Poly[bis(μ-4-aminobenzenesulfonato-κ²N:O)diaquacobalt(II)]

Antoine Blaise Kama,[a]* Mamadou Sidibe,[a] Cheikh Abdoul Khadre Diop[a] and Florent Blanchard[b]

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The title compound, $[Co(C_6H_6NO_3S)_2(H_2O)_2]_n$, was obtained from a mixture of $Co(NO_3)_2 \cdot 6H_2O$ and a previously synthesized salt, namely $CyNH_3 \cdot NH_2PhSO_3$, in a 1:1 ratio (Cy = cyclohexyl; Ph = phenyl). The crystal structure consists of a three-dimensional supramolecular framework, in which polymeric layers are interconnected via $N—H \cdots O$ and $O—H \cdots O$ hydrogen bonding. The polymeric layers are formed by an interconnection of neighbouring cobalt(II) cations via $NH_2PhSO_3^-$ bridges. Each cobalt(II) cation is surrounded by four $NH_2PhSO_3^-$ moieties and two water molecules, leading to a distorted octahedral environment.

3D view
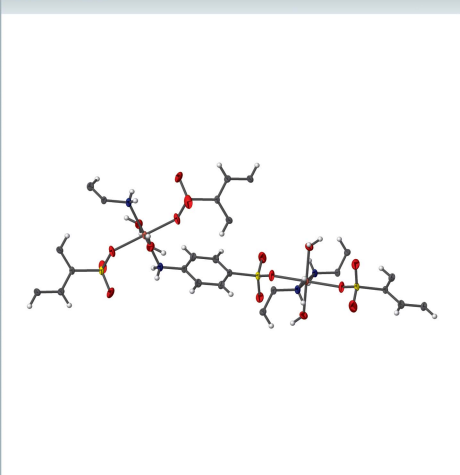
Chemical scheme
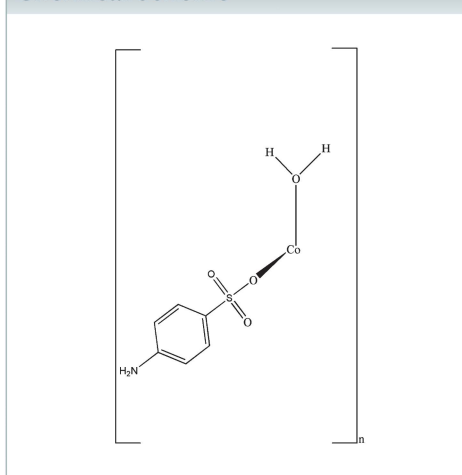
Structure description

Mononuclear or polynuclear cobalt complexes formed by electron-donating groups have been widely studied (Liu *et al.*, 2017; Leung *et al.*, 2012; McCool *et al.*, 2011; Nakazono *et al.*, 2013; Pizzolato *et al.*, 2013; Wang *et al.*, 2014; Xu *et al.*, 2017) owing to their capacities for water oxidation. Indeed, it has been frequently observed that ligand dissociation of cobalt complexes occurs, generating CoO_x nanoparticles that act as water oxidation catalysts (Wasylenko *et al.*, 2011; Hong *et al.*, 2012). For the design of new cobalt complexes, we target the synthesis of a new material from $Co(NO_3)_2 \cdot 6H_2O$ and a previously synthesized ligand. In this case, $CyNH_3 \cdot NH_2PhSO_3$ (Cy = cyclohexyl; Ph = phenyl) yielded the title compound $[Co(NH_2PhSO_3)_2(H_2O)_2]_n$ via the elimination of the NO_3^- group and the substitution of four water molecules by $NH_2PhSO_3^-$. If we consider the reagents and the resulting material, a notable fact is the elimination of some water molecules and the nitrate, probably in the form of $CyNH_3 \cdot NO_3$, leading to the substitution complex $[Co(NH_2PhSO_3)_2(H_2O)_2]_n$. The crystal structure is reported herein. A
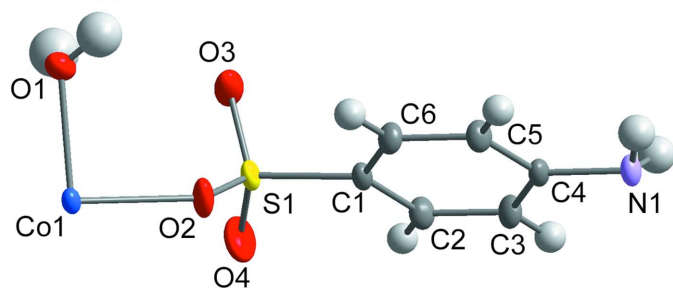
Figure 1
The asymmetric unit of the title compound. Displacement ellipsoids are drawn at 50% probability level.

similar tetrahydrate cobalt complex has been previously reported (Shakeri & Haussühl, 1992).

