O(3)—Ca(1)—O(7)	173.4 (1)	Ca(1^{iii})—O(5^{iii})—C(1^{iv})	168.9 (3)
O(4)—Ca(1)—O(5)	96.9 (1)	Ca(1^{iv})—O(6^{iv})—C(1^{iv})	141.1 (3)
O(4)—Ca(1)—O(6)	89.3 (1)	O(5^{iii})—C(1^{iv})—O(6^{iv})	125.0 (4)
O(4)—Ca(1)—O(7)	79.8 (1)	O(5^{iii})—C(1^{iv})—C(2)	118.9 (3)
O(5)—Ca(1)—O(6)	170.5 (1)	O(6^{iv})—C(1^{iv})—C(2)	116.0 (3)
O(5)—Ca(1)—O(7)	91.9 (1)	N(1)—C(2)—C(1^{iv})	109.9 (3)
O(6)—Ca(1)—O(7)	96.3 (1)	N(1)—C(2)—C(3)	111.8 (3)
O(1)—P(1)—O(2^i)	107.3 (2)	C(1^{iv})—C(2)—C(3)	108.2 (3)
O(1)—P(1)—O(3)	101.7 (2)	O(1)—C(3)—C(2)	113.5 (3)

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

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1985). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985) and *DIRDIF* (Beurskens, 1984). Program(s) used to refine structure: *TEXSAN*. Molecular graphics: *ORTEPII* (Johnson, 1976).

References

Beurskens, P. T. (1984). *DIRDIF. Direct Methods for Difference Structures – an Automatic Procedure for Phase Extension and Refinement of Difference Structure Factors*. Technical Report 1984/1. Crystallography Laboratory, Toernooiveld, 6525 ED Nijmegen, The Netherlands.

Cohen, P. (1982). *Nature (London)*, **296**, 613–620.

Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

McCallum, G. H., Robertson, J. M. & Sim, G. A. (1959). *Nature (London)*, **184**, 1863–1864.

Martin, D. W., Mayes, P. A. & Rodwell, V. W. (1983). *Harper's Review of Biochemistry*, pp. 464–479. Tokyo: Maruzen Asia.

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.

North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A24, 351–359.

Putkey, E. & Sundaralingam, M. (1970). *Acta Cryst.* B26, 782–789.

Rubin, C. S. & Rosen, O. M. (1975). *Annu. Rev. Biochem.* **44**, 831–887.

Sheldrick, G. M. (1985). *SHELXS86. Crystallographic Computing 3*, edited by G. M. Sheldrick, C. Krüger & R. Goddard, pp. 175–189. Oxford University Press.

Taborsky, G. (1974). *Adv. Protein Chem.* **28**, 1–187.

Two Calcium Salts of o-Tolidine-6,6'-disulfonate

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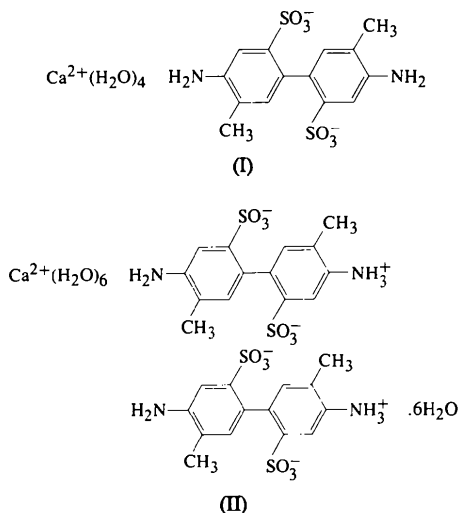
Abstract

The dibasic and monobasic calcium salts of o-tolidine-6,6'-disulfonic acid, tetraaqua(4,4'-diamino-5,5'-dimethyl-1,1'-biphenyl-2,2'-disulfonato-O:O')calcium, $[Ca(C_{14}H_{14}N_2O_6S_2)(H_2O)_4]$, (I), and hexaaqua(4-amino-4'-ammonio-5,5'-dimethyl-1,1'-biphenyl-2,2'-disulfonato-O)calcium 4-amino-4'-ammonio-5,5'-dimethyl-1,1'-biphenyl-2,2'-disulfonate hexahydrate, $[Ca(C_{14}H_{15}N_2O_6S_2)(H_2O)_6](C_{14}H_{15}N_2O_6S_2).6H_2O$, (II), have structures built upon layers of anions, with the calcium cations and water molecules between these layers. The calcium ions are seven-coordinate. The coordination sphere in compound (I) contains three sulfonate O atoms and four water molecules, while that in (II) contains one sulfonate O atom and six water molecules. Both structures are held together by a network of hydrogen bonds involving the amine, sulfonate and water groups. The biphenyl rings in the anions are approximately 75° out of parallel and the *ortho*-sulfonate groups are in an *anti* conformation.

