Molecular Structure Corporation (1985). *TEXSAN. TEXRAY Structure Analysis Package*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
Molecular Structure Corporation (1988). *MSC/AFC Diffractometer Control Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
Mullica, D. F., Sappenfield, E. L., Tippin, D. B. & Leschnitzer, D. H. (1989). *Inorg. Chim. Acta*, **164**, 99–103.
Mullica, D. F., Tippin, D. B. & Sappenfield, E. L. (1990). *Inorg. Chim. Acta*, **174**, 129–135.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
Siemens (1994). *XP. Molecular Graphics Program*. Version 5.03. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Acta Cryst. (1997). C**53**, 17–19

Hexaaquacobalt(II) Bis(2-aminotoluene-4-sulfonate)

BRIAN J. GUNDERMAN,[a] SURENDRA N. DUBEY[b] AND PHILIP J. SQUATTRITO[a]*

[a]*Department of Chemistry, Central Michigan University, Mount Pleasant, Michigan 48859, USA, and* [b]*Department of Chemistry, Kurukshetra University, Kurukshetra 132119, Haryana, India. E-mail: 3clwp5s@cmuvm.csv.cmich.edu*

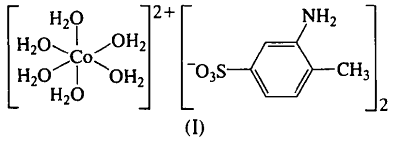
(*Received 22 July 1996; accepted 16 September 1996*)

Abstract

The title compound, $[Co(H_2O)_6](C_7H_8NO_3S)_2$, has a structure built of segregated layers of hexaaquacobalt(II) cations and 2-aminotoluene-4-sulfonate anions. The Co atom is in a fairly regular octahedral coordination environment of water molecules [Co—O range 2.046 (3)–2.111 (3) Å]. The anions are arranged with the sulfonate groups directed to opposite faces of the layer in an alternating fashion. The layers are held together by a series of O—H···O hydrogen bonds between the water molecules and sulfonate O atoms [H···O range 1.89 (4)–2.10 (4) Å]. The Mn and Zn salts are isostructural. These features are similar to those of other divalent metal organosulfonate salts.

Comment

The title compound, (I), was prepared and characterized as part of a larger study (Shubnell, Kosnic & Squattrito, 1994) of the coordination behavior and structural trends of transition metal organosulfonate salts. Our studies (Kosnic, McClymont, Hodder & Squattrito, 1996) and others (Aquino, Clegg, Liu & Sykes, 1995; Couldwell, Prout, Robey, Taylor & Rossotti, 1978; Henderson & Nicholson, 1995) have shown that the first-row transition metal cations tend to crystallize as hexaaqua complexes in the presence of a variety of organosulfonate anions. The resulting structures have alternating layers of hexaaqua cations and organosulfonate anions. The anions are usually interleaved, having the sulfonate groups directed to both faces of the layer, though double layers are also sometimes observed. The layers are held together by hydrogen bonding between the coordinated water molecules and sulfonate O atoms. One sulfonate which does readily coordinate to transition metal cations is sulfanilate (4-aminobenzenesulfonate), which forms structures in which the anion layers are linked by direct bonding between the metal and both sulfonate O and amine N atoms (Shakeri & Haussuhl, 1992*a*; Gunderman, Squattrito & Dubey, 1996). Consequently, we were interested in the reactions of other amino-substituted benzenesulfonic acids and the possibility of obtaining structures similar to those of the sulfanilate salts.



(I)

The cobalt 2-aminotoluene-4-sulfonate salt has no direct bonding between the Co atom and the O or N atoms of the anion (Fig. 1). The cation rests on a center of inversion in a fairly regular octahedral environment of water molecules. Although there is some variation in the Co—O bond distances (Table 2), they are all within the reported range for $[Co(H_2O)_6]^{2+}$ complexes (Cotton, Daniels, Murillo & Quesada, 1993). The geometry of the sulfonate anion is as expected and similar to that of the parent acid (Shubnell & Squattrito, 1994). The extended structure of this salt (Fig. 2) has its essential features in common with the previously reported structures of non-coordinating sulfonates. The hexaaqua complexes form planar layers in between slabs of anions. The phenyl rings of the anions are approximately perpendicular to the plane of the layer. Alternating anions have the sulfonate group directed to the opposite face of the layer, with the long axes of the anions canted slightly in opposite directions. This packing affords the formation of a short almost linear O—H···$O_{sulfonate}$ hydrogen bond involving each water H atom (Table 3). The amine groups are somewhat in the interior of the layer and the H atoms have no short contacts (< 2.3 Å) with the O atoms. The Mn and Zn salts are isostructural with the Co salt on the basis of their unit-cell parameters [Mn: a = 7.095 (2), b = 6.301 (2), c = 24.715 (8) Å, β = 90.07 (2)°; Zn: a = 7.012 (2), b = 6.271 (2), c = 24.455 (5) Å, β = 90.17 (2)°] and Laue symmetry as determined in this laboratory.

