metal-organic papers

Bis(2-aminonaphthalene-1-sulfonato-κO)-bis(1,10-phenanthroline-$\kappa^2 N,N'$)cobalt(II)

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The title molecule, $[Co(C_{10}H_8NO_3S)_2(C_{12}H_{10}N_2)_2]$, lies on a crystallographic twofold axis with the Co^{II} atom coordinated by four N atoms from two chelating 1,10-phenanthroline ligands and two sulfonate O atoms from two 2-aminonaphthalene-1-sulfonate ligands in a distorted octahedral geometry. In the crystal structure, intermolecular C—H···O and N—H···O hydrogen bonds link the mononuclear units into a three-dimensional network. There is also a single N—H···O hydrogen bond and an intramolecular π–π stacking interaction.

Comment

The design and synthesis of metal-organic frameworks (MOFs) by the mixed-ligand strategy is currently an active research area due to their intriguing structural architectures as well as their potential applications in catalysis, gas adsorption, and separation (Kitagawa *et al.*, 2004). The mixed-ligand strategy has been proven to be an effective method for the preparation of metal–sulfonate complexes (Cai, Chen, Liao, Feng *et al.*, 2001; Cai, Chen, Liao, Yao *et al.*, 2001; Chen *et al.*, 2002; Dai *et al.*, 2006).

(I)
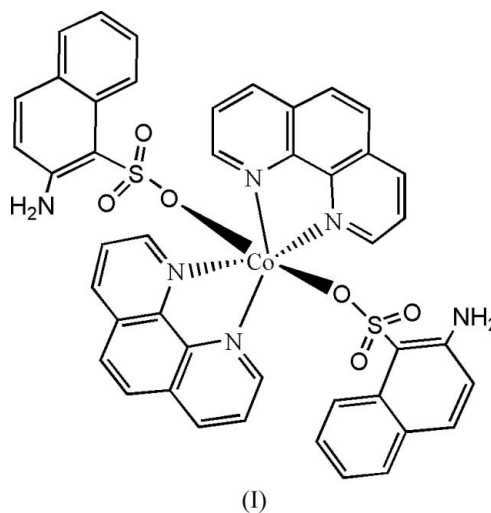
As part of our further investigation of the coordination chemistry of aromatic sulfonate anions, we report here the crystal structure of a Co^{II} complex, (I), with mixed ligands of 1,10-phenanthroline and 2-aminonaphthalene-1-sulfonate. The molecular structure of (I) is shown in Fig. 1 and selected bond lengths and angles are listed in Table 1. The Co^{II} atom exhibits a distorted octahedral coordination geometry involving four N-atom donors from two chelating 1,10-phenanthroline ligands, and two sulfonate O atoms from two
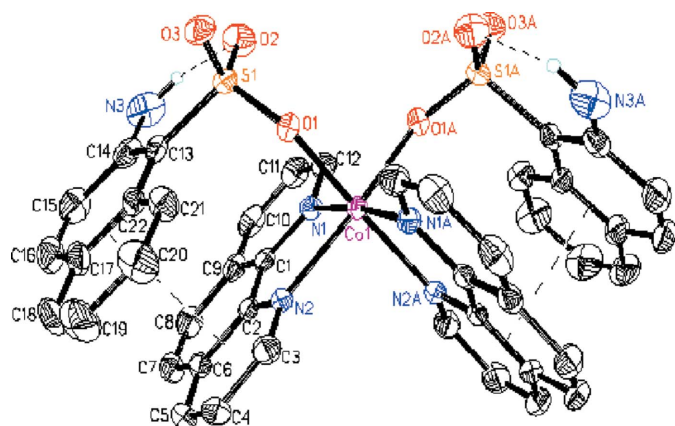
Figure 1
The molecular structure of (I). Displacement ellipsoids are drawn at the 30% probability level. Only H atoms involved in hydrogen bonds have been included. The short-dashed lines indicate intramolecular hydrogen bonds and the long-dashed lines indicate π–π stacking interactions [symmetry code: (A) $y, x, -z$].

monodentate 2-aminonaphthalene-1-sulfonate ligands. The molecule lies on a crystallographic twofold axis.

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 3.670 (1) Å and a dihedral angle between the rings of 5.20 (4)°. In the crystal structure, intermolecular N—H ⋯O and C—H ⋯O hydrogen bonds link complex molecules, forming a three-dimensional network (Table 2 and Fig. 2).