Comment

We have previously examined the structural trends in various arenesulfonates (Gunderman & Squattrito, 1994) and naphthalenesulfonates (Gunderman & Squattrito, 1995). As an extension of this study of aromatic sulfonic acids and their salts, we have characterized two salts of an *ortho*-disulfonated biphenyl derivative. Despite the presence of numerous references to such compounds in the patent literature, no crystal structures of either the sulfonic acids or their salts have been reported. There are relatively few structural studies of *ortho*-substituted biphenyls of any kind (Lesser & Rabinovich, 1978). The closest reported compound to the title compounds, (I) and (II), is biphenyl-2,2'-dicarboxylic acid (Fronczek, Davis, Gehrig & Gandour, 1987). The dihedral angles between the phenyl rings of the *o*-tolidine-6,6'-disulfonate anions [(I) 78.8 (2); (II) 72.5 (4) and 75.0 (4)°] are within the range reported for the two independent molecules of the dicarboxylic acid (71.3 and 83.6°). The torsion angles between the sulfonate groups [(I): C(6)—C(1)—C(7)—C(12)

−106.3 (5); (II): C(6)—C(1)—C(7)—C(12) 116.1 (9) and C(20)—C(15)—C(21)—C(26) −110.5 (8)°] are also in the range of those in the dicarboxylic acid. These are apparently the only reported examples in which the *ortho* substituents adopt an *anti* conformation (torsion angle > 90°).

(I)

(II)

Fig. 1. An *ORTEP*II (Johnson, 1976) diagram of (I) showing the *o*-tolidinedisulfonate anion, the coordination sphere about the Ca ion and the atom-labelling scheme. The displacement ellipsoids of the non-H atoms are shown at the 50% probability level in this and subsequent figures.

The calcium ions are seven-coordinate in both salts. In compound (I), the cation is coordinated to O atoms from three different *o*-tolidinedisulfonate anions and four water molecules, while in (II), the cation bonds to only one sulfonate O atom and six water molecules. While the bond distances are very consistent, in neither case does the geometry conform to a regular shape, such as the pentagonal bipyramid found in other sulfonate salts (Shubnell, Kosnic & Squattrito, 1994). In compound (I) (Fig. 1), all the water molecules are directly attached to the cation. As shown in the packing diagram (Fig. 2), the anions pack in layers with half having the sulfonate groups directed towards the next layer up and half having the sulfonate groups directed towards the layer below. This aspect of the packing is typical of the aromatic sulfonates we have studied, though here the organic portions of the oppositely oriented anions are segregated in double layers rather than interleaved, as is the case in the benzene and naphthalene derivatives. The cations and water molecules are located between the organic layers. The structure is extensively hydrogen bonded, with N—H···O$_{sulfonate}$, O—H···O$_{sulfonate}$, O—H···N and O—H···O$_{water}$ interactions all reinforcing the crystal packing. There is a particularly short hydrogen bond between H(19) and O(1) of 1.69 (4) Å, which has presumably contributed to the elongation of the O(9)—H(19) bond to 1.11 (4) Å and the shortening of the O(9)—H(20) bond to 0.55 (5) Å. Given the known tendency of metal ions to increase the acidity of water H atoms, one can think of this interaction as somewhat along the continuum to a hydroxyl···sulfonic acid hydrogen bond.
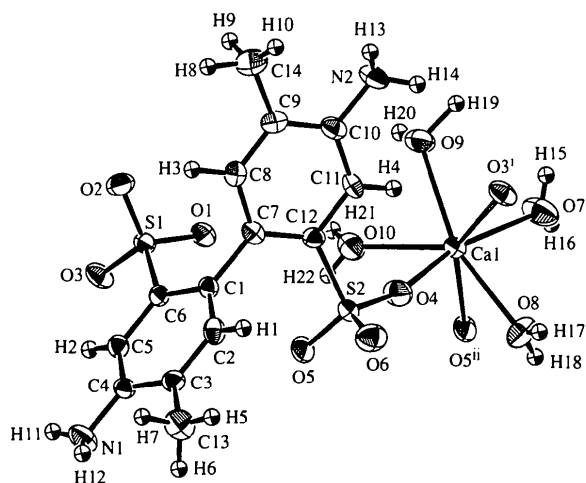

Fig. 2. An *ORTEP*II (Johnson, 1976) packing diagram of (I) showing the outline of the unit cell. The Ca ions are shown with octant shading and the bonds to oxygen omitted.

Compound (II) (Figs. 3 and 4), with two organic anions per calcium ion, represents the monobasic salt of *o*-tolidinedisulfonic acid. One of the amine groups on each anion is apparently protonated. Three reasonable H-atom positions were found around N(2). While a set of three protons could not be located on any other N atom, it is

evident from the longer C—N distances [1.465 (8) and 1.462 (8) Å] that N(2) and N(4) are the ammonium N atoms. The calcium ion is only bonded directly to one of the anions through a single O atom. The balance of the coordination sphere is water molecules. This arrangement has been observed in calcium 2-aminotoluene-4-sulfonate heptahydrate (Shubnell, Kosnic & Squattrito, 1994). Both coordinated and non-coordinated sulfonate anions are also found in several trivalent lanthanide sulfonate hydrates (Ohki, Suzuki, Takeuchi & Ouchi, 1988; Starynowicz, 1992). Like the dibasic salt, this compound adopts a layered structure (Fig. 5), with the cations and water molecules, including six not coordinated to the cation, sandwiched by the anions. The packing of the anions is less regular in this case. The anion which coordinates to the Ca^{2+} ion has both sulfonate groups oriented towards the same face of the layer, while the free anion straddles the layer so that one sulfonate group is directed towards each face. There are many hydrogen bonds in the structure; Table 6 lists only those with donor–acceptor distances less than 3 Å for which the H atoms were located on difference maps.