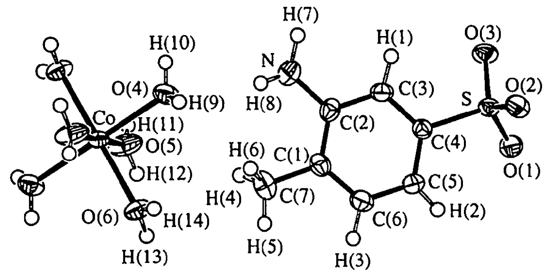


Fig. 1. An *ORTEP*II diagram (Johnson, 1976) showing the 2-aminotoluene-4-sulfonate, the coordination sphere around the Co atom and the atom-labelling scheme. The displacement ellipsoids of the non-H atoms are shown at the 50% probability level.

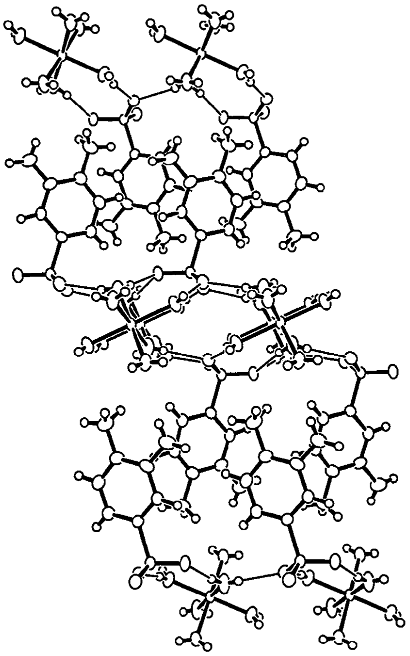


Fig. 2. An *ORTEP*II diagram (Johnson, 1976) showing the crystal packing as viewed down the *a* axis with the *c* axis vertical. Hydrogen bonds are shown by narrow lines. The displacement ellipsoids of the non-H atoms are shown at the 50% probability level.

A comparison of (I) with the structures of hexaaquacobalt(II) benzenesulfonate (Kosnic *et al.*, 1996) and hexaaquamagnesium sulfanilate (Shakeri & Haussuhl, 1992*b*) shows that all have the same space group and almost the same *a* and *b* cell lengths. Moreover, a progressive lengthening in the *c* axis corresponds to an increase in the interlayer spacing (benzenesulfonate 11.21, sulfanilate 12.08 and 2-aminotoluene-4-sulfonate 12.24 Å) due to the substitution of the phenyl ring. These observations indicate that the layers are essentially the same in these compounds. The packing within the layers is evidently driven primarily by the water–sulfonate interactions and is not significantly affected by the presence of relatively small substituents on the phenyl rings.

Experimental

An aggregate of large red slab-like crystals with irregular six-sided faces grew upon evaporation of solvent from a water–methanol (80:20 by volume) solution of 4.98 g cobalt acetate tetrahydrate and 3.75 g 2-aminotoluene-4-sulfonic acid monohydrate. A total of 4.80 g of (I) was isolated from this reaction.

Crystal data

$[Co(H_2O)_6](C_7H_8NO_3S)_2$
$M_r = 539.43$
Monoclinic
$P2_1/n$
$a = 7.046\ (4)$ Å
$b = 6.287\ (4)$ Å
$c = 24.486\ (5)$ Å
$\beta = 90.04\ (4)°$
$V = 1084.7\ (8)$ Å^3
$Z = 2$
$D_x = 1.651$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.7107$ Å
Cell parameters from 24 reflections
$\theta = 11.6–17.7°$
$\mu = 1.034$ mm^{-1}
$T = 296$ K
Slab
0.30 × 0.25 × 0.20 mm
Dark red

