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Acta Cryst. (1996). C**52**, 1131–1134

Copper and Manganese Sulfanilate Hydrates

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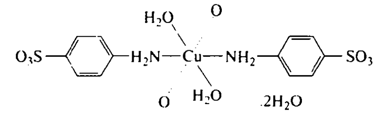
(*Received 23 August 1995; accepted 6 November 1995*)

Abstract

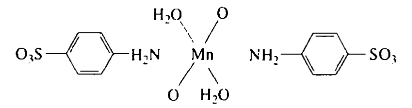
The title compounds, bis(4-aminobenzenesulfonato)-diaquacopper(II) dihydrate, $[Cu(C_6H_6NO_3S)_2(H_2O)_2].2H_2O$, and bis(4-aminobenzenesulfonato)diaquamanganese(II), $[Mn(C_6H_6NO_3S)_2(H_2O)_2]$, have structures in which the sulfanilate anions are arranged in layers with the functional groups directed towards adjacent layers. Between these slabs are the metal cations and water molecules. The Cu atom sits in a tetragonally distorted octahedron, with short contacts to two amine N atoms and two water molecules. Two sulfonate O atoms provide the longer interactions. The other water molecules are anchored by hydrogen bonds to the sulfonate groups. The Mn atom also displays a tetragonal distortion of its octahedral coordination to two sulfonate O atoms, two water molecules and, at the elongated vertices, two amine N atoms. The manganese salt contains no free water molecules. Both structures differ from those of the reported cobalt and zinc salts.

Comment

The copper and manganese sulfanilate salts, (I) and (II), respectively, were prepared as part of a continuing study of the coordination chemistry and layering patterns of functionalized sulfonic acids (Gunderman & Squattrito, 1995).



(I)



(II)

As shown in Fig. 1, the Cu cation, which rests on a center of inversion, is coordinated to the amine N atoms of two sulfanilate anions and to two water molecules in a square-planar arrangement. Two O atoms from the sulfonate groups of other anions are at the remaining vertices of the octahedron, approximately 0.4 Å further away. Thus, the copper coordination shows a classic Jahn–Teller distortion similar to many reported examples (Melnik, 1982). The packing diagram (Fig. 2) shows that the sulfanilate anions occur in layers that stack along the *b* axis. Neighboring anions in a layer have the polar groups oriented towards opposite faces of the layer. In addition, they are canted slightly with respect to each other and the rings are approximately 16° out of parallel. This type of anion packing arrangement is also observed in sodium sulfanilate dihydrate (Bats, 1977). The layers are held together by the Cu cations, each of which is bonded to four different anions, two from each adjacent layer. The structure is further reinforced by hydrogen bonds (Table 3) involving the amine group, both water molecules and the sulfonate group. This structure is quite similar to that of the cobalt (Shakeri & Haussuhl, 1992*a*) and zinc (Shakeri & Haussuhl, 1992*b*) sulfanilate tetrahydrates, but is distinguished by the distorted coordination of the Cu atom. In contrast, the octahedral environments of the cobalt (Co—*L* 2.06–2.19 Å) and zinc (Zn—*L* 2.09–2.18 Å) atoms are far more regular.

The manganese compound is a dihydrate, with all water molecules directly coordinated to the metal ion. The Mn cation (Fig. 3) also sits on an inversion center and coordinates to two amine N atoms, two water molecules and two sulfonate O atoms. The octahedron about Mn is distorted as the Mn—N distances are longer than the four Mn—O distances. Similar distortions have been observed in other mixed-ligand Mn^{II} complexes (Stephens, 1977), though the elongated contacts are often *cis* rather than *trans*. The packing pattern of the anions also differs from that found in the tetrahydrates. Here again, neighboring anions have the amine and sulfonate groups flipped, but they are not tilted with respect