Fig. 3. An ORTEPII (Johnson, 1976) diagram of (II) showing the coordination sphere about the Ca ion, including one of the independent o-tolidinedisulfonate anions.

Fig. 4. An ORTEPII (Johnson, 1976) diagram of the other independent o-tolidinedisulfonate anion in (II).
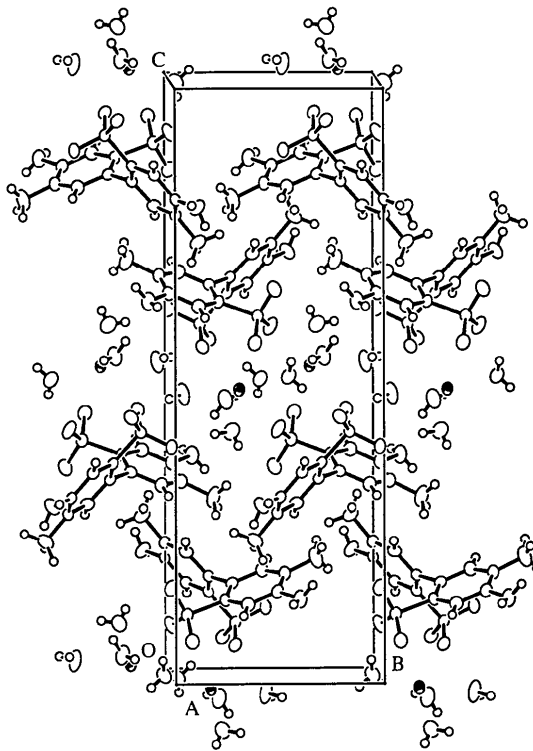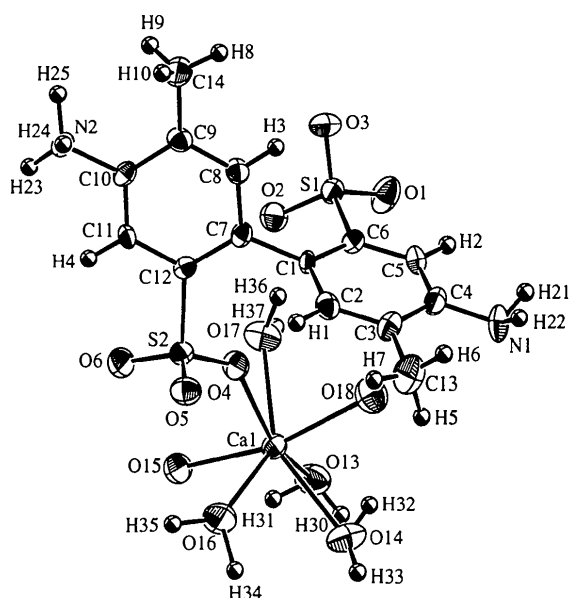

Fig. 5. An ORTEPII (Johnson, 1976) packing diagram of (II) showing the outline of the unit cell. The Ca ions are shown with octant shading and the bonds to oxygen omitted.

Experimental

Many small (< 1 mm) tan plate-shaped crystals of compound (I) grew upon evaporation of solvent from an equimolar aqueous solution of o-tolidine-6,6'-disulfonic acid and either calcium hydroxide or acetate. Small plate-shaped crystals of compound (II) were isolated as a minor product in the reaction that produced compound (I).

Compound (I)

Crystal data

[Ca(C$_{14}$H$_{14}$N$_2$O$_6$S$_2$)(H$_2$O)$_4$]	Mo $K\alpha$ radiation
$M_r = 482.54$	$\lambda = 0.7107$ Å
Monoclinic	Cell parameters from 20
$P2_1/c$	reflections
$a = 9.003 (3)$ Å	$\theta = 15.0–19.6°$
$b = 8.896 (5)$ Å	$\mu = 0.563$ mm^{-1}
$c = 24.832 (4)$ Å	$T = 296$ K
$\beta = 94.29 (3)°$	Plate
$V = 1983 (1)$ Å^3	$0.30 \times 0.25 \times 0.10$ mm
$Z = 4$	Tan
$D_x = 1.616$ Mg m^{-3}	
D_m not measured	

Data collection

Rigaku AFC-6S diffractom-
eter

ω scans

Absorption correction:
none

3967 measured reflections

3715 independent reflections

2343 observed reflections
$[I > 3\sigma(I)]$

$R_{int} = 0.034$

$\theta_{max} = 24.95°$

$h = 0 \rightarrow 10$

$k = 0 \rightarrow 10$

$l = -29 \rightarrow 29$

3 standard reflections
monitored every 150
reflections

intensity decay: 0.05%

Refinement

Refinement on F

$R = 0.036$

$wR = 0.037$

$S = 1.87$

2343 reflections

328 parameters

Only coordinates of H atoms
refined

$w = 4F_o^2/\sigma^2(F_o^2)$

$(\Delta/\sigma)_{max} = 0.26$

$\Delta\rho_{max} = 0.28$ e Å^{-3}

$\Delta\rho_{min} = -0.41$ 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)*