Data collection

Rigaku AFC-6*S* diffractometer
ω scans
Absorption correction: empirical *via* ψ scans of three reflections (North, Phillips & Mathews, 1968)
$T_{min} = 0.704$, $T_{max} = 0.813$
2280 measured reflections
2098 independent reflections

1349 observed reflections $[I > 3\sigma(I)]$
$R_{int} = 0.035$
$\theta_{max} = 25°$
$h = 0 \rightarrow 8$
$k = 0 \rightarrow 7$
$l = -28 \rightarrow 28$
3 standard reflections monitored every 150 reflections
intensity decay: 0.30%

Refinement

Refinement on *F*
$R = 0.032$
$wR = 0.030$
$S = 1.76$
1349 reflections
184 parameters
Only coordinates of H atoms refined
$w = 4F_o^2/\sigma^2(F_o^2)$

$(\Delta/\sigma)_{max} = 0.0011$
$\Delta\rho_{max} = 0.34$ e Å^{-3}
$\Delta\rho_{min} = -0.34$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Co	1	0	1/2	0.0235 (2)
S	1.0168 (1)	0.1042 (2)	0.09493 (4)	0.0250 (3)
O(1)	0.8543 (3)	0.0143 (4)	0.06654 (9)	0.0327 (7)
O(2)	1.1966 (3)	0.0162 (4)	0.07542 (9)	0.0344 (7)
O(3)	1.0168 (3)	0.3370 (4)	0.09380 (10)	0.0329 (8)
O(4)	1.1793 (4)	0.1024 (4)	0.4362 (1)	0.0375 (9)
O(5)	0.7552 (4)	0.0981 (5)	0.4593 (1)	0.0457 (10)
O(6)	0.9812 (4)	−0.2953 (4)	0.4653 (1)	0.0351 (8)
N	1.0895 (5)	0.2326 (7)	0.3017 (1)	0.047 (1)

C(1)	0.9750 (5)	−0.1129 (7)	0.2718 (2)	0.030 (1)
C(2)	1.0424 (5)	0.0921 (7)	0.2602 (2)	0.030 (1)
C(3)	1.0534 (5)	0.1594 (6)	0.2057 (2)	0.029 (1)
C(4)	0.9965 (5)	0.0244 (6)	0.1643 (1)	0.0246 (10)
C(5)	0.9313 (5)	−0.1788 (6)	0.1752 (2)	0.032 (1)
C(6)	0.9209 (5)	−0.2426 (7)	0.2293 (2)	0.034 (1)
C(7)	0.9568 (7)	−0.1862 (8)	0.3304 (2)	0.043 (1)

Table 2. *Selected geometric parameters (Å, °)*

Co—O(4)	2.111 (3)	S—O(2)	1.463 (2)
Co—O(5)	2.085 (3)	S—O(3)	1.464 (2)
Co—O(6)	2.046 (3)	S—C(4)	1.776 (3)
S—O(1)	1.454 (2)	N—C(2)	1.387 (5)
O(4)—Co—O(5)	92.9 (1)	O(2)—S—C(4)	106.0 (2)
O(4)—Co—O(6)	90.5 (1)	O(3)—S—C(4)	107.5 (2)
O(5)—Co—O(6)	90.9 (1)	N—C(2)—C(1)	121.1 (4)
O(1)—S—O(2)	112.3 (2)	N—C(2)—C(3)	119.5 (4)
O(1)—S—O(3)	112.3 (2)	S—C(4)—C(3)	120.3 (3)
O(1)—S—C(4)	106.5 (2)	S—C(4)—C(5)	118.2 (3)
O(2)—S—O(3)	111.8 (2)		

Table 3. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O(4)—H(9)···O(3^{i})	0.84 (4)	1.97 (4)	2.813 (4)	176 (4)
O(4)—H(10)···O(2^{ii})	0.80 (4)	1.97 (4)	2.759 (4)	168 (4)
O(5)—H(11)···O(1^{iii})	0.71 (4)	2.10 (4)	2.800 (4)	173 (5)
O(5)—H(12)···O(3^{iv})	0.86 (4)	1.98 (4)	2.838 (4)	174 (4)
O(6)—H(13)···O(1^{iv})	0.88 (4)	1.89 (4)	2.762 (4)	174 (3)
O(6)—H(14)···O(2^{i})	0.83 (4)	1.92 (4)	2.749 (4)	172 (4)

Symmetry codes: (i) $\frac{5}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$; (ii) $\frac{5}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$; (iii) $\frac{3}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$; (iv) $\frac{3}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$.

