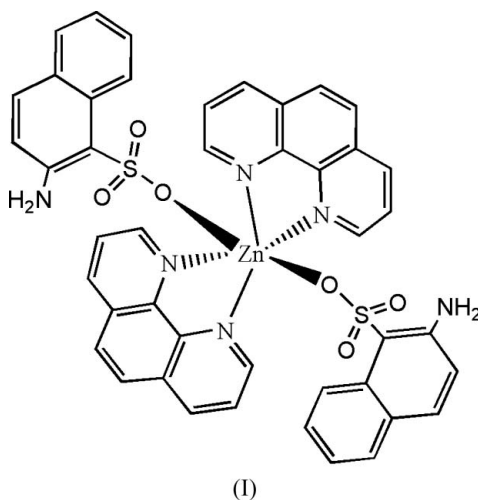
Single-crystal X-ray study
 $T = 293\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.004\text{ \AA}$
 R factor = 0.023
 wR factor = 0.060
Data-to-parameter ratio = 12.6For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.Bis(2-aminonaphthalene-1-sulfonato- κO)-
bis(1,10-phenanthroline)zinc(II)

In the title compound, $[\text{Zn}(\text{C}_{10}\text{H}_8\text{NO}_3\text{S})_2(\text{C}_{12}\text{H}_8\text{N}_2)_2]$, the Zn^{II} atom lies on a crystallographic twofold axis and is in a distorted octahedral coordination geometry formed by four N atoms from two chelating 1,10-phenanthroline ligands and two O atoms from two 2-aminonaphthalene-1-sulfonate ligands. In the crystal structure, intermolecular $\text{N}-\text{H}\cdots\text{O}$ and $\text{C}-\text{H}\cdots\text{O}$ hydrogen bonds link molecules to form a three-dimensional network. In addition, there is a single intramolecular $\pi-\pi$ stacking interaction.

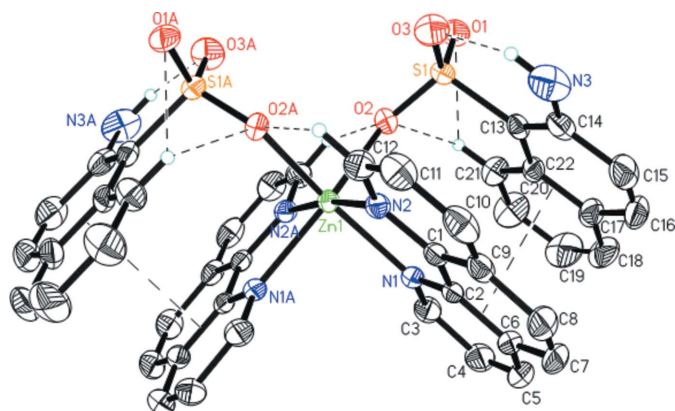
Received 14 July 2006
Accepted 20 July 2006

Comment

Sulfonates are not widely used as ligands, as the sulfonate group was traditionally thought to be a poor ligand and it was difficult for it to form stable coordinate bonds with transition metal ions (Kosnic *et al.*, 1992; Dalrymple *et al.*, 2002; Dalrymple & Shimizu, 2002). Recently some transition metal complexes with sulfonate anion-based ligands have been obtained by introducing other organic ligands to the metal centers as auxiliaries (Cai, Chen, Liao, Feng *et al.*, 2001; Cai, Chen, Liao, Yao *et al.*, 2001; Chen *et al.*, 2002), indicating that the coordination strength of sulfonate anions is tunable. As part of our investigation of the coordination chemistry of aromatic sulfonate anions, we report here the crystal structure of a Zn^{II} complex with 1,10-phenanthroline and 2-aminonaphthalene-1-sulfonate, (I).



The molecular structure of the title mononuclear complex is shown in Fig. 1 and selected bond lengths and angles are listed in Table 1. The Zn^{II} center exhibits a distorted octahedral coordination geometry involving four N-atom donors from two chelating 1,10-phenanthroline ligands, and two sulfonate

**Figure 1**

The molecular structure of (I). Displacement ellipsoids are drawn at the 30% probability level. Only H atoms involved in hydrogen bonds have been included. The short dashed lines indicate intramolecular hydrogen bonds and the long dashes indicate π - π stacking interactions [Symmetry code: (A) $y - 1, 1 + x, -z$].

O atoms from two 2-aminonaphthalene-1-sulfonate ligands. 1,10-Phenanthroline acts as a typical asymmetric chelating ligand coordinating to the Zn^{II} atom with the Zn1–N2 bond 0.023 Å shorter than Zn1–N1. The 2-aminonaphthalene-1-sulfonate ligand coordinates in a monodentate mode. There is a single intramolecular π - π stacking interaction between the naphthalene ring system and the quinoline ring system of the 1,10-phenanthroline ligand, with a centroid–centroid distance of 3.6812 (2) Å and a dihedral angle between rings of 4.99 (5)°. In the crystal structure, intermolecular N–H \cdots O and C–H \cdots O hydrogen bonds link complex molecules to form a three-dimensional network (Table 2 and Fig. 2).