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

	x	y	z	U_{eq}
Ca(1)	0.70312 (8)	0.18035 (9)	0.98488 (3)	0.0250 (2)
S(1)	0.01731 (10)	0.3335 (1)	1.07777 (4)	0.0233 (3)
S(2)	0.48845 (10)	0.0789 (1)	1.10340 (4)	0.0251 (3)
O(1)	0.1404 (3)	0.3268 (3)	1.04290 (10)	0.0308 (8)
O(2)	0.0007 (3)	0.4805 (3)	1.1026 (1)	0.0335 (8)
O(3)	−0.1206 (3)	0.2811 (3)	1.04969 (10)	0.0327 (8)
O(4)	0.5904 (3)	0.0981 (3)	1.0611 (1)	0.0412 (9)
O(5)	0.3490 (3)	0.0104 (3)	1.0825 (1)	0.0372 (9)
O(6)	0.5576 (3)	0.0018 (3)	1.1499 (1)	0.0426 (10)
O(7)	0.8866 (5)	0.2262 (4)	0.9202 (2)	0.054 (1)
O(8)	0.8387 (4)	−0.0506 (4)	1.0113 (1)	0.043 (1)
O(9)	0.6641 (4)	0.4461 (4)	0.9770 (2)	0.050 (1)
O(10)	0.4422 (3)	0.2335 (4)	0.9613 (2)	0.045 (1)
N(1)	−0.1497 (4)	−0.0981 (5)	1.1955 (2)	0.039 (1)
N(2)	0.6745 (4)	0.6122 (4)	1.1340 (2)	0.041 (1)
C(1)	0.1966 (4)	0.1965 (4)	1.1602 (2)	0.022 (1)
C(2)	0.2144 (4)	0.0897 (5)	1.2015 (2)	0.027 (1)
C(3)	0.1020 (4)	−0.0080 (4)	1.2150 (2)	0.025 (1)
C(4)	−0.0349 (4)	−0.0001 (4)	1.1850 (2)	0.023 (1)
C(5)	−0.0543 (4)	0.1030 (5)	1.1429 (2)	0.023 (1)
C(6)	0.0584 (4)	0.2022 (4)	1.1308 (1)	0.021 (1)
C(7)	0.3232 (4)	0.3025 (4)	1.1515 (2)	0.024 (1)
C(8)	0.3197 (4)	0.4471 (5)	1.1733 (2)	0.030 (1)
C(9)	0.4351 (4)	0.5503 (5)	1.1706 (2)	0.031 (1)
C(10)	0.5592 (4)	0.5095 (5)	1.1436 (2)	0.029 (1)
C(11)	0.5669 (4)	0.3667 (5)	1.1221 (2)	0.028 (1)
C(12)	0.4510 (4)	0.2637 (4)	1.1264 (2)	0.023 (1)
C(13)	0.1238 (5)	−0.1154 (6)	1.2616 (2)	0.041 (1)
C(14)	0.4231 (6)	0.7019 (6)	1.1965 (3)	0.054 (2)

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

Ca(1)—O(3^i)	2.352 (3)	S(1)—O(3)	1.454 (3)
Ca(1)—O(4)	2.331 (3)	S(1)—C(6)	1.778 (4)
Ca(1)—O(5^{ii})	2.405 (3)	S(2)—O(4)	1.456 (3)
Ca(1)—O(7)	2.424 (4)	S(2)—O(5)	1.456 (3)
Ca(1)—O(8)	2.454 (4)	S(2)—O(6)	1.444 (3)
Ca(1)—O(9)	2.396 (4)	S(2)—C(12)	1.781 (4)
Ca(1)—O(10)	2.424 (3)	N(1)—C(4)	1.392 (5)
S(1)—O(1)	1.457 (3)	N(2)—C(10)	1.417 (5)
S(1)—O(2)	1.459 (3)		

