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Key indicators

Single-crystal X-ray study
T = 293 K
Mean $\sigma(\text{C}-\text{C}) = 0.004 \text{ \AA}$
R factor = 0.037
wR factor = 0.100
Data-to-parameter ratio = 9.9For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.*trans*-Tetraaquabis(*p*-nitrobenzoxasulfamato)-
cobalt(II)

The structure of the title complex consists of neutral molecules of $[\text{Co}(\text{nbs})_2(\text{H}_2\text{O})_4]$ (nbs is the *p*-nitrobenzoxasulfamate anion, $\text{C}_6\text{H}_3\text{N}_2\text{O}_5\text{S}^-$). The Co^{2+} ion occupies an inversion centre and exhibits a distorted octahedral geometry, involving two monodentate nbs (N_{imine}) anions and four water molecules. The crystal structure is stabilized by hydrogen bonding and weak aromatic $\pi-\pi$ stacking interactions between the benzene rings of nbs ligands, forming a three-dimensional network.

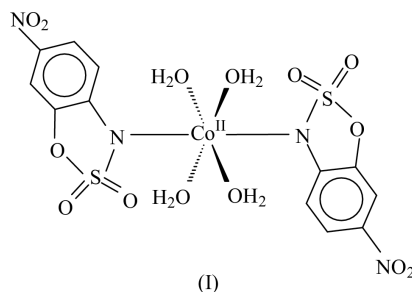
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Comment

Sulfamate derivatives have considerable commercial importance as artificial sweeteners (Spillane *et al.*, 1996; Drew *et al.*, 1998) and drugs (Howarth *et al.*, 1994; Maryanoff *et al.*, 1998; Gautun *et al.*, 1999) and have been used in the preparation of flame retarding (Lewin, 1997) and antistatic polymers (Spiridonov & Malushko, 2000). Recently, we have started the synthesis and spectroscopic and crystallographic characterization of metal salts and complexes of a cyclic sulfamate, the *p*-nitrobenzoxasulfamate ion (nbs) ($\text{C}_6\text{H}_3\text{N}_2\text{O}_5\text{S}^-$). We have previously reported the X-ray crystal structures of the sodium (Yazicilar *et al.*, 2002) and potassium (Bekdemir *et al.*, 2002) salts of nbs, and the first aqua-metal complexes of nbs with copper(II), *viz.* $[\text{Cu}(\text{nbs})_2(\text{H}_2\text{O})_3]\cdot\text{H}_2\text{O}$ (Yilmaz, Andac *et al.*, 2002), cadmium(II), $[\text{Cd}(\text{nbs})_2(\text{H}_2\text{O})_4]$ and mercury(II), $[\text{Hg}(\text{nbs})_2(\text{H}_2\text{O})_3]$ (Yilmaz, Yazicilar *et al.*, 2002). As a part of our research project, in this paper, we report the synthesis and crystal structure of the title compound, (I).



A molecular view of (I) is shown in Fig. 1 and Table 1 lists selected geometric data. The structure of (I) consists of neutral molecules of $[\text{Co}(\text{nbs})_2(\text{H}_2\text{O})_4]$, in which the Co^{2+} ion occupies an inversion centre and is coordinated by a pair of anionic nbs ligands and four water molecules, exhibiting distorted octahedral geometry. The nbs ions act as monodentate ligands through the imine N atom, occupying *trans* positions of the coordination polyhedron. Previous studies showed that the nbs ligand exhibits two types of coordination *via* the N or O_{nitro} sites. N-coordination was observed in the

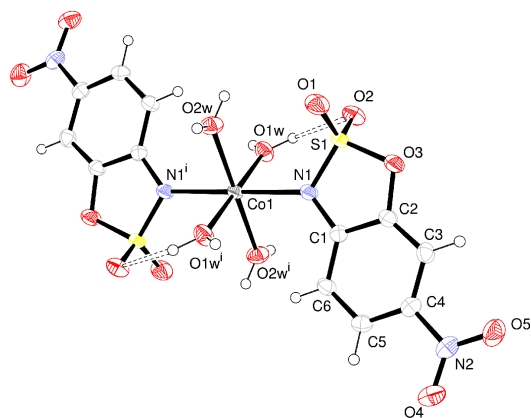


Figure 1
Molecular view of (I) (40% probability displacement ellipsoids). The symmetry code is as in Table 1.

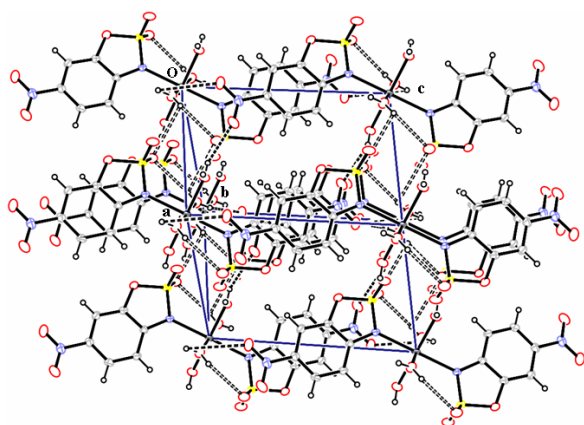


Figure 2
Packing diagram of (I), projected approximately on to $(\bar{1}10)$, showing hydrogen bonds as dashed lines (50% probability displacement ellipsoids).

case of copper(II) and cadmium(II), whereas nbs behaves as an ambidentate ligand in $[\text{Hg}(\text{nbs})_2(\text{H}_2\text{O})_3]$; one of the nbs ions is N-bonded, while the other one is O-coordinated. Slight distortion of the metal coordination from regular octahedral geometry is apparent, as seen in the O—Co—O angles (Table 1).

