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Hexaaquacobalt(II) bis(4-toluenesulfonate)

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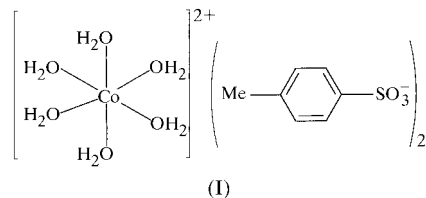
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The title compound, $[\text{Co}(\text{H}_2\text{O})_6](\text{CH}_3\text{C}_6\text{H}_4\text{SO}_3)_2$, has a structure where the metal atom is surrounded by six molecules of water forming the cation and the anion is deprotonated 4-toluenesulfonic acid. The Co atom is in a nearly regular octahedral coordination geometry, with Co–O distances between 2.0529 (14) and 2.0810 (16) Å, and angles ranging from 87.25 (9) to 92.75 (9)°. The supramolecular structure consists of parallel layers of cations and anions. The anions are arranged with their sulfonate groups directed towards the cation layer in an alternating fashion and form hydrogen bonds with the water molecules of the cation.

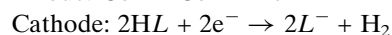
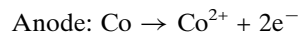
Comment

The structural features of transition and non-transition metal organosulfonate salts have been studied in the last few years (Gunderman, Kabell *et al.*, 1997; Leonard *et al.*, 1999). In our group, research has been directed towards the electrochemical synthesis of neutral sulfonamide metal complexes. Neutral complexes can be easily obtained when a sacrificial anode is oxidized in a cell containing an appropriate proligand with a weak acidic character, *e.g.* sulfonamides (Cabaleiro *et al.*, 1999).



The title compound, (I), was obtained (see *Experimental*) by electrolysis of a solution of 4-toluenesulfonic acid monohydrate in a mixture of acetonitrile and dichloromethane of commercial grade, using a cobalt plate as the anode. The value

of the electrochemical efficiency, defined as the amount of cobalt dissolved per number of Faradays, was close to 0.5 mol F⁻¹. This fact and the formation of hydrogen gas at the cathode are compatible with a reaction mechanism involving the anodic oxidation to cobalt(II) and the deprotonation of the ligand at the cathode,



where HL and L⁻ are 4-toluenesulfonic acid and its anion, respectively.

The isolated compound consists of a hexaaquacobalt(II) cation and the 4-toluenesulfonate anion. Its main features are similar to those of other sulfonate derivatives (Gunderman, Dubey & Squatrrito, 1997). There is no direct bonding between the Co atom and the O atoms of the anion, but there are important hydrogen bonds joining the cation and the anion. The Co atom is on a centre of inversion, in an octahedral geometry, with Co–O distances ranging between 2.0529 (14) and 2.0810 (16) Å, and angles ranging from 87.25 (9) to 92.75 (7)°.

The structure is composed of alternating layers of cations and anions. A similar compound with benzenesulfonate anions was described previously by Kosnic *et al.* (1996). The rows of anions are canted in opposite directions with the sulfonate groups pointing towards the cations. In the title compound, each phenyl ring forms with its neighbour in another row a dihedral angle of 37.00 (6)°. The distance between the theoretical centres of two neighbouring rings is rather long, between 4.982 and 4.988 Å.

Packing is provided by an interaction between the sulfonyl groups and the aqua ligands of the cation *via* strong almost linear hydrogen bonds involving all the H atoms of the aqua cation (see the geometric parameters).

The *a* and *b* unit-cell parameters of (I) are similar to those found in the benzenesulfonate salt (Kosnic *et al.*, 1996) and other substituted phenyl sulfonates (Gunderman, Dubey & Squatrrito, 1997; Leonard *et al.*, 1999). As a consequence of the substitution in the phenyl ring, there is a progressive increase of the interlayer spacing [calculated as $(\frac{1}{2}\text{c}\sin\beta)$, with values of 11.21 Å for benzenesulfonate (Kosnic *et al.*, 1996), 12.24 Å for 2-amino-4-toluenesulfonate (Gunderman, Dubey & Squatrrito, 1997), 12.61 Å for the title compound and 13.41 Å for 4-styrenesulfonate (Leonard *et al.*, 1999)].

Experimental

The electrochemical oxidation of a cobalt anode in an acetonitrile/dichloromethane solution (25 + 25 ml) containing 4-toluenesulfonic acid monohydrate (237.8 mg, 1.38 mmol) and tetramethylammonium perchlorate (*ca* 10 mg) for 2 h at 8 V and 10 mA, resulted in a loss of 21.5 mg of cobalt from the anode and the formation of a pink solution. Concentration by slow evaporation at room temperature gave a well crystallized solid which was identified as the title compound. Analysis found: C 33.0, H 4.9, S 12.2%; calculated for C₁₄H₂₆CoO₁₂S₂: C 33.0, H 5.1, S 12.6%.

