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Tetraaquabis[2-(thiosemicarbazonomethyl)benzenesulfonato]calcium(II)

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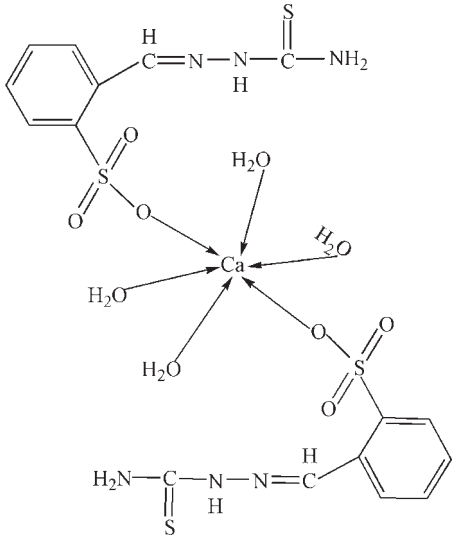
Key indicators: single-crystal X-ray study; T = 298 K; mean σ(C–C) = 0.009 Å; R factor = 0.078; wR factor = 0.227; data-to-parameter ratio = 13.1.

In the title compound, $[Ca(C_8H_8N_3O_3S_2)_2(H_2O)_4]$, the Ca atom (site symmetry $\bar{1}$) adopts a slightly distorted octahedral CaO_6 geometry and the molecular conformation is stabilized by intramolecular N—H···N interactions. In the crystal, the molecules are linked by O—H···O, O—H···S, N—H···O and N—H···S hydrogen bonds.

Related literature

For background to Schiff bases, see: Sawant *et al.* (2009).



Experimental

Crystal data

$[Ca(C_8H_8N_3O_3S_2)_2(H_2O)_4]$
M_r = 628.73
Triclinic, $P\bar{1}$
a = 6.9123 (11) Å
b = 9.6383 (13) Å
c = 10.9481 (17) Å
α = 64.372 (1)°
β = 87.708 (2)°
γ = 83.225 (2)°
V = 652.99 (17) Å^3
Z = 1
Mo $K\alpha$ radiation
μ = 0.62 mm^{-1}
T = 298 K
0.31 × 0.15 × 0.12 mm

Data collection

Bruker SMART CCD diffractometer
Absorption correction: multi-scan *SADABS* (Bruker, 2000)
T_{min} = 0.831, T_{max} = 0.929
2223 measured reflections
2223 independent reflections
1781 reflections with $I > 2\sigma(I)$

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.078
$wR(F^2)$ = 0.227
S = 1.04
2223 reflections
170 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.60 e Å^{-3}
$\Delta\rho_{min}$ = −0.55 e Å^{-3}

Table 1
Selected bond lengths (Å).

Ca1—O4	2.310 (4)	Ca1—O1	2.362 (4)
Ca1—O5	2.313 (6)		

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

D—H···A	D—H	H···A	D···A	D—H···A
N3—H3A···N2	0.86	2.28	2.636 (7)	105
O5—H5C···O2^{i}	0.85	2.07	2.840 (9)	150
N1—H1···S2^{ii}	0.86	2.60	3.441 (6)	166
N3—H3B···O2^{iii}	0.86	2.34	3.035 (7)	138
O4—H4C···S2^{iv}	0.85	2.42	3.261 (6)	173
O4—H4D···O3^{v}	0.85	1.87	2.712 (8)	171
O5—H5D···S2^{ii}	0.85	2.42	3.197 (8)	152

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

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB5075).