Acta Crystallographica Section C
ISSN 0108-2701 ©1996

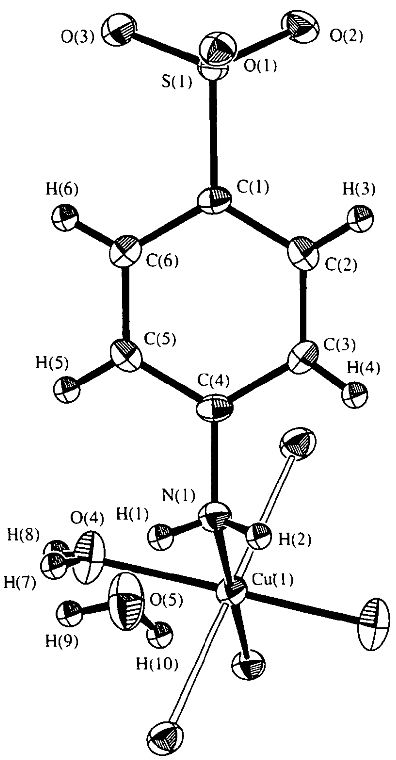


Fig. 1. An *ORTEP*II diagram (Johnson, 1976) of compound (I) showing the sulfanilate ion, the coordination sphere about the Cu atom and the atom-labelling scheme. The elongated contacts to the sulfonate O atoms are shown with open bonds. The displacement ellipsoids of the non-H atoms are shown at the 50% probability level in this and subsequent figures.

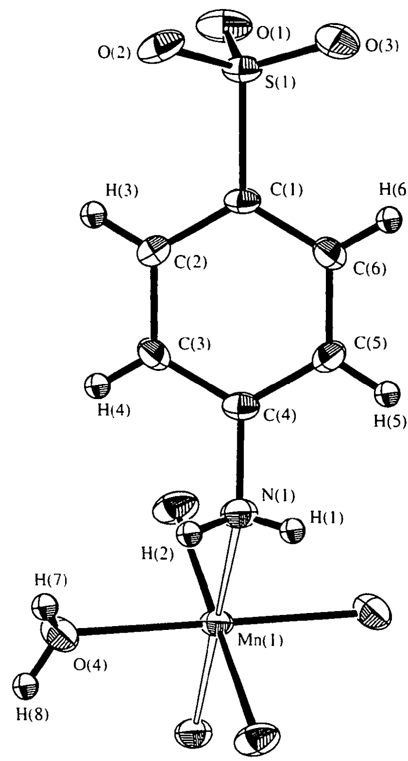


Fig. 3. An *ORTEP*II diagram (Johnson, 1976) of compound (II) showing the sulfanilate ion, the coordination sphere about the Mn atom and the atom-labelling scheme. The elongated bonds to the amine N atoms are shown with open bonds.

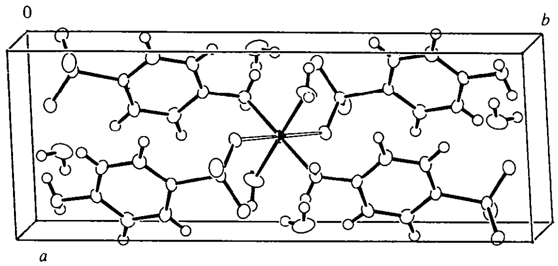


Fig. 2. An *ORTEP*II packing diagram (Johnson, 1976) of compound (I) showing the outline of the unit cell.

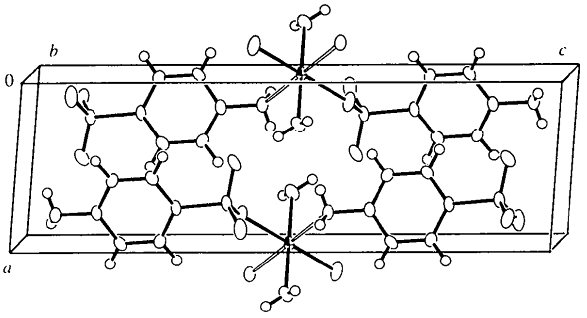


Fig. 4. An *ORTEP*II packing diagram (Johnson, 1976) of compound (II) showing the outline of the unit cell.

to each other along the long axis (*i.e.* the line bisecting the ring through the N and S atoms) of the molecules. This arrangement is like that found in magnesium sulfanilate hexahydrate (Shakeri & Haussuhl, 1992*c*). The anions are, however, rotated about those axes so that the rings of neighboring anions are about 42° out of parallel. The Mn cations hold the layers together through bonds to four different anions. There are also hydrogen bonds from the amine and water H atoms to the sulfonate O atoms (Table 6). These structures demonstrate the types of subtle variations that can occur in organosulfonate salts having different metal and water content.