Experimental

The title complex was synthesized by dissolving a reaction mixture of Co(CH₃COO)₂·4H₂O (99.6 mg, 0.4 mmol), 1,10-phenanthroline (39.6 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, the mixture was cooled slowly to room temperature at a rate of 5 K h⁻¹; red block-shaped crystals suitable for X-ray analysis were obtained in 30% yield. Analysis calculated for $C_{44}H_{32}CoN_6O_6S_2$: C 61.18, H 3.73, N 9.73%; found: C 61.35, H 3.89, N 9.89%.

Crystal data

[Co(C₁₀H₈NO₃S)₂(C₁₂H₈N₂)₂]	$D_x = 1.506$ Mg m⁻³
$M_r = 863.81$	Mo $K\alpha$ radiation
Tetragonal, $P4_12_12$	$\mu = 0.62$ mm⁻¹
$a = 12.468$ (3) Å	$T = 294$ (2) K
$c = 24.510$ (9) Å	Block, red
$V = 3810.3$ (19) Å³	$0.44 \times 0.28 \times 0.20$ mm
$Z = 4$	

Data collection

Bruker APEX-II CCD diffractometer	20658 measured reflections
	3363 independent reflections
φ and ω scans	3105 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	$R_{int} = 0.038$
$T_{min} = 0.812$, $T_{max} = 0.883$	$\theta_{max} = 25.0°$

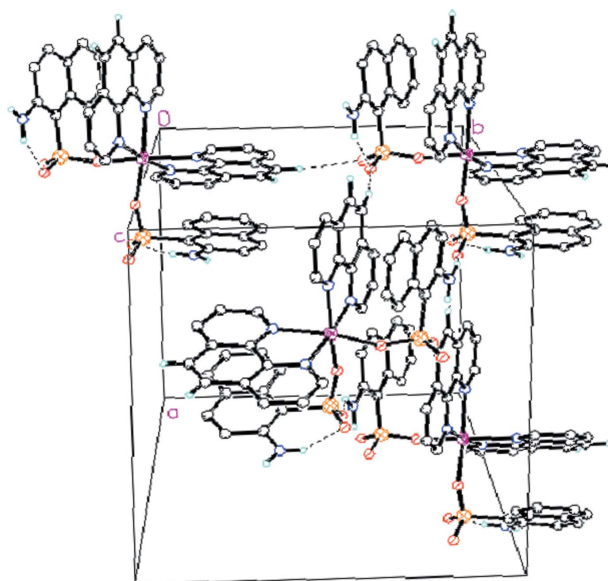**Figure 2**
Part of the crystal structure of (I), showing N—H⋯O and C—H⋯O hydrogen bonds as dashed lines. Only H atoms involved in hydrogen bonds are shown.

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0406P)^2 + 0.043P]$
$R[F^2 > 2\sigma(F^2)] = 0.024$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.063$	$(\Delta/\sigma)_{max} = 0.001$
$S = 1.04$	$\Delta\rho_{max} = 0.13$ e Å⁻³
3363 reflections	$\Delta\rho_{min} = -0.26$ e Å⁻³
267 parameters	Absolute structure: Flack (1983), 1364 Friedel pairs
H-atom parameters constrained	Flack parameter: −0.034 (12)

Table 1
Selected geometric parameters (Å, °).

Co1—O1	2.0716 (14)	Co1—N2	2.1523 (16)
Co1—N1	2.1520 (16)		
O1^i—Co1—O1	90.19 (8)	O1—Co1—N2	93.65 (6)
O1^i—Co1—N1	86.50 (6)	N1^i—Co1—N2	98.66 (6)
O1—Co1—N1	97.47 (6)	N1—Co1—N2	77.21 (6)
N1^i—Co1—N1	174.40 (9)	N2—Co1—N2^i	87.12 (8)
O1^i—Co1—N2	163.61 (6)		

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

Table 2
Hydrogen-bond geometry (Å, °).

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
N3—H3B⋯O3^{ii}	0.86	2.22	2.901 (3)	137
N3—H3A⋯O2	0.86	1.95	2.650 (3)	137
C21—H21⋯O1	0.93	2.47	3.027 (3)	119
C21—H21⋯O3	0.93	2.50	3.063 (3)	119
C7—H7⋯O3^{iii}	0.93	2.57	3.471 (3)	163
C8—H8⋯O2^{iv}	0.93	2.53	3.385 (3)	154
C12—H12⋯O1^i	0.93	2.48	3.025 (3)	117

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

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, with U_{iso}(H) = 1.2U_{eq}(C, N).

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