References

Bruker (2000). *SMART*, *SAINT* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
Sawant, S. K., Gaikwad, G. A., Sawant, V. A., Yamgar, B. A. & Chavan, S. S. (2009). *Inorg. Chem. Commun.* **12**, 632–633.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

supporting information

Acta Cryst. (2009). E**65**, m1195 [doi:10.1107/S1600536809035971]

Tetraaquabis[2-(thiosemicarbazonomethyl)benzenesulfonato]calcium(II)

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S1. Comment

Schiff base metal complexes have been of interest in coordination chemistry for many years due to their facile synthesis, strong coordination function and wide applications (*e.g.* Sawant, *et al.*, 2009). Ca complexes with Schiff base ligand have received little attention. In this paper, we report on the synthesis and crystal structure of the title compound, (I), (Scheme I).

The Ca(II) center is Six-coordinate with two O donors of 2-formyl-benzenesulfonate-thiosemicarbazide ligands and four O donors of coordinated water molecules, and adopts distorted octahedral coordination. The bond distances of Ca—O are in the range of 2.310 (4)–2.362 (4), which are consistent with the bond lengths reported previously. In the crystal packing, the molecules form a one-dimensional chain structure by the interaction of hydrogen bonds.

S2. Experimental

A solution of 1.0 mmol 2-formyl-benzenesulfonate-thiosemicarbazide was added to a solution of 0.5 mmol $Ca(ClO_4)_2.4H_2O$ in 5 ml e thanol at room temperature. The mixture was refluxed for 4 h with stirring, then the resulting precipitate was filtered, washed, and dried *in vacuo* over P_4O_{10} for 48 h. Colourless blocks of (I) were obtained by slowly evaporating from methanol at room temperature.

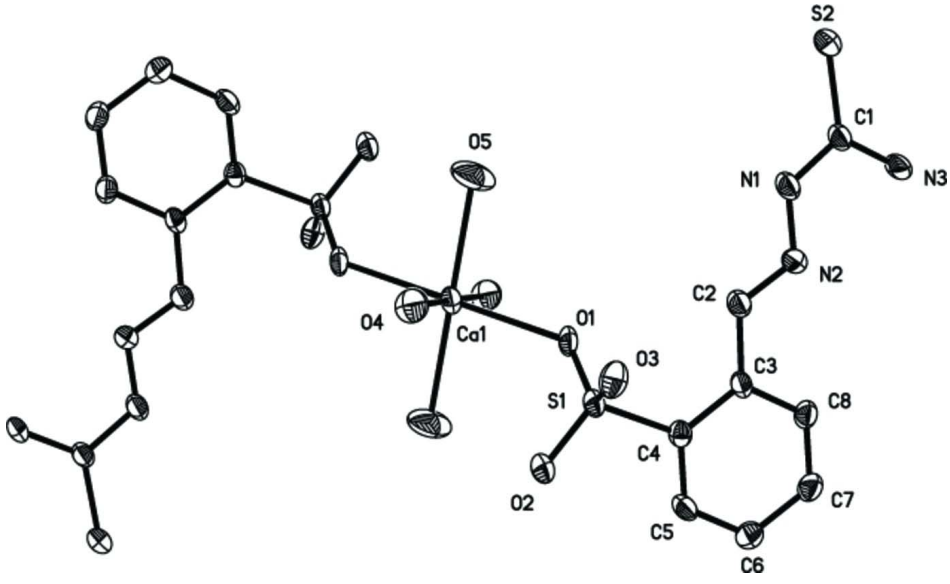

Figure 1

The molecular structure of (I) showing 30% displacement ellipsoids. Unlabelled atoms are generated by the symmetry operation (1–x, 1–y, 1–z).