Experimental

For the preparation of the copper sulfanilate salt, (I), a 5.204 g sample of sulfanilic acid was dissolved in 200 ml of water. This solution was heated to boiling, at which time 1.235 g of copper(II) carbonate was added. The solid dissolved with evolution of carbon dioxide to give a dark green solution. The solution was heated until the volume was reduced to about 175 ml. Dark green block-shaped crystals of copper sulfanilate tetrahydrate (4.540 g) grew from the solution on standing in an open evaporating dish. For the preparation of the manganese sulfanilate salt, (II), a 4.997 g sample of sulfanilic acid was added to 200 ml of water. The mixture was heated and stirred until most of the solid dissolved. Then 3.530 g of manganese(II) acetate tetrahydrate was added, dissolving quickly to produce a clear colorless solution. Large tan needles of manganese sulfanilate dihydrate (1.982 g) grew upon evaporation of the solvent.

Compound (I)

Crystal data

$[Cu(C_6H_6NO_3S)_2(H_2O)_2]$.-$2H_2O$
M_r = 479.96
Monoclinic
$P2_1/n$
a = 7.428 (2) Å
b = 17.376 (2) Å
c = 7.632 (2) Å
β = 116.67 (1)°
V = 880.2 (3) Å^3
Z = 2
D_x = 1.811 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.7107 Å
Cell parameters from 19 reflections
θ = 23.6–24.9°
μ = 1.525 mm^{-1}
T = 296.2 K
Block
0.30 × 0.25 × 0.25 mm
Green

Data collection

Rigaku AFC-6*S* diffractometer
ω scans
Absorption correction: ψ scans of three reflections
$T_{\min}$ = 0.891, $T_{\max}$ = 1.000
1725 measured reflections
1600 independent reflections

1311 observed reflections [$I > 3\sigma(I)$]
$R_{\rm int}$ = 0.021
$\theta_{\max}$ = 24.92°
$h = 0 \rightarrow 8$
$k = 0 \rightarrow 20$
$l = -8 \rightarrow 8$
3 standard reflections monitored every 150 reflections intensity decay: 0.61%

Refinement

Refinement on F
R = 0.025
wR = 0.028
S = 2.46
1311 reflections
154 parameters
Only coordinates of H atoms refined
$w = 4F_o^2/\sigma^2(F_o^2)$

$(\Delta/\sigma)_{\max}$ = 0.01
$\Delta\rho_{\max}$ = 0.44 e Å^{-3}
$\Delta\rho_{\min}$ = −0.30 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) for (I)*

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

	x	y	z	$U_{\rm eq}$
Cu(1)	1	0	1	0.0184 (1)
S(1)	0.65933 (10)	0.39764 (4)	0.94552 (10)	0.0171 (2)
O(1)	0.4928 (3)	0.42290 (10)	0.7608 (3)	0.0228 (5)
O(2)	0.6018 (3)	0.3973 (1)	1.1049 (3)	0.0265 (6)
O(3)	0.8423 (3)	0.44198 (10)	0.9927 (3)	0.0240 (6)
O(4)	1.2304 (3)	0.0559 (1)	0.9925 (3)	0.0313 (7)
O(5)	0.6090 (4)	0.0669 (2)	0.2587 (4)	0.0413 (8)
N(1)	0.8138 (4)	0.0740 (1)	0.7860 (4)	0.0201 (7)
C(1)	0.7124 (4)	0.3013 (2)	0.9106 (4)	0.0170 (7)
C(2)	0.5906 (4)	0.2422 (2)	0.9180 (4)	0.0228 (8)
C(3)	0.6266 (4)	0.1675 (2)	0.8804 (4)	0.0217 (8)
C(4)	0.7829 (4)	0.1516 (2)	0.8337 (4)	0.0177 (7)
C(5)	0.9079 (4)	0.2103 (2)	0.8325 (4)	0.0241 (9)
C(6)	0.8727 (4)	0.2854 (2)	0.8698 (4)	0.0238 (8)
H(1)	0.866 (4)	0.076 (2)	0.712 (4)	
H(2)	0.700 (4)	0.054 (2)	0.728 (4)	
H(3)	0.485 (4)	0.254 (2)	0.942 (4)	
H(4)	0.552 (4)	0.129 (2)	0.873 (4)	
H(5)	1.016 (4)	0.199 (2)	0.807 (4)	
H(6)	0.961 (4)	0.323 (2)	0.872 (4)	
H(7)	1.220 (5)	0.064 (2)	0.894 (5)	
H(8)	1.356 (5)	0.059 (2)	1.082 (5)	
H(9)	0.707 (5)	0.071 (2)	0.245 (5)	
H(10)	0.625 (5)	0.030 (2)	0.327 (5)	