The nbs ligand (C1—C6/C21/O3/N1/S1) is essentially planar, with an r.m.s. deviation of 0.09 Å. The nitro group is almost coplanar with the nbs backbone, although one of the O atoms (O4) of the nitro group deviates from the mean plane of the nbs ligand by 0.20 (1) Å. The packing of (I) is shown in Fig. 2. It exhibits parallel stacking of pairs of nbs ions, resulting in weak aromatic π — π interactions [$Cg \cdots Cg^{\text{vii}} = 3.828$ (2) Å; symmetry code: (vii) $2 - x, -y, 1 - z$; Cg is the centroid of the ring]. The H atoms of one of the water molecules (O1W) form intramolecular hydrogen bonds with the sulfonyl O atoms (O2). The individual molecules are connected by intermolecular hydrogen bonds (Table 2) between water H atoms and the O atoms of the nitro groups. These include a trifurcated interaction involving atom H1B. The hydrogen bonds and weak π — π interactions stabilize the crystal structure, thereby forming a three-dimensional network (Fig. 2).

Experimental

$\text{Na}(\text{nbs}) \cdot \text{H}_2\text{O}$ (0.51 g, 2.0 mmol) dissolved in a tetrahydrofuran/water mixture (1:1, v/v, 20 ml) was added to an aqueous solution (10 ml) of $\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$ (0.24 g, 1.0 mmol) and the mixture stirred for 15 min at room temperature. The resulting solution was allowed to evaporate slowly for crystallization at room temperature and X-ray quality brown single crystals were obtained within a week.

Crystal data

$[\text{Co}(\text{C}_6\text{H}_3\text{N}_2\text{O}_5\text{S})_2(\text{H}_2\text{O})_4]$
 $M_r = 561.32$
 Triclinic, $P\bar{1}$
 $a = 7.2079$ (9) Å
 $b = 7.3251$ (10) Å
 $c = 10.4032$ (14) Å
 $\alpha = 88.760$ (11)°
 $\beta = 77.191$ (10)°
 $\gamma = 62.442$ (9)°
 $V = 472.75$ (11) Å³

$Z = 1$
 $D_x = 1.972$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 11439 reflections
 $\theta = 2.0$ – 25.2 °
 $\mu = 1.22$ mm⁻¹
 $T = 293$ (2) K
 Prism, brown
 $0.5 \times 0.4 \times 0.1$ mm

Data collection

Stoe IPDS-II diffractometer
 ω scans
 Absorption correction: by integration (*X-RED*; Stoe & Cie, 2002)
 $T_{\text{min}} = 0.563$, $T_{\text{max}} = 0.885$
 5264 measured reflections
 1647 independent reflections

1571 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.064$
 $\theta_{\text{max}} = 25.0$ °
 $h = -8 \rightarrow 8$
 $k = -8 \rightarrow 8$
 $l = -12 \rightarrow 12$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.037$
 $wR(F^2) = 0.100$
 $S = 1.05$
 1647 reflections
 167 parameters
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0729P)^2 + 0.0979P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 0.93$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.67$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

Co1—O1W	2.0713 (18)	Co1—N1	2.1653 (16)
Co1—O2W	2.0951 (16)		
O1W—Co1—O2W	92.89 (8)	O1W ⁱ —Co1—N1	89.05 (7)
O1W ⁱ —Co1—O2W	87.11 (8)	O2W—Co1—N1	91.55 (7)
O1W—Co1—N1	90.95 (7)	O2W ⁱ —Co1—N1	88.45 (7)

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

Table 2

Hydrogen-bonding geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O1W—H1A...O5 ⁱⁱ	0.88 (3)	1.99 (3)	2.853 (2)	171 (4)
O1W—H1B...O2	0.88 (5)	2.46 (4)	3.031 (2)	123 (3)
O1W—H1B...O1 ⁱⁱⁱ	0.88 (5)	2.59 (5)	3.141 (3)	121 (3)
O1W—H1B...O5 ^{iv}	0.88 (5)	2.50 (4)	3.020 (3)	118 (4)
O2W—H2A...O4 ^v	0.86 (3)	2.34 (3)	2.908 (2)	124 (3)
O2W—H2A...O2 ⁱⁱⁱ	0.86 (3)	2.31 (3)	3.109 (3)	156 (3)
O2W—H2B...O1 ^{vi}	0.86 (3)	2.09 (3)	2.927 (3)	164 (4)

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

H atoms of the hydroxy group and water molecules were refined freely [O—H = 0.857 (19)–0.88 (5) Å], while H atoms bonded to C

atoms were included using a riding model, starting from calculated positions [$C-H = 0.93 \text{ \AA}$ and $U_{iso}(H) = 1.2U_{eq}(C)$].

Data collection: *X-AREA* (Stoe & Cie, 2002); cell refinement: *X-AREA*; data reduction: *X-RED* (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* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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