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Triclinic, $P\overline{1}$
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$\alpha = 64.372$ (1)°
$\beta = 87.708$ (2)°
$\gamma = 83.225$ (2)°
$V = 652.99$ (17) Å^3
$Z = 1$
$F(000) = 326$
$D_x = 1.599$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 1563 reflections
$\theta = 3.6$–27.6°
$\mu = 0.62$ mm^{-1}
$T = 298$ K
Block, colourless
0.31 × 0.15 × 0.12 mm

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Graphite monochromator
ω scans
Absorption correction: multi-scan *SADABS* (Bruker, 2000)
$T_{min} = 0.831$, $T_{max} = 0.929$
2223 measured reflections
2223 independent reflections
1781 reflections with $I > 2\sigma(I)$
$R_{int} = 0.000$
$\theta_{max} = 25.0°$, $\theta_{min} = 2.1°$
$h = -8 \rightarrow 8$
$k = -10 \rightarrow 11$
$l = -9 \rightarrow 13$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.078$
$wR(F^2) = 0.227$
$S = 1.04$
2223 reflections
170 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.1501P)^2 + 0.6556P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.60$ e Å^{-3}
$\Delta\rho_{min} = -0.55$ e Å^{-3}

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	U_{iso}*/U_{eq}
Ca1	0.5000	0.5000	0.5000	0.0345 (5)
S1	0.7458 (2)	0.67806 (16)	0.65974 (13)	0.0354 (4)
S2	1.0140 (3)	−0.13332 (17)	1.21326 (16)	0.0449 (5)

O1	0.6451 (7)	0.5503 (5)	0.6662 (4)	0.0438 (11)
O2	0.6760 (7)	0.8251 (5)	0.5486 (4)	0.0501 (12)
O3	0.9554 (7)	0.6437 (6)	0.6624 (5)	0.0507 (12)
O4	0.7857 (7)	0.5634 (6)	0.3822 (5)	0.0556 (13)
H4C	0.8364	0.6474	0.3401	0.083*
H4D	0.8592	0.4914	0.3730	0.083*
O5	0.6194 (10)	0.2408 (6)	0.5851 (8)	0.096 (3)
H5C	0.5528	0.1878	0.5611	0.143*
H5D	0.7093	0.1806	0.6394	0.143*
N1	0.9136 (7)	0.1670 (6)	1.0860 (5)	0.0354 (11)
H1	0.9541	0.1587	1.0139	0.043*
N2	0.8339 (7)	0.3076 (5)	1.0789 (5)	0.0337 (11)
N3	0.8802 (9)	0.0645 (6)	1.3157 (5)	0.0506 (14)
H3A	0.8420	0.1565	1.3071	0.061*
H3B	0.8874	−0.0123	1.3947	0.061*
C1	0.9278 (8)	0.0419 (6)	1.2074 (6)	0.0353 (13)
C2	0.8137 (8)	0.4179 (6)	0.9586 (6)	0.0352 (12)
H2	0.8529	0.4001	0.8838	0.042*
C3	0.7269 (8)	0.5739 (6)	0.9407 (5)	0.0309 (12)
C4	0.6848 (8)	0.6971 (6)	0.8118 (5)	0.0311 (12)
C5	0.6039 (9)	0.8407 (7)	0.7991 (6)	0.0390 (13)
H5	0.5791	0.9211	0.7133	0.047*
C6	0.5592 (9)	0.8668 (7)	0.9128 (7)	0.0429 (14)
H6	0.5031	0.9635	0.9034	0.052*
C7	0.5998 (9)	0.7453 (8)	1.0420 (7)	0.0441 (15)
H7	0.5721	0.7615	1.1190	0.053*
C8	0.6807 (9)	0.6020 (7)	1.0545 (6)	0.0369 (13)
H8	0.7054	0.5219	1.1406	0.044*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ca1	0.0392 (9)	0.0391 (9)	0.0220 (8)	−0.0068 (7)	−0.0025 (6)	−0.0094 (7)
S1	0.0473 (9)	0.0352 (8)	0.0200 (7)	−0.0087 (6)	−0.0001 (6)	−0.0074 (6)
S2	0.0613 (11)	0.0331 (8)	0.0317 (8)	−0.0016 (7)	−0.0043 (7)	−0.0066 (7)
O1	0.069 (3)	0.044 (2)	0.0195 (19)	−0.016 (2)	−0.0045 (18)	−0.0119 (18)
O2	0.080 (3)	0.040 (2)	0.023 (2)	−0.011 (2)	−0.005 (2)	−0.0059 (19)
O3	0.053 (3)	0.066 (3)	0.042 (3)	−0.011 (2)	0.008 (2)	−0.031 (2)
O4	0.056 (3)	0.058 (3)	0.053 (3)	−0.017 (2)	0.019 (2)	−0.023 (2)
O5	0.103 (5)	0.043 (3)	0.123 (6)	0.013 (3)	−0.073 (4)	−0.018 (3)
N1	0.042 (3)	0.034 (2)	0.022 (2)	0.001 (2)	−0.0021 (19)	−0.005 (2)
N2	0.038 (3)	0.030 (2)	0.029 (3)	−0.0019 (19)	−0.0006 (19)	−0.009 (2)
N3	0.082 (4)	0.034 (3)	0.024 (3)	0.000 (3)	0.000 (2)	−0.004 (2)
C1	0.040 (3)	0.035 (3)	0.025 (3)	−0.007 (2)	−0.003 (2)	−0.006 (2)
C2	0.039 (3)	0.034 (3)	0.027 (3)	−0.004 (2)	−0.004 (2)	−0.008 (2)
C3	0.032 (3)	0.031 (3)	0.026 (3)	−0.008 (2)	−0.005 (2)	−0.007 (2)
C4	0.032 (3)	0.033 (3)	0.025 (3)	−0.010 (2)	0.002 (2)	−0.008 (2)
C5	0.045 (3)	0.031 (3)	0.032 (3)	−0.005 (2)	−0.003 (2)	−0.005 (2)