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

Cu(1)—O(4)	1.991 (2)	S(1)—O(2)	1.459 (2)
Cu(1)—N(1)	2.050 (2)	S(1)—O(3)	1.460 (2)
Cu(1)—O(1$^{\rm i}$)	2.420 (2)	S(1)—C(1)	1.767 (3)
S(1)—O(1)	1.465 (2)	N(1)—C(4)	1.442 (3)
O(4)—Cu(1)—N(1$^{\rm ii}$)	92.7 (1)	O(2)—S(1)—O(3)	112.6 (1)
O(4)—Cu(1)—O(1$^{\rm i}$)	95.18 (8)	O(2)—S(1)—C(1)	106.9 (1)
N(1)—Cu(1)—O(1$^{\rm i}$)	92.98 (8)	O(3)—S(1)—C(1)	106.9 (1)
O(1)—S(1)—O(2)	111.5 (1)	Cu(1)—N(1)—C(4)	120.8 (2)
O(1) S(1) O(3)	111.7 (1)	Cu(1)···O(1$^{\rm i}$)—S(1$^{\rm i}$)	129.5 (1)
O(1)—S(1)—C(1)	106.7 (1)		

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

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

D—H···A	D—H	H···A	D···A	D—H···A
N(1)—H(1)···O(2$^{\rm i}$)	0.82 (3)	2.29 (3)	3.064 (3)	158 (3)
O(4)—H(7)···O(2$^{\rm i}$)	0.73 (3)	2.09 (3)	2.790 (3)	161 (4)
O(4)—H(8)···O(5$^{\rm ii}$)	0.88 (3)	1.76 (3)	2.635 (3)	179 (3)
O(5)—H(9)···O(1$^{\rm i}$)	0.78 (3)	2.08 (4)	2.849 (3)	170 (4)
O(5)—H(10)···O(3$^{\rm iii}$)	0.81 (3)	1.99 (4)	2.798 (3)	176 (4)

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

Compound (II)

Crystal data

$[Mn(C_6H_6NO_3S)_2(H_2O)_2]$
M_r = 435.32
Monoclinic
$P2_1/c$
a = 5.910 (3) Å
b = 7.103 (3) Å
c = 18.790 (2) Å
β = 94.77 (2)°
V = 786.1 (5) Å^3
Z = 2
D_x = 1.839 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.7107 Å
Cell parameters from 21 reflections
θ = 12.4–18.8°
μ = 1.107 mm^{-1}
T = 296.2 K
Flat needle
0.25 × 0.15 × 0.15 mm
Tan

Data collection

Rigaku AFC-6*S* diffractometer
ω scans
Absorption correction: ψ scans of three reflections
$T_{\min}$ = 0.889, $T_{\max}$ = 1.000
1652 measured reflections
1498 independent reflections

1040 observed reflections [$I > 3\sigma(I)$]
$R_{\rm int}$ = 0.022
$\theta_{\max}$ = 24.97°
$h = 0 \rightarrow 7$
$k = 0 \rightarrow 8$
$l = -22 \rightarrow 22$
3 standard reflections monitored every 150 reflections intensity decay: 0.50%

Refinement

Refinement on F
$R = 0.028$
$wR = 0.027$
$S = 1.69$
1040 reflections
140 parameters
Only coordinates of H atoms refined
$w = 4F_o^2/\sigma^2(F_o^2)$
$(\Delta/\sigma)_{\max} = 0.01$
$\Delta\rho_{\max} = 0.25$ e Å^{-3}
$\Delta\rho_{\min} = -0.34$ e Å^{-3}
Extinction correction: Zachariasen (1968) Type II, Gaussian isotropic
Extinction coefficient: 0.00000268 (19)
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 4. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for (II)*