The asymmetric unit comprises of a cobalt(II) cation (situated at an inversion centre), one $NH_2PhSO_3^-$ anion and one water molecule (Fig. 1). The *trans* coordination of the ligands around the Co^{II} ion leads to a distorted octahedral coordination sphere with O—Co—N and O—Co—O angles in the range 88.42 (5)–91.58 (5)°. The Co—N [2.2424 (14) Å] and Co—O [in the range 2.0800 (12)–2.1049 (10) Å] bond length are similar to those found in the literature (Co—N = 2.256 and Co—O = 2.118 Å; Li *et al.*, 2007]. The three S—O bond lengths are different [S1—O2 = 1.4652 (12), S1—O3 = 1.4512 (13) and S1—O4 = 1.4463 (15) Å] because O2 is involved in covalent bonding while O3 and O4 are involved in hydrogen bonding (Table 1, Fig. 2).
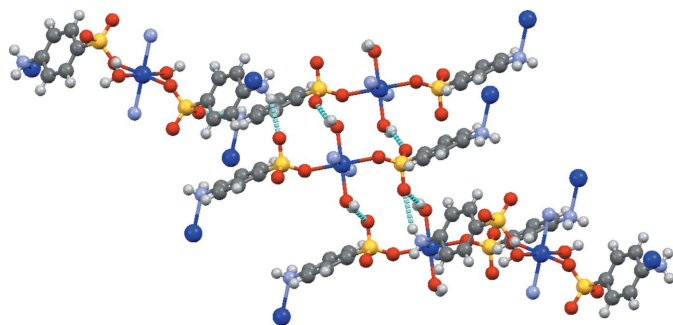

Figure 2
Hydrogen bonds (shown as light-blue dashed lines) between water molecules and SO_3^- groups in the title compound.
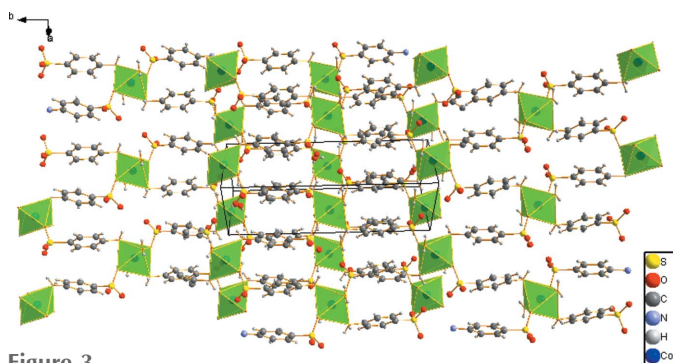

Figure 3
Polymeric layers formed by interconection of neighbouring cobalt(II) cations.

Table 1
Hydrogen-bond geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O1—H$O1A\cdots$O4^i	0.84 (3)	1.85 (3)	2.660 (2)	161 (3)
O1—H$O1B\cdots$O3^{ii}	0.80 (3)	1.97 (3)	2.7647 (18)	176 (3)
N1—H$N1A\cdots$O3^{iii}	0.85 (2)	2.21 (2)	3.008 (2)	156 (2)
N1—H$N1B\cdots$O1^{iv}	0.84 (2)	2.48 (2)	3.309 (2)	171 (2)
C3—H3$\cdots$O3^{iii}	0.93	2.59	3.2123 (19)	124
C5—H5$\cdots$O2^v	0.93	2.60	3.501 (2)	163

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

In the crystal structure, the cobalt(II) cation is surrounded by four $NH_2PhSO_3^-$ moieties. Each $NH_2PhSO_3^-$ unit is a bridge connecting two neighboring cobalt(II) cations through the NH_2 groups on the one hand and the SO_3^- group on the other, leading to polymeric layers (Fig. 3). The layers are connected *via* N—H$\cdots$O (sulfanilate–sulfanilate interaction through SO_3^- and NH_2 groups) and O—H$\cdots$O (sulfanilate–water interaction) hydrogen bonding. The resulting structure can be described as a three-dimensional supramolecular framework built from layers (Fig. 4).

