Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

mer-(4-Aminobenzenesulfonato-κN)triaqua(1,10-phenanthroline-$\kappa^2 N,N'$)cobalt(**II**) chloride

Ming-Hua Huang, Li-Hua Bi and Shao-Jun Dong*

State Key Laboratory of Electroanalytical Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun, Jilin 130022, People's Republic of China
Correspondence e-mail: dongsj@ns.ciac.jl.cn

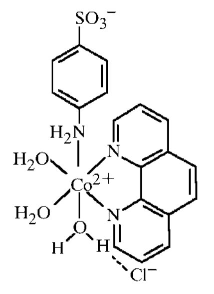
Received 29 October 2003
Accepted 24 November 2003
Online 20 December 2003

Both coordination and hydrogen bonds contribute to networking in the supramolecular title compound, $[Co(C_6H_6NO_3S)(C_{12}H_8N_2)(H_2O)_3]Cl$, which contains a discrete $[Co(C_6H_6NO_3S)(C_{12}H_8N_2)(H_2O)_3]^+$ complex cation, formed by one 4-aminobenzenesulfonate ligand, one 1,10-phenanthroline ligand and three coordinated water molecules, together with one uncoordinated chloride anion. These discrete cations and chloride anions are connected by hydrogen-bonding interactions into a two-dimensional supramolecular motif. Further hydrogen-bonding interactions consolidate the structural architecture and extend the two-dimensional supramolecular structure into a three-dimensional network.

Comment

Supramolecular frameworks based on metal and organic building blocks that contain diverse topologies with desired features are receiving increasing attention because of their promising potential uses in catalysis (Fujita *et al.*, 1994), gas storage (Kitaura *et al.*, 2003) and magnetism (Inoue *et al.*, 1996). However, there have been few reports of metal-based organosulfonate anions containing supramolecular compounds to date (Cai, Chen, Feng *et al.*, 2001; Cai, Chen, Liao *et al.*, 2001; Wang *et al.*, 2002). We present here a novel compound, $[Co(C_6H_6NO_3S)(C_{12}H_8N_2)(H_2O)_3]Cl$, (I), built from discrete $[Co(C_6H_6NO_3S)(C_{12}H_8N_2)(H_2O)_3]^+$ cations, each formed by one 4-aminobenzenesulfonate (4-abs) ligand, one 1,10-phenanthroline (1,10-phen) ligand and three coordinated water molecules, together with one uncoordinated chloride anion.

As depicted by Fig. 1, the Co^{II} center exhibits a slightly distorted octahedral coordination geometry, defined by three aqua O atoms [Co—O*W*1 = 2.065 (2) Å, Co—O*W*2 = 2.083 (2) Å and Co—O*W*3 = 2.091 (2) Å], two N atoms from a 1,10-phen ligand [Co—N1 = 2.119 (2) Å and Co—N2 = 2.116 (2) Å] and an N-atom donor from a 4-abs ligand [Co—N3 = 2.270 (2) Å; Table 1]. The coordination environment and mode of coordination of 4-abs differ from that observed in $[Co(4\text{-abs})_2(4,4'\text{-bipy})(H_2O)_4]\cdot H_2O$ (Wang *et al.*, 2002), in which the 4-abs ligands are not coordinated to Co^{II} and form one-dimensional head-to-tail zigzag chains *via* hydrogen-bonding interactions. The rings of the 4-abs and 1,10-phen groups are not completely parallel to one another, the dihedral angle between their planes being 12.6° and the average ring separation being 3.324 Å.