O(3^i)—Ca(1)—O(4)	82.9 (1)	O(9)—Ca(1)—O(10)	69.8 (1)
O(3^i)—Ca(1)—O(5^{ii})	146.28 (10)	O(1)—S(1)—O(2)	113.2 (2)
O(3^i)—Ca(1)—O(7)	86.0 (1)	O(1)—S(1)—O(3)	111.2 (2)
O(3^i)—Ca(1)—O(8)	80.8 (1)	O(1)—S(1)—C(6)	106.7 (2)
O(3^i)—Ca(1)—O(9)	76.5 (1)	O(2)—S(1)—O(3)	112.3 (2)
O(3^i)—Ca(1)—O(10)	133.1 (1)	O(2)—S(1)—C(6)	107.4 (2)
O(4)—Ca(1)—O(5^{ii})	105.6 (1)	O(3)—S(1)—C(6)	105.5 (2)
O(4)—Ca(1)—O(7)	162.0 (1)	O(4)—S(2)—O(5)	111.4 (2)
O(4)—Ca(1)—O(8)	76.0 (1)	O(4)—S(2)—O(6)	112.1 (2)
O(4)—Ca(1)—O(9)	107.8 (1)	O(4)—S(2)—C(12)	105.6 (2)
O(4)—Ca(1)—O(10)	77.5 (1)	O(5)—S(2)—O(6)	113.2 (2)
O(5^{ii})—Ca(1)—O(7)	76.4 (1)	O(5)—S(2)—C(12)	108.8 (2)
O(5^{ii})—Ca(1)—O(8)	70.3 (1)	O(6)—S(2)—C(12)	105.2 (2)
O(5^{ii})—Ca(1)—O(9)	128.3 (1)	S(1)—C(6)—C(1)	122.6 (3)
O(5^{ii})—Ca(1)—O(10)	80.5 (1)	S(1)—C(6)—C(5)	117.5 (3)
O(7)—Ca(1)—O(8)	88.2 (1)	C(1)—C(6)—C(5)	119.9 (4)
O(7)—Ca(1)—O(9)	83.3 (1)	S(2)—C(12)—C(7)	123.7 (3)
O(7)—Ca(1)—O(10)	120.2 (1)	S(2)—C(12)—C(11)	114.8 (3)
O(8)—Ca(1)—O(9)	156.2 (1)	C(7)—C(12)—C(11)	121.2 (4)
O(8)—Ca(1)—O(10)	132.9 (1)		

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

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

D—H···A	D—H	H···A	D···A	D—H···A
N(1)—H(12)···O(6^i)	0.70 (4)	2.24 (4)	2.927 (5)	164 (5)
N(2)—H(14)···O(2^{ii})	0.95 (4)	2.36 (4)	3.308 (5)	175 (3)
O(7)—H(15)···O(2^{iii})	0.79 (5)	2.08 (5)	2.871 (5)	173 (5)
O(8)—H(18)···O(1^{iv})	0.76 (4)	2.08 (4)	2.815 (4)	161 (5)
O(9)—H(19)···O(1^{iii})	1.11 (4)	1.69 (4)	2.749 (5)	158 (3)
O(10)—H(21)···N(2^{iii})	0.90 (4)	1.99 (4)	2.867 (5)	164 (4)
O(10)—H(22)···O(8^{iv})	0.79 (4)	2.34 (4)	3.124 (5)	170 (5)

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

Compound (II)

Crystal data

$[Ca(C_{14}H_{15}N_2O_6S_2)(H_2O)_6]$-
$(C_{14}H_{15}N_2O_6S_2).6H_2O$

$M_r = 999.07$

Triclinic

$P\bar{1}$

$a = 13.163$ (7) Å

$b = 16.122$ (7) Å

$c = 11.814$ (5) Å

$\alpha = 93.23$ (4)°

$\beta = 112.97$ (4)°

$\gamma = 106.50$ (4)°

$V = 2173$ (2) Å^3

$Z = 2$

$D_x = 1.527$ Mg m^{-3}

D_m not measured

Mo $K\alpha$ radiation

$\lambda = 0.7107$ Å

Cell parameters from 25
reflections

$\theta = 3.5-7.8°$

$\mu = 0.410$ mm^{-1}

$T = 296$ K

Plate

$0.30 \times 0.25 \times 0.07$ mm

Tan

Data collection

Rigaku AFC-6S diffractom-
eter

$\omega/2\theta$ scans

Absorption correction:
empirical *via* ψ scans of
three reflections (North,
Phillips & Mathews,
1968)

$T_{min} = 0.90$, $T_{max} = 1.00$

8003 measured reflections

7638 independent reflections

3574 observed reflections
$[I > 3\sigma(I)]$

$R_{int} = 0.046$

$\theta_{max} = 25°$

$h = 0 \rightarrow 15$

$k = -19 \rightarrow 18$

$l = -14 \rightarrow 12$

3 standard reflections
monitored every 150
reflections

intensity decay: 0.11%

Refinement

Refinement on F
$R = 0.049$
$wR = 0.050$
$S = 1.87$
3574 reflections
550 parameters
H-atom parameters not refined
$w = 4F_o^2/\sigma^2(F_o^2)$

$(\Delta/\sigma)_{max} = 0.013$
$\Delta\rho_{max} = 0.36$ e Å^{-3}
$\Delta\rho_{min} = -0.39$ e Å^{-3}
Extinction correction: none
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)*