Synthesis and crystallization

The title compound was obtained by mixing cyclohexyl-ammonium sulfanilate (0.78 g, 3 mmol) and cobalt nitrate hexahydrate, $Co(NO_3)_2\cdot 6H_2O$ (0.6 g, 3 mmol) in ethanol as solvent. The solution was stirred for about two h and filtered. Slow evaporation of the filtrate at room temperature afforded red crystals suitable for single-crystal X-ray diffraction analysis.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.
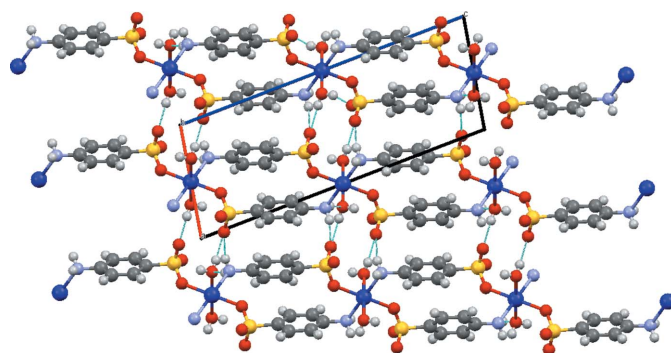
Acknowledgements

Figure 4
Three-dimensional supramolecular framework built from polymeric layers connected *via* hydrogen bonds.

Table 2
Experimental details.

Crystal data	
Chemical formula	$[Co(C_6H_6NO_3S)_2(H_2O)_2]$
M_r	439.32
Crystal system, space group	Monoclinic, $P2_1/n$
Temperature (K)	293
a, b, c (Å)	7.0768 (3), 5.9601 (3), 18.6738 (8)
β (°)	100.494 (4)
V (Å^3)	774.46 (6)
Z	2
Radiation type	Mo $K\alpha$
μ (mm^{-1})	1.43
Crystal size (mm)	$0.7 \times 0.5 \times 0.1$
Data collection	
Diffractometer	Rigaku Pilatus 200K
Absorption correction	Multi-scan (*CrysAlis PRO*; Rigaku OD, 2015)
T_{min}, T_{max}	0.837, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	7932, 1931, 1780
R_{int}	0.024
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.696
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.024, 0.065, 1.07
No. of reflections	1931
No. of parameters	131
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.30, −0.48

Computer programs: *CrysAlis PRO* (Rigaku OD, 2015), *SHELXT* (Sheldrick, 2015*a*), *SHELXL2016* (Sheldrick, 2015*b*) and *OLEX2* (Dolomanov *et al.*, 2009).

Funding information

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full crystallographic data

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Poly[bis(*μ*-4-aminobenzenesulfonato-*κ²N:O*)diaquacobalt(II)]

Crystal data

$[Co(C_6H_6NO_3S)_2(H_2O)_2]$	$F(000) = 450$
$M_r = 439.32$	$D_x = 1.884$ Mg m^{-3}
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 7.0768 (3)$ Å	Cell parameters from 5404 reflections
$b = 5.9601 (3)$ Å	$\theta = 4.5$–$29.6°$
$c = 18.6738 (8)$ Å	$\mu = 1.43$ mm^{-1}
$\beta = 100.494 (4)°$	$T = 293$ K
$V = 774.46 (6)$ Å^3	Block, red
$Z = 2$	$0.7 \times 0.5 \times 0.1$ mm

Data collection

Rigaku Pilatus 200K diffractometer	1931 independent reflections
Detector resolution: 5.8140 pixels mm^{-1}	1780 reflections with $I > 2\sigma(I)$
profile data from ω–scans	$R_{int} = 0.024$
Absorption correction: multi-scan (CrysAlis PRO; Rigaku OD, 2015)	$\theta_{max} = 29.7°$, $\theta_{min} = 4.0°$
$T_{min} = 0.837$, $T_{max} = 1.000$	$h = -9 \rightarrow 8$
7932 measured reflections	$k = -8 \rightarrow 7$
	$l = -25 \rightarrow 22$