A statistical comparison of the intensities of 18 $hkl/\bar{h}kl$ pairs prior to data collection revealed the absence of a mirror plane perpendicular to **a**, confirming the crystal system as monoclinic. Phenyl C—C distances were in the range 1.375 (5)–1.403 (5), with a mean of 1.389 (5) Å. All H atoms were located on difference electron-density maps and their positions refined with fixed isotropic *B* values equal to 1.2 times those of the attached atoms at the time of their inclusion. Bond distances were C—H 0.89 (3)–1.02 (4), N—H(7) 0.96 (4) and N—H(8) 0.85 (4) Å.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1991). Program(s) used to solve structure: *MITHRIL* (Gilmore, 1983). Program(s) used to refine structure: *TEXSAN*. Software used to prepare material for publication: *TEXSAN*.

The Center for International Education and the College of Arts and Sciences at Central Michigan University provided funding to support SND's stay at CMU. The Herbert H. and Grace A. Dow Foundation and The Dow Chemical Company Foundation provided funding for the establishment of the CMU X-ray facility.

Lists of structure factors, least-squares-planes data, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: FR1012). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Aquino, M. A. S., Clegg, W., Liu, Q. & Sykes, A. G. (1995). *Acta Cryst.* C**51**, 560–562.
Cotton, F. A., Daniels, L. M., Murillo, C. A. & Quesada, J. F. (1993). *Inorg. Chem.* **32**, 4861–4867.
Couldwell, C., Prout, K., Robey, D., Taylor, R. & Rossotti, F. J. C. (1978). *Acta Cryst.* B**34**, 1491–1499.
Gilmore, C. J. (1983). *MITHRIL. Computer Program for the Automatic Solution of Crystal Structures from X-ray Data.* Department of Chemistry, University of Glasgow, Scotland.
Gunderman, B. J., Squattrito, P. J. & Dubey, S. N. (1996). *Acta Cryst.* C**52**, 1131–1134.
Henderson, W. & Nicholson, B. K. (1995). *Acta Cryst.* C**51**, 37–40.
Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Kosnic, E. J., McClymont, E. L., Hodder, R. A. & Squattrito, P. J. (1996). *Inorg. Chim. Acta*, **244**, 253–254.
Molecular Structure Corporation (1988). *MSC/AFC Diffractometer Control Software.* MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
Molecular Structure Corporation (1991). *TEXSAN. TEXRAY Structure Analysis Package.* MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.
Shakeri, V. & Haussuhl, S. (1992*a*). *Z. Kristallogr.* **198**, 165–166.
Shakeri, V. & Haussuhl, S. (1992*b*). *Z. Kristallogr.* **198**, 169–170.
Shubnell, A. J., Kosnic, E. J. & Squattrito, P. J. (1994). *Inorg. Chim. Acta*, **216**, 101–112.
Shubnell, A. J. & Squattrito, P. J. (1994). *Acta Cryst.* C**50**, 1296–1299.

Acta Cryst. (1997). C**53**, 19–22

[2,2,2-Crypt-Na]$_2$[Cr$_2$(CO)$_{10}$]: a Chromium(−1) Carbonyl Structure with a Very Weakly Coordinating Cation

Horst Borrmann,[a] Ayaaz M. Pirani[b] and Gary J. Schrobilgen[b]

[a]*Max Planck Institut für Festkörperforschung, Heisenbergstrasse 1, Stuttgart D-70569, Germany, and* [b]*Department of Chemistry, McMaster University, Hamilton, Ontario L8S 4M1, Canada. E-mail: schrobil@mcmail.cis.mcmaster.ca*

(*Received 22 July 1996; accepted 16 September 1996*)

Abstract

The title compound, bis[(1,10-diaza-4,7,13,16,21,24-hexaoxabicyclo[8.8.8]hexacosane)sodium(+)] decacarbonyldichromate(*Cr*—*Cr*)(2−), [Na($C_{18}H_{36}N_2O_6$)]$_2$[Cr$_2$(CO)$_{10}$], has been prepared by the reduction of [Cr(CO)$_6$] with Na$_2$Tl in dimethylformamide followed by the addition of the macrobicyclic ligand 2,2,2-crypt in ethylenediamine (en) solvent. The geometric parameters observed for the anion in the title salt differ significantly from those reported previously for the DME-solvated (DME = 1,2-dimethoxyethane) K$^+$ and