(I)

As shown in Fig. 2, the discrete $[Co(C_6H_6NO_3S)(C_{12}H_8N_2)(H_2O)_3]^+$ cations and chloride anions are connected into a two-dimensional supramolecular motif. The rings of two

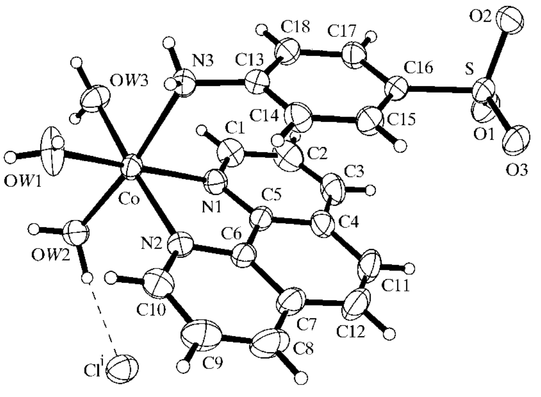


Figure 1
The molecular structure of the title compound, with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. (The symmetry code is as in Table 2.)

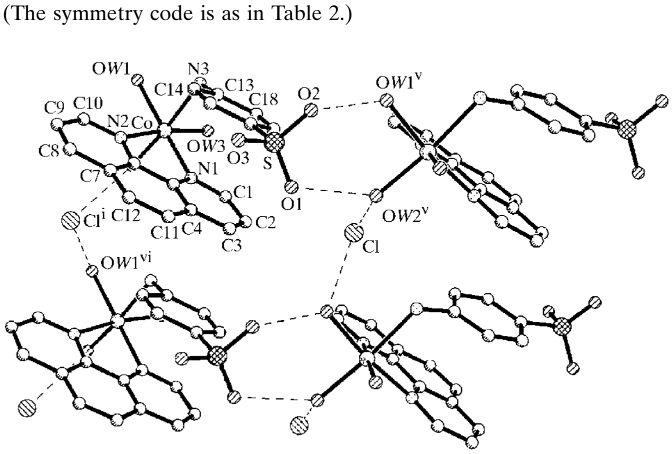


Figure 2
The two-dimensional network of $[Co(4\text{-abs})(1,10\text{-phen})(H_2O)_3]^+$ cations and chloride anions formed *via* hydrogen-bonding interactions. The symmetry codes are as in Table 2, plus (v) $x-\frac{1}{2}, \frac{1}{2}-y, z-\frac{1}{2}$; (vi) $1+x, y, z$.

DOI: 10.1107/S0108270103026957

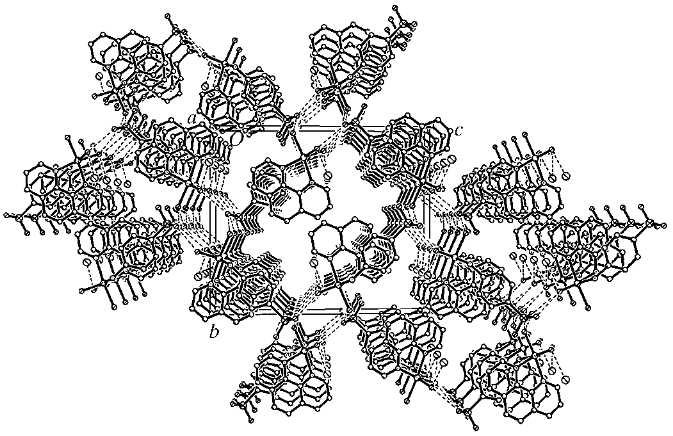


Figure 3
A packing diagram, showing the three-dimensional structure viewed along the *a* axis.