Refinement

Refinement on F^2	Hydrogen site location: mixed
Least-squares matrix: full	H atoms treated by a mixture of independent and constrained refinement
$R[F^2 > 2\sigma(F^2)] = 0.024$	
$wR(F^2) = 0.065$	$w = 1/[\sigma^2(F_o^2) + (0.0326P)^2 + 0.403P]$
$S = 1.07$	where $P = (F_o^2 + 2F_c^2)/3$
1931 reflections	$(\Delta/\sigma)_{max} < 0.001$
131 parameters	$\Delta\rho_{max} = 0.30$ e Å^{-3}
0 restraints	$\Delta\rho_{min} = -0.47$ e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
Co1	1.000000	0.500000	0.500000	0.01583 (9)
S1	0.61895 (5)	0.27748 (7)	0.39481 (2)	0.01899 (10)
O1	0.81064 (18)	0.7558 (2)	0.51451 (7)	0.0250 (3)
HO1A	0.761 (3)	0.833 (5)	0.4782 (14)	0.052 (7)*
HO1B	0.727 (4)	0.711 (5)	0.5342 (16)	0.062 (9)*
O2	0.81062 (15)	0.3792 (2)	0.40793 (6)	0.0285 (3)
O3	0.48036 (17)	0.4192 (3)	0.42166 (6)	0.0349 (3)
N1	0.3584 (2)	0.2190 (3)	0.07238 (7)	0.0201 (3)
HN1A	0.245 (3)	0.166 (4)	0.0662 (12)	0.036 (6)*
HN1B	0.359 (3)	0.351 (4)	0.0570 (12)	0.034 (6)*
O4	0.6175 (2)	0.0504 (3)	0.42203 (7)	0.0429 (4)
C1	0.5497 (2)	0.2593 (2)	0.29930 (7)	0.0167 (3)
C2	0.4574 (2)	0.0664 (3)	0.26903 (8)	0.0204 (3)
H2	0.436669	−0.052910	0.298746	0.024*
C3	0.3963 (2)	0.0531 (3)	0.19415 (8)	0.0212 (3)
H3	0.336171	−0.076396	0.173539	0.025*
C5	0.5176 (2)	0.4255 (3)	0.18059 (8)	0.0205 (3)
C4	0.4249 (2)	0.2329 (2)	0.14997 (7)	0.0169 (3)
H5	0.537318	0.545480	0.150979	0.025*
C6	0.5808 (2)	0.4383 (3)	0.25555 (8)	0.0205 (3)
H6	0.643504	0.566272	0.276156	0.025*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Co1	0.01436 (15)	0.02289 (16)	0.00953 (14)	0.00224 (10)	0.00027 (10)	−0.00099 (9)
S1	0.01725 (19)	0.0298 (2)	0.00910 (16)	0.00209 (13)	0.00034 (12)	0.00003 (13)
O1	0.0220 (6)	0.0298 (6)	0.0232 (6)	0.0067 (5)	0.0040 (5)	0.0020 (5)
O2	0.0173 (5)	0.0521 (8)	0.0147 (5)	−0.0029 (5)	−0.0010 (4)	−0.0078 (5)
O3	0.0242 (6)	0.0608 (9)	0.0204 (6)	0.0104 (6)	0.0062 (5)	−0.0093 (6)
N1	0.0209 (7)	0.0273 (7)	0.0110 (6)	−0.0005 (5)	−0.0001 (5)	−0.0003 (5)
O4	0.0648 (10)	0.0370 (7)	0.0220 (6)	−0.0013 (7)	−0.0051 (6)	0.0121 (5)
C4	0.0161 (7)	0.0243 (7)	0.0104 (6)	0.0012 (5)	0.0023 (5)	−0.0012 (5)
C1	0.0146 (6)	0.0245 (7)	0.0106 (6)	0.0009 (5)	0.0010 (5)	−0.0005 (5)
C6	0.0224 (7)	0.0213 (7)	0.0168 (7)	−0.0048 (6)	0.0012 (5)	−0.0023 (6)
C2	0.0226 (7)	0.0233 (7)	0.0151 (6)	−0.0039 (6)	0.0031 (5)	0.0028 (6)
C5	0.0238 (7)	0.0224 (7)	0.0151 (6)	−0.0035 (6)	0.0035 (5)	0.0026 (6)
C3	0.0226 (7)	0.0231 (7)	0.0165 (7)	−0.0060 (6)	−0.0002 (5)	−0.0021 (6)

Geometric parameters (Å, º)

Co1—O1[i]	2.0800 (12)	N1—C4	1.4420 (17)
Co1—O1	2.0800 (12)	N1—HN1A	0.85 (2)
Co1—O2[i]	2.1048 (10)	N1—HN1B	0.84 (2)
Co1—O2	2.1049 (10)	C4—C5	1.392 (2)