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

	x	y	z	$U_{\rm eq}$
Mn(1)	1	0	1	0.0192 (2)
S(1)	0.7300 (1)	0.1686 (1)	1.38918 (4)	0.0222 (2)
O(1)	0.8667 (4)	0.0174 (3)	1.4227 (1)	0.0351 (7)
O(2)	0.8204 (4)	0.3527 (3)	1.4125 (1)	0.0302 (7)
O(3)	0.4905 (4)	0.1483 (4)	1.3989 (1)	0.0400 (8)
O(4)	1.2762 (4)	0.2062 (3)	1.0070 (1)	0.0267 (7)
N(1)	0.7995 (5)	0.1922 (4)	1.0743 (1)	0.0235 (8)
C(1)	0.7554 (5)	0.1623 (4)	1.2964 (2)	0.0186 (8)
C(2)	0.9563 (5)	0.2220 (4)	1.2698 (2)	0.0229 (9)
C(3)	0.9710 (6)	0.2264 (5)	1.1966 (2)	0.0232 (9)
C(4)	0.7869 (5)	0.1750 (4)	1.1504 (2)	0.0196 (8)
C(5)	0.5915 (5)	0.1076 (5)	1.1772 (2)	0.0225 (9)
C(6)	0.5764 (5)	0.1015 (4)	1.2503 (2)	0.0228 (9)
H(1)	0.670 (5)	0.182 (5)	1.056 (2)	
H(2)	0.861 (5)	0.306 (4)	1.064 (2)	
H(3)	1.075 (5)	0.271 (4)	1.301 (2)	
H(4)	1.094 (5)	0.272 (4)	1.179 (2)	
H(5)	0.471 (5)	0.071 (4)	1.145 (2)	
H(6)	0.445 (5)	0.057 (4)	1.268 (2)	
H(7)	1.247 (5)	0.305 (4)	1.027 (2)	
H(8)	1.346 (5)	0.249 (4)	0.973 (2)	

Table 5. *Selected geometric parameters (Å, °) for (II)*

Mn(1)—O(2$^{\rm i}$)	2.152 (2)	S(1)—O(2)	1.466 (2)
Mn(1)—O(4)	2.189 (2)	S(1)—O(3)	1.449 (2)
Mn(1)—N(1)	2.343 (3)	S(1)—C(1)	1.762 (3)
S(1)—O(1)	1.456 (2)	N(1)—C(4)	1.444 (4)
O(2$^{\rm i}$)—Mn(1)—O(4)	92.22 (9)	O(2)—S(1)—O(3)	112.7 (1)
O(2$^{\rm ii}$)—Mn(1)—N(1)	94.02 (9)	O(2)—S(1)—C(1)	105.1 (1)
O(4)—Mn(1)—N(1$^{\rm iii}$)	90.8 (1)	O(3)—S(1)—C(1)	106.7 (1)
O(1)—S(1)—O(2)	110.7 (1)	Mn(1)—N(1)—C(4)	127.7 (2)
O(1)—S(1)—O(3)	112.6 (1)	Mn(1)—O(2$^{\rm i}$)—S(1$^{\rm i}$)	143.8 (1)
O(1)—S(1)—C(1)	108.6 (1)		

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

Table 6. *Hydrogen-bonding geometry (Å, °) for (II)*

D—H···A	D—H	H···A	D···A	D—H···A
N(1)—H(2)···O(1$^{\rm i}$)	0.91 (3)	2.20 (3)	3.035 (3)	152 (3)
O(4)—H(7)···O(1$^{\rm i}$)	0.82 (3)	1.93 (3)	2.744 (3)	171 (3)
O(4)—H(8)···O(3$^{\rm ii}$)	0.85 (3)	1.84 (3)	2.688 (3)	177 (3)

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

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: (I) N—H 0.82 (3)–0.83 (3), C—H 0.86 (3)–0.93 (3) Å; (II) N—H 0.81 (3)–0.91 (3), C—H 0.88 (3)–0.95 (3) Å.

For both compounds, 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 structures: *MITHRIL* (Gilmore, 1983); program(s) used to refine structures: *TEXSAN*; software used to prepare material for publication: *TEXSAN*.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry, including intermolecular distances involving both H and non-H atoms, have been deposited with the IUCr (Reference: BK1192). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1996). C**52**, 1134–1136

A Copper(II) Complex of a Macrocyclic Schiff Base Ligand with a Polyether Bridge

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(*Received 20 December 1995; accepted 29 January 1996*)

Abstract

In the structure of aquachloro[7,10,13-trioxa-3,17,23-triazabicyclo[17.3.1]tricosa-1(23),2,17,19,21-pentaene-N,N',N'']copper(II) hexafluorophosphate acetonitrile solvate, the Cu$^{\rm II}$ ion is pentacoordinate with square-pyramidal coordination geometry, with a relatively long axial bond to water [2.244 (5) Å] and with the shortest