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

	x	y	z	U_{eq}
Ca(1)	0.2645 (1)	0.51852 (10)	0.8869 (1)	0.0275 (5)
S(1)	0.1931 (2)	0.3010 (1)	0.4853 (2)	0.0296 (6)
S(2)	0.2538 (2)	0.2950 (1)	0.9181 (2)	0.0267 (6)
S(3)	0.2060 (2)	−0.1584 (1)	0.9584 (2)	0.0297 (6)
S(4)	0.5004 (2)	0.1248 (1)	1.2041 (2)	0.0252 (6)
O(1)	0.1808 (5)	0.3687 (4)	0.4090 (5)	0.048 (2)
O(2)	0.2973 (4)	0.3317 (3)	0.6032 (5)	0.039 (2)
O(3)	0.1852 (5)	0.2211 (3)	0.4136 (5)	0.046 (2)
O(4)	0.2347 (4)	0.3655 (3)	0.8504 (4)	0.036 (2)
O(5)	0.1647 (4)	0.2596 (3)	0.9618 (4)	0.036 (2)
O(6)	0.3717 (4)	0.3189 (3)	1.0162 (4)	0.039 (2)
O(7)	0.2318 (4)	−0.0749 (3)	0.9186 (5)	0.038 (2)
O(8)	0.2085 (5)	−0.2292 (3)	0.8801 (5)	0.046 (2)
O(9)	0.0973 (4)	−0.1808 (3)	0.9738 (5)	0.043 (2)
O(10)	0.5737 (4)	0.0955 (3)	1.3090 (4)	0.036 (2)
O(11)	0.4993 (4)	0.0899 (3)	1.0883 (4)	0.039 (2)
O(12)	0.5281 (4)	0.2191 (3)	1.2250 (5)	0.045 (2)
O(13)	0.3409 (5)	0.6681 (3)	0.8643 (5)	0.051 (2)
O(14)	0.1278 (5)	0.5904 (4)	0.8969 (5)	0.058 (2)
O(15)	0.4630 (4)	0.5723 (3)	1.0523 (5)	0.043 (2)
O(16)	0.2297 (5)	0.4814 (4)	1.0629 (5)	0.055 (2)
O(17)	0.3759 (5)	0.4960 (3)	0.7657 (5)	0.043 (2)
O(18)	0.1074 (5)	0.4743 (4)	0.6835 (5)	0.067 (2)
O(19)	0.5243 (5)	0.3764 (4)	0.3449 (5)	0.058 (2)
O(20)	0.8801 (5)	0.4798 (4)	0.5956 (6)	0.066 (2)
O(21)	0.9070 (5)	0.4622 (4)	0.8419 (5)	0.058 (2)
O(22)	0.9770 (5)	0.3289 (4)	0.9295 (7)	0.075 (3)
O(23)	0.2992 (6)	0.3901 (5)	1.2593 (7)	0.094 (3)
O(24)	0.6215 (6)	0.4064 (5)	0.5992 (6)	0.095 (3)
N(1)	−0.2094 (5)	0.3179 (4)	0.4186 (6)	0.044 (2)
N(2)	0.3714 (5)	0.0295 (4)	0.8330 (5)	0.028 (2)
N(3)	0.4884 (5)	−0.2870 (4)	1.2716 (6)	0.039 (2)
N(4)	0.1305 (5)	0.1868 (4)	1.1694 (5)	0.027 (2)
C(1)	0.0706 (6)	0.2301 (4)	0.6208 (6)	0.023 (2)
C(2)	−0.0259 (6)	0.2186 (5)	0.6496 (7)	0.030 (2)
C(3)	−0.1193 (6)	0.2456 (6)	0.5841 (7)	0.032 (2)
C(4)	−0.1188 (6)	0.2859 (5)	0.4831 (7)	0.030 (2)
C(5)	−0.0230 (6)	0.3011 (5)	0.4560 (7)	0.030 (2)
C(6)	0.0706 (6)	0.2746 (4)	0.5239 (6)	0.025 (2)
C(7)	0.1570 (6)	0.1852 (4)	0.6830 (6)	0.023 (2)
C(8)	0.1477 (6)	0.1100 (4)	0.6095 (7)	0.027 (2)
C(9)	0.2160 (6)	0.0571 (4)	0.6551 (7)	0.027 (2)
C(10)	0.2989 (6)	0.0836 (4)	0.7779 (7)	0.024 (2)
C(11)	0.3102 (6)	0.1563 (5)	0.8533 (6)	0.022 (2)
C(12)	0.2390 (6)	0.2067 (4)	0.8076 (6)	0.023 (2)
C(13)	−0.2215 (7)	0.2299 (6)	0.6182 (8)	0.050 (3)
C(14)	0.1988 (7)	−0.0248 (5)	0.5722 (7)	0.046 (3)
C(15)	0.3541 (6)	−0.0756 (4)	1.2065 (7)	0.022 (2)
C(16)	0.4381 (6)	−0.0774 (5)	1.3229 (7)	0.029 (2)
C(17)	0.4849 (6)	−0.1447 (5)	1.3471 (6)	0.023 (2)
C(18)	0.4476 (6)	−0.2146 (5)	1.2498 (7)	0.026 (2)
C(19)	0.3648 (6)	−0.2144 (4)	1.1333 (6)	0.026 (2)
C(20)	0.3185 (6)	−0.1473 (5)	1.1116 (6)	0.024 (2)
C(21)	0.3004 (6)	−0.0045 (4)	1.1941 (6)	0.024 (2)
C(22)	0.1887 (6)	−0.0255 (5)	1.1898 (7)	0.031 (2)
C(23)	0.1273 (6)	0.0335 (5)	1.1811 (6)	0.027 (2)
C(24)	0.1850 (6)	0.1190 (5)	1.1732 (6)	0.023 (2)
C(25)	0.2955 (6)	0.1425 (4)	1.1778 (6)	0.022 (2)
C(26)	0.3545 (6)	0.0833 (4)	1.1903 (6)	0.021 (2)
C(27)	0.5704 (7)	−0.1445 (5)	1.4779 (7)	0.042 (3)
C(28)	0.0087 (7)	0.0069 (5)	1.1807 (8)	0.046 (3)