4-abs and two 1,10-phen ligands from two different discrete cations lie parallel to one another. In the supramolecular architecture, unusual hydrogen-bonding interactions play a crucial role. The O*W*2 and O*W*1 water molecules from one $[\mathrm{Co(4\text{-}abs)(1,10\text{-}phen)(H_2O)_3}]^+$ cation interact with the $\mathrm{SO_3}^-$ group of the 4-abs ligand from another, thus forming hydrogen-bonding interactions [O*W*2···O1$^{\rm i}$ = 2.875 (3) Å and O*W*1···O2$^{\rm i}$ = 2.664 (3) Å; see Table 2 for all symmetry codes]. Furthermore, the O*W*2 and O*W*1 water molecules from two adjacent cations are bridged *via* hydrogen-bonding interactions with a chloride anion [Cl$^{\rm ii}$···O*W*1 = 3.072 (2) Å and Cl$^{\rm i}$···O*W*2 = 3.018 (2) Å]. In addition, there are hydrogen-bonding interactions between the O*W*3 water molecules and the $\mathrm{SO_3}^-$ groups of 4-abs anions from two adjacent building blocks [O1$^{\rm iv}$···O*W*3 = 2.824 (3) Å and O2$^{\rm iii}$···O*W*3 = 2.748 (3) Å]. Therefore, such hydrogen-bonding interactions consolidate the structural architecture and further extend the two-dimensional supramolecular structure into a three-dimensional network (see Fig. 3).

Experimental

To an aqueous solution of $\mathrm{CoCl_2{\cdot}6H_2O}$ (0.2379 g, 1.00 mmol) was added 4-aminobenzenesulfonic acid (0.074 g, 0.54 mmol) with stirring at 298 K. After the pH of the solution had been adjusted to ~5.5 with dilute NaOH, 1,10-phen (0.078 g, 0.50 mmol) was added slowly and the mixture was stirred for 30 min at 333 K. After filtration, a clear orange solution was obtained, which was allowed to stand at room temperature. Orange crystals were obtained after two weeks.

Crystal data

$[\mathrm{Co(C_6H_6NO_3S)(C_{12}H_8N_2)}$-
$\mathrm{(H_2O)_3]Cl}$
M_r = 500.81
Monoclinic, $P2_1/n$
a = 7.0148 (10) Å
b = 15.896 (4) Å
c = 18.587 (5) Å
β = 96.548 (18)°
V = 2059.0 (8) Å^3

Z = 4
D_x = 1.616 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 24 reflections
θ = 5.2–10.2°
μ = 1.11 mm^{-1}
T = 293 (2) K
Block, orange
0.50 × 0.38 × 0.32 mm

Data collection

Siemens *P*4 diffractometer
ω scans
Absorption correction: ψ scan
(*SHELXTL*; Siemens, 1994)
$T_{\rm min}$ = 0.561, $T_{\rm max}$ = 0.687
5562 measured reflections
4060 independent reflections
2959 reflections with $I > 2\sigma(I)$