Crystal data

[Co(H₂O)₆](C₇H₇O₃S)₂
M_r = 509.40
 Monoclinic, *P*2₁/*n*
a = 6.9867 (1) Å
b = 6.3049 (1) Å
c = 25.2330 (1) Å
 β = 91.7544 (8)°
V = 1111.00 (2) Å³
Z = 2

D_x = 1.523 Mg m⁻³
 Mo *K*α radiation
 Cell parameters from 54 reflections
 θ = 3–27°
 μ = 1.016 mm⁻¹
T = 293 (2) K
 Plate, pink
 0.55 × 0.45 × 0.05 mm

Data collection

Siemens CCD diffractometer
 ω scans
 Absorption correction: empirical
 (*SADABS*; Sheldrick, 1996)
T_{min} = 0.567, *T_{max}* = 0.953
 7307 measured reflections
 2753 independent reflections
 2430 reflections with *I* > 2σ(*I*)

R_{int} = 0.032
 θ_{max} = 28.28°
h = -9 → 8
k = -8 → 6
l = -33 → 32
 50 first frames standard reflections
 every set of frames reflections
 intensity decay: 0.37%

Refinement

Refinement on *F*²
R [*F*² > 2σ(*F*²)] = 0.036
wR (*F*²) = 0.098
S = 1.012
 2753 reflections
 185 parameters
 H atoms treated by a mixture of
 independent and constrained
 refinement

w = 1/[σ²(*F_o*²) + (0.0578*P*)²
 + 0.2261*P*]
 where *P* = (*F_o*² + 2*F_c*²)/3
 (Δ/σ)_{max} = 0.006
 Δρ_{max} = 0.28 e Å⁻³
 Δρ_{min} = -0.52 e Å⁻³

Table 1

Selected geometric parameters (Å, °).

Co—O1 <i>W</i>	2.0529 (14)	Co—O3 <i>W</i>	2.0810 (16)
Co—O2 <i>W</i>	2.0770 (16)		
O1 <i>W</i> —Co—O2 <i>W</i> ⁱ	89.10 (7)	O2 <i>W</i> —Co—O3 <i>W</i> ⁱ	87.25 (9)
O1 <i>W</i> —Co—O2 <i>W</i>	90.90 (7)	O1 <i>W</i> —Co—O3 <i>W</i>	91.10 (7)
O1 <i>W</i> —Co—O3 <i>W</i> ⁱ	88.90 (7)	O2 <i>W</i> —Co—O3 <i>W</i>	92.75 (9)

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

H atoms in the anion were refined using a riding model (*HFIX*43 for aromatic and *HFIX*137 for methyl groups). Aqua H atoms of the cation were located on difference electron-density maps and were refined with the distance O—H fixed at 0.82 Å.

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>
O1 <i>W</i> —H1 <i>A</i> ...O2 ⁱ	0.823 (16)	1.934 (17)	2.756 (2)	179 (3)
O1 <i>W</i> —H1 <i>B</i> ...O3 ⁱⁱ	0.821 (17)	1.925 (17)	2.745 (2)	177 (3)
O2 <i>W</i> —H2 <i>A</i> ...O2	0.773 (17)	2.008 (17)	2.767 (2)	167 (3)
O1 <i>W</i> —H1 <i>A</i> ...O1 ⁱ	0.823 (16)	3.24 (2)	3.845 (2)	132 (2)
O3 <i>W</i> —H3 <i>A</i> ...O3 ⁱⁱⁱ	0.809 (13)	1.968 (14)	2.773 (2)	174 (3)
O3 <i>W</i> —H3 <i>B</i> ...O1 ⁱⁱ	0.82 (4)	1.98 (4)	2.795 (2)	178 (3)

Symmetry codes: (i) *x*, *y* - 1, *z*; (ii) *x* - 1, *y* - 1, *z*; (iii) *x* - 1, *y*, *z*.

Data collection: *SMART* (Siemens, 1995); cell refinement: *SMART*; data reduction: *SAINT* (Siemens, 1996); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); software used to prepare material for publication: *SHELXL97*.

Intensity measurements were performed at the SXAIN, Universidade de A. Coruña. All crystallographic calculations were performed at the site angus.uvigo.es (<http://angus.uvigo.es>). This study was carried out with financial support from the Xunta de Galicia (XUGA 20302B97).

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