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

Ca(1)—O(4)	2.371 (5)	S(2)—C(12)	1.790 (7)
Ca(1)—O(13)	2.408 (6)	S(3)—O(7)	1.444 (5)
Ca(1)—O(14)	2.436 (6)	S(3)—O(8)	1.443 (5)
Ca(1)—O(15)	2.436 (5)	S(3)—O(9)	1.459 (5)
Ca(1)—O(16)	2.371 (5)	S(3)—C(20)	1.795 (7)
Ca(1)—O(17)	2.493 (5)	S(4)—O(10)	1.442 (5)
Ca(1)—O(18)	2.377 (6)	S(4)—O(11)	1.443 (5)
S(1)—O(1)	1.459 (5)	S(4)—O(12)	1.442 (5)
S(1)—O(2)	1.454 (5)	S(4)—C(26)	1.782 (7)
S(1)—O(3)	1.456 (5)	N(1)—C(4)	1.398 (8)
S(1)—C(6)	1.788 (7)	N(2)—C(10)	1.465 (8)
S(2)—O(4)	1.450 (5)	N(3)—C(18)	1.414 (8)
S(2)—O(5)	1.447 (5)	N(4)—C(24)	1.462 (8)
S(2)—O(6)	1.452 (5)		
O(4)—Ca(1)—O(13)	153.3 (2)	O(1)—S(1)—C(6)	106.1 (3)
O(4)—Ca(1)—O(14)	128.3 (2)	O(2)—S(1)—O(3)	112.5 (3)
O(4)—Ca(1)—O(15)	100.5 (2)	O(2)—S(1)—C(6)	106.6 (3)
O(4)—Ca(1)—O(16)	80.9 (2)	O(3)—S(1)—C(6)	107.3 (3)
O(4)—Ca(1)—O(17)	72.8 (2)	O(4)—S(2)—O(5)	112.5 (3)
O(4)—Ca(1)—O(18)	79.7 (2)	O(4)—S(2)—O(6)	112.7 (3)
O(13)—Ca(1)—O(14)	73.9 (2)	O(4)—S(2)—C(12)	106.4 (3)
O(13)—Ca(1)—O(15)	76.1 (2)	O(5)—S(2)—O(6)	112.9 (3)
O(13)—Ca(1)—O(16)	123.2 (2)	O(5)—S(2)—C(12)	105.6 (3)
O(13)—Ca(1)—O(17)	80.6 (2)	O(6)—S(2)—C(12)	105.9 (3)
O(13)—Ca(1)—O(18)	95.0 (2)	O(7)—S(3)—O(8)	113.3 (3)
O(14)—Ca(1)—O(15)	117.8 (2)	O(7)—S(3)—O(9)	111.9 (3)
O(14)—Ca(1)—O(16)	74.2 (2)	O(7)—S(3)—C(20)	107.8 (3)
O(14)—Ca(1)—O(17)	143.4 (2)	O(8)—S(3)—O(9)	112.0 (3)
O(14)—Ca(1)—O(18)	75.0 (2)	O(8)—S(3)—C(20)	106.0 (3)
O(15)—Ca(1)—O(16)	79.0 (2)	O(9)—S(3)—C(20)	105.3 (3)
O(15)—Ca(1)—O(17)	79.8 (2)	O(10)—S(4)—O(11)	111.6 (3)
O(15)—Ca(1)—O(18)	160.4 (2)	O(10)—S(4)—O(12)	112.6 (3)
O(16)—Ca(1)—O(17)	142.4 (2)	O(10)—S(4)—C(26)	107.7 (3)
O(16)—Ca(1)—O(18)	120.0 (2)	O(11)—S(4)—O(12)	112.9 (3)
O(17)—Ca(1)—O(18)	81.6 (2)	O(11)—S(4)—C(26)	107.3 (3)
O(1)—S(1)—O(2)	113.0 (3)	O(12)—S(4)—C(26)	104.1 (3)
O(1)—S(1)—O(3)	110.9 (3)		

Table 6. *Hydrogen-bonding distances (Å) for (II)*

D—H$\cdots A$	$D\cdots A$	D—H$\cdots A$	$D\cdots A$
N(2)—H(23)$\cdots$O(11)	2.767 (8)	O(16)—H(34)$\cdots$O(21^v)	2.779 (8)
N(2)—H(24)$\cdots$O(7)	2.668 (8)	O(16)—H(35)$\cdots$O(23)	2.807 (8)
N(2)—H(25)$\cdots$O(10^i)	2.964 (7)	O(17)—H(36)$\cdots$O(2)	2.844 (7)
N(3)—H(26)$\cdots$O(2^i)	2.946 (8)	O(17)—H(37)$\cdots$O(19^{vi})	2.789 (8)
N(4)—H(28)$\cdots$O(9^{ii})	2.779 (7)	O(19)—H(38)$\cdots$O(12^{vii})	2.857 (8)
N(4)—H(29)$\cdots$O(5)	2.912 (8)	O(19)—H(39)$\cdots$O(24)	2.716 (9)
O(13)—H(30)$\cdots$O(8^{iii})	2.770 (7)	O(20)—H(40)$\cdots$N(1^{viii})	2.880 (9)
O(13)—H(31)$\cdots$O(15)	2.984 (8)	O(23)—H(41)$\cdots$O(16)	2.807 (8)
O(14)—H(32)$\cdots$O(18)	2.931 (8)	O(23)—H(42)$\cdots$O(19^{ix})	2.812 (9)
O(14)—H(33)$\cdots$O(21^{iv})	2.846 (9)	O(24)—H(44)$\cdots$N(3^i)	2.932 (9)