Co1—N1ⁱⁱ	2.2424 (14)	C4—C3	1.390 (2)
Co1—N1ⁱⁱⁱ	2.2424 (14)	C1—C6	1.385 (2)
S1—O2	1.4652 (12)	C1—C2	1.391 (2)
S1—O3	1.4512 (13)	C6—H6	0.9300
S1—O4	1.4463 (15)	C6—C5	1.392 (2)
S1—C1	1.7648 (14)	C2—H2	0.9300
O1—HO1A	0.84 (3)	C2—C3	1.389 (2)
O1—HO1B	0.80 (3)	C5—H5	0.9300
N1—Co1ⁱᵛ	2.2424 (13)	C3—H3	0.9300
O1ⁱ—Co1—O1	180.0	Co1ⁱᵛ—N1—HN1A	102.4 (15)
O1ⁱ—Co1—O2	88.42 (5)	Co1ⁱᵛ—N1—HN1B	108.0 (15)
O1ⁱ—Co1—O2ⁱ	91.58 (5)	C4—N1—Co1ⁱᵛ	122.62 (10)
O1—Co1—O2	91.58 (5)	C4—N1—HN1A	106.6 (15)
O1—Co1—O2ⁱ	88.42 (5)	C4—N1—HN1B	105.6 (15)
O1ⁱ—Co1—N1ⁱⁱ	91.20 (6)	HN1A—N1—HN1B	111 (2)
O1ⁱ—Co1—N1ⁱⁱⁱ	88.80 (6)	C5—C4—N1	120.19 (13)
O1—Co1—N1ⁱⁱ	88.80 (6)	C3—C4—N1	119.75 (13)
O1—Co1—N1ⁱⁱⁱ	91.20 (6)	C3—C4—C5	120.05 (13)
O2ⁱ—Co1—O2	180.0	C6—C1—S1	120.28 (11)
O2—Co1—N1ⁱⁱⁱ	89.70 (5)	C6—C1—C2	120.67 (13)
O2—Co1—N1ⁱⁱ	90.30 (5)	C2—C1—S1	119.01 (11)
O2ⁱ—Co1—N1ⁱⁱ	89.70 (5)	C1—C6—H6	120.2
O2ⁱ—Co1—N1ⁱⁱⁱ	90.30 (5)	C1—C6—C5	119.64 (14)
N1ⁱⁱ—Co1—N1ⁱⁱⁱ	180.0	C5—C6—H6	120.2
O2—S1—C1	105.81 (7)	C1—C2—H2	120.2
O3—S1—O2	111.38 (8)	C3—C2—C1	119.59 (14)
O3—S1—C1	107.71 (7)	C3—C2—H2	120.2
O4—S1—O2	113.22 (9)	C4—C5—H5	120.0
O4—S1—O3	112.01 (10)	C6—C5—C4	119.95 (14)
O4—S1—C1	106.22 (8)	C6—C5—H5	120.0
Co1—O1—HO1A	118.7 (17)	C4—C3—H3	120.0
Co1—O1—HO1B	111 (2)	C2—C3—C4	120.09 (14)
HO1A—O1—HO1B	108 (2)	C2—C3—H3	120.0
S1—O2—Co1	135.27 (7)		

Symmetry codes: (i) −x+2, −y+1, −z+1; (ii) x+1/2, −y+1/2, z+1/2; (iii) −x+3/2, y+1/2, −z+1/2; (iv) −x+3/2, y−1/2, −z+1/2.

Hydrogen-bond geometry (Å, º)

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
O1—HO1A⋯O4ᵛ	0.84 (3)	1.85 (3)	2.660 (2)	161 (3)
O1—HO1B⋯O3ᵛⁱ	0.80 (3)	1.97 (3)	2.7647 (18)	176 (3)
N1—HN1A⋯O3ᵛⁱⁱ	0.85 (2)	2.21 (2)	3.008 (2)	156 (2)
N1—HN1B⋯O1ᵛⁱⁱⁱ	0.84 (2)	2.48 (2)	3.309 (2)	171 (2)
C3—H3⋯O3ᵛⁱⁱ	0.93	2.59	3.2123 (19)	124
C5—H5⋯O2ⁱⁱⁱ	0.93	2.60	3.501 (2)	163

Symmetry codes: (iii) −x+3/2, y+1/2, −z+1/2; (v) x, y+1, z; (vi) −x+1, −y+1, −z+1; (vii) −x+1/2, y−1/2, −z+1/2; (viii) x−1/2, −y+3/2, z−1/2.