$R_{\rm int}$ = 0.026
$\theta_{\rm max}$ = 26.0°
$h = -1 \rightarrow 8$
$k = -1 \rightarrow 19$
$l = -22 \rightarrow 22$
3 standard reflections
every 97 reflections
intensity decay: 8.0%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.034
$wR(F^2)$ = 0.073
S = 1.09
4060 reflections
271 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.02P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max}$ = 0.001
$\Delta\rho_{\rm max}$ = 0.31 e Å^{-3}
$\Delta\rho_{\rm min}$ = −0.37 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Co—O*W*1	2.065 (2)	S—O3	1.4415 (18)
Co—O*W*2	2.083 (2)	S—C16	1.767 (2)
Co—O*W*3	2.091 (2)	N1—C1	1.329 (3)
Co—N1	2.119 (2)	N1—C5	1.361 (3)
Co—N2	2.116 (2)	N2—C10	1.333 (3)
Co—N3	2.270 (2)	N2—C6	1.360 (3)
S—O1	1.461 (2)	N3—C13	1.428 (3)
S—O2	1.469 (2)		
O*W*1—Co—O*W*2	90.81 (8)	O2—S—C16	105.35 (12)
O*W*1—Co—O*W*3	92.55 (8)	O3—S—C16	106.85 (11)
O*W*1—Co—N1	170.16 (8)	Co—N1—C5	112.67 (16)
O*W*1—Co—N2	94.96 (8)	C1—N1—C5	117.8 (2)
O*W*1—Co—N3	82.49 (8)	Co—N1—C1	128.30 (18)
O*W*2—Co—O*W*3	86.49 (8)	C6—N2—C10	117.8 (2)
O*W*2—Co—N1	96.43 (8)	Co—N2—C6	113.19 (16)
O*W*2—Co—N2	92.36 (8)	Co—N2—C10	128.86 (18)
O*W*2—Co—N3	172.50 (8)	Co—N3—C13	118.20 (17)
O*W*3—Co—N1	94.52 (8)	N1—C1—C2	122.4 (3)
O*W*3—Co—N2	172.41 (8)	N1—C5—C6	117.1 (2)
O*W*3—Co—N3	90.43 (8)	N1—C5—C4	123.3 (2)
N1—Co—N2	78.14 (8)	N2—C6—C5	117.1 (2)
N1—Co—N3	90.62 (8)	N2—C6—C7	122.8 (2)
N2—Co—N3	91.58 (8)	N2—C10—C9	122.4 (2)
O1—S—O2	111.23 (11)	N3—C13—C18	120.4 (2)
O1—S—O3	114.76 (12)	N3—C13—C14	120.1 (2)
O1—S—C16	106.28 (12)	S—C16—C15	119.86 (18)
O2—S—O3	111.67 (12)	S—C16—C17	120.25 (19)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O*W*1—H*W*1···O2$^{\rm i}$	0.84	1.82	2.664 (3)	177
O*W*1—H*W*2···Cl$^{\rm ii}$	0.95	2.17	3.072 (2)	158
O*W*2—H*W*3···Cl$^{\rm i}$	0.97	2.06	3.018 (2)	170
N3—H3*A*···O3$^{\rm iii}$	0.90	2.18	3.062 (3)	167
N3—H3*B*···Cl$^{\rm ii}$	0.90	2.53	3.392 (2)	160
O*W*2—H*W*4···O1$^{\rm i}$	0.90	2.01	2.875 (3)	161
O*W*3—H*W*5···O2$^{\rm iii}$	0.91	1.84	2.748 (3)	174
O*W*3—H*W*6···O1$^{\rm iv}$	0.93	1.90	2.824 (3)	170

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

Water H atoms were located from difference maps and their positions were fixed during refinement. Other H atoms were placed in geometric positions using a riding model, with C—H distances of 0.93 Å and N—H distances of 0.90 Å, and with $U_{\rm iso}$(H) values equal to $1.2U_{\rm eq}$(C, N).

Data collection: *XSCANS* (Siemens, 1994); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXTL* (Siemens, 1994); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

This work was supported by the National Natural Science Foundation of China (grant Nos. 20275036 and 2021130506).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1550). Services for accessing these data are described at the back of the journal.

References

Cai, J. W., Chen, C. H., Feng, X. L., Liao, C. Z. & Chen, X. M. (2001). *J. Chem. Soc. Dalton Trans.* pp. 2370–2375.

Cai, J. W., Chen, C. H., Liao, C. Z., Yao, J. H., Hu, H. P. & Chen, X. M. (2001). *J. Chem. Soc. Dalton Trans.* pp. 1137–1142.

Fujita, M., Kwon, Y. J., Washizu, S. & Ogura, K. (1994). *J. Am. Chem. Soc.* **116**, 1151–1152.

Inoue, K., Hayamizu, T., Iwamura, H., Hashizume, D. & Ohashi, Y. (1996). *J. Am. Chem. Soc.* **118**, 1803–1804.

Kitaura, R., Seki, K., Akiyama, G. & Kitagawa, S. (2003). *Angew. Chem. Int. Ed.* **42**, 428–431.

Siemens (1994). *XSCANS* (Version 2.1) and *SHELXTL* (Release 5.03). Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Wang, Y. H., Feng, L. Y., Li, Y. G., Hu, C. W., Wang, E. B., Hu, N. H. & Jia, H. Q. (2002). *Inorg. Chem.* **41**, 6351–6357.