Experimental

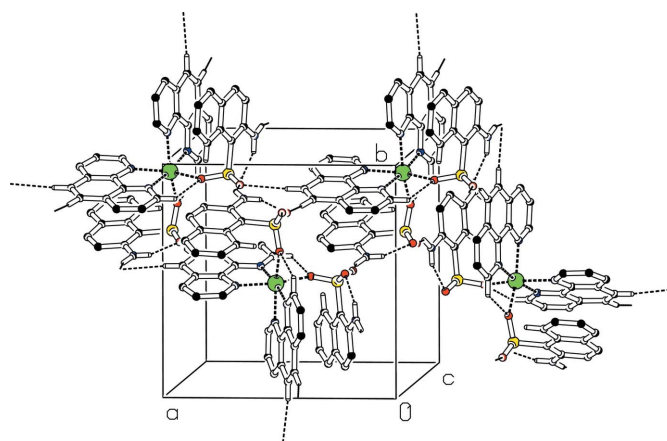
The title complex was synthesized by heating a mixture of Zn(NO₃)₂·6H₂O (87.8 mg, 0.4 mmol), 1,10-phenanthroline (39.64 mg, 0.2 mmol), 2-aminonaphthalene-1-sulfonic acid (89.3 mg, 0.4 mmol), NaOH (0.6 mmol) and H₂O (12 ml) in a 23 ml Teflon-lined autoclave under autogenous pressure at 413 K for 2 d. After the reaction mixture was slowly cooled to room temperature at a rate of 5 K h⁻¹, pale-yellow block crystals suitable for X-ray analysis were obtained in 40% yield. Analysis calculated for C₄₄H₃₂ZnN₆O₆S₂: C 60.73, H 3.71, N 9.66%; found: C 60.50, H 3.65, N 9.76%.

Crystal data

[Zn(C ₁₀ H ₈ NO ₃ S) ₂ (C ₁₂ H ₈ N ₂) ₂]	$D_x = 1.517 \text{ Mg m}^{-3}$
$M_r = 870.25$	Mo $K\alpha$ radiation
Tetragonal, $P4_12_12$	$\mu = 0.82 \text{ mm}^{-1}$
$a = 12.4631 (7) \text{ \AA}$	$T = 293 (2) \text{ K}$
$c = 24.538 (3) \text{ \AA}$	Block, pale yellow
$V = 3811.4 (6) \text{ \AA}^3$	$0.28 \times 0.20 \times 0.18 \text{ mm}$
$Z = 4$	

Data collection

Bruker APEX-II CCD area-detector diffractometer	20667 measured reflections
φ and ω scans	3362 independent reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	3176 reflections with $I > 2\sigma(I)$
$T_{\min} = 0.822, T_{\max} = 0.864$	$R_{\text{int}} = 0.029$
	$\theta_{\text{max}} = 25.0^\circ$

**Figure 2**

Part of the crystal structure of (I), showing N–H \cdots O and C–H \cdots O hydrogen bonds as dashed lines. Only H atoms involved in hydrogen bonds have been included.

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.023$
 $wR(F^2) = 0.060$
 $S = 1.05$
 3362 reflections
 267 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0281P)^2 + 0.6697P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 0.19 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.23 \text{ e \AA}^{-3}$
 Absolute structure: Flack (1983),
 1365 Friedel pairs
 Flack parameter: 0.017 (10)

Table 1

Selected geometric parameters (Å, °).

Zn1–O2	2.0855 (14)	Zn1–N1	2.1865 (16)
Zn1–N2	2.1634 (16)		
O2 ⁱ –Zn1–O2	89.89 (8)	N2–Zn1–N1 ⁱ	97.97 (6)
O2–Zn1–N2 ⁱ	85.99 (6)	O2–Zn1–N1	93.60 (6)
O2–Zn1–N2	99.42 (6)	N2–Zn1–N1	76.48 (7)
N2 ⁱ –Zn1–N2	172.41 (9)	N1 ⁱ –Zn1–N1	88.23 (9)
O2–Zn1–N1 ⁱ	162.46 (6)		

Symmetry code: (i) $y - 1, x + 1, -z$.

Table 2

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N3–H3A \cdots O3	0.86	1.95	2.646 (3)	137
N3–H3B \cdots O1 ⁱⁱ	0.86	2.19	2.894 (3)	139
C12–H12 \cdots O2 ⁱ	0.93	2.45	3.004 (3)	118
C21–H21 \cdots O1	0.93	2.49	3.055 (3)	120
C21–H21 \cdots O2	0.93	2.48	3.033 (3)	118
C7–H7 \cdots O1 ⁱⁱⁱ	0.93	2.56	3.453 (3)	162
C8–H8 \cdots O3 ^{iv}	0.93	2.54	3.394 (4)	153

Symmetry codes: (i) $y - 1, x + 1, -z$; (ii) $y - \frac{1}{2}, -x + \frac{1}{2}, z - \frac{1}{4}$; (iii) $y, x + 1, -z$; (iv) $x + \frac{1}{2}, -y + \frac{3}{2}, -z - \frac{1}{4}$.

H atoms were located in difference maps, but were subsequently placed in calculated positions and treated as riding, with C–H = 0.93 Å and N–H = 0.86 Å. All H atoms were allocated displacement parameters related to those of their parent atoms [$U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C,N})$].

Data collection: *APEXII* (Bruker, 2003); cell refinement: *SAINTE* (Bruker, 2001); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2001) and *DIAMOND* (Brandenburg & Berndt, 1999); software used to prepare material for publication: *SHELXTL*.

The authors gratefully acknowledge financial support from the Natural Science Foundation of Tianjin (No. 06YFJMJC03900) and the doctoral fund from Tianjin Normal University (to ECY).

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