Symmetry codes: (i) $1 - x, -y, 2 - z$; (ii) $-x, -y, 2 - z$; (iii) $x, 1 + y, z$; (iv) $x - 1, y, z$; (v) $1 - x, 1 - y, 2 - z$; (vi) $1 - x, 1 - y, 1 - z$; (vii) $x, y, z - 1$; (viii) $1 + x, y, z$; (ix) $x, y, 1 + z$.

Phenyl C—C bond distances: (I) 1.382 (5)–1.398 (5), mean 1.393 (5) Å; (II) 1.368 (9)–1.406 (9), mean 1.388 (9) Å. All H atoms in compound (I) were located on difference electron density maps and refined with fixed isotropic U values equal to 1.2 times those of the attached atoms at the time of their inclusion. Bond distance ranges: C—H 0.84 (4)–1.08 (4),

N—H 0.70 (4)–0.95 (4) and O—H 0.55 (5)–1.11 (4) Å. For compound (II), some H atoms attached to N and O atoms could not be located. Those which could be positioned were included as fixed isotropic scatterers. No absorption correction was applied for (I) because ψ scans of three reflections indicated a transmission range of less than 5%. As a result of the generally weak reflection intensities for (II), the θ range for the unit cell is unusually low which may cause systematic errors in the cell parameters.

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, 1993); 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, complete geometry, least-squares-planes data and torsion angles have been deposited with the IUCr (Reference: BK1220). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Fronczek, F., Davis, S., Gehrig, L. & Gandour, R. (1987). *Acta Cryst.* C43, 1615–1618.

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. (1994). *Inorg. Chem.* 33, 2924–2931.

Gunderman, B. J. & Squattrito, P. J. (1995). *Inorg. Chem.* 34, 2399–2406.

Johnson, C. K. (1976). *ORTEPII.* Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Lesser, J. & Rabinovich, D. (1978). *Acta Cryst.* B34, 2260–2263.

Molecular Structure Corporation (1988). *MSC/AFC Diffractometer Control Software.* MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Molecular Structure Corporation (1993). *TEXSAN. Single Crystal Structure Analysis Software.* Version 1.6c. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A24, 351–359.

Ohki, Y., Suzuki, Y., Takeuchi, T. & Ouchi, A. (1988). *Bull. Chem. Soc. Jpn,* 61, 393–405.

Shubnell, A., Kosnic, E. & Squattrito. P. (1994). *Inorg. Chim. Acta,* 216, 101–112.

Starynowicz, P. (1992). *Acta Cryst.* C48, 1414–1416.

Aqua[bis(3-aminopropyl)amine-N',N',N'']-(glutarato-O)copper(II) Tetrahydrate

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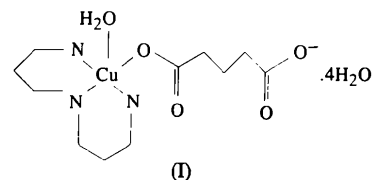
Abstract

The title compound, $[Cu(C_5H_6O_4)(C_6H_{17}N_3)(H_2O)]$.-$4H_2O$, consists of monomeric complex molecules in which the central Cu atom is coordinated by three N atoms from the amine ligand and by one glutarate and one water O atom. The coordination polyhedron is square pyramidal.

Comment

Only a few structures containing copper(II) and glutarate ions have been reported. The coordination of the glutarate anion in the title compound, (I), is of particular interest because glutarate can form both polymeric (Pajunen & Pajunen, 1977) and dimeric (Pajunen & Pajunen, 1979) complexes.

(I)

The coordination polyhedron of the Cu atom is a square pyramid whose base is formed by three N atoms from the amine ligand and the O1 atom of the glutarate ion (Fig. 1). The O5 atom of a coordinated water molecule occupies the apex of the pyramid at a distance of 2.482 (2) Å. The Cu atom also has two long contacts to the water O6 and glutarate O2 atoms. Even though these distances are long [3.061 (3) and 3.102 (2) Å, respectively], the atoms must have some interaction with the Cu atom since the Cu atom lies 0.013 (1) Å from the mean plane defined by the amine N and O1 atoms towards the O6 atom. This is in contrast to the situation found in most square-pyramidal structures, where the Cu atom is lifted *ca* 0.2 Å towards the apex of the pyramid (Hathaway & Billing, 1970). An interesting feature of the structure is the dissimilar conformations of the two six-membered chelate rings. The ring including the N2