C6	0.047 (3)	0.040 (3)	0.045 (4)	0.000 (3)	0.000 (3)	−0.021 (3)
C7	0.055 (4)	0.047 (3)	0.037 (3)	−0.013 (3)	0.007 (3)	−0.023 (3)
C8	0.045 (3)	0.037 (3)	0.028 (3)	−0.008 (2)	−0.001 (2)	−0.012 (2)

Geometric parameters (Å, º)

Ca1—O4^{i}	2.310 (4)	N1—H1	0.8600
Ca1—O4	2.310 (4)	N2—C2	1.286 (7)
Ca1—O5	2.313 (6)	N3—C1	1.318 (8)
Ca1—O5^{i}	2.313 (6)	N3—H3A	0.8599
Ca1—O1	2.362 (4)	N3—H3B	0.8599
Ca1—O1^{i}	2.362 (4)	C2—C3	1.484 (8)
S1—O3	1.446 (5)	C2—H2	0.9300
S1—O2	1.455 (4)	C3—C8	1.403 (8)
S1—O1	1.459 (4)	C3—C4	1.410 (8)
S1—C4	1.781 (6)	C4—C5	1.380 (9)
S2—C1	1.698 (6)	C5—C6	1.389 (9)
O4—H4C	0.8497	C5—H5	0.9300
O4—H4D	0.8503	C6—C7	1.405 (10)
O5—H5C	0.8504	C6—H6	0.9300
O5—H5D	0.8499	C7—C8	1.378 (9)
N1—C1	1.351 (7)	C7—H7	0.9300
N1—N2	1.372 (7)	C8—H8	0.9300
O4^{i}—Ca1—O4	180.0	H5C—O5—H5D	108.9
O4^{i}—Ca1—O5	90.5 (2)	C1—N1—N2	119.3 (5)
O4—Ca1—O5	89.5 (2)	C1—N1—H1	120.4
O4^{i}—Ca1—O5^{i}	89.5 (2)	N2—N1—H1	120.3
O4—Ca1—O5^{i}	90.5 (2)	C2—N2—N1	115.2 (5)
O5—Ca1—O5^{i}	180.0	C1—N3—H3A	119.7
O4^{i}—Ca1—O1	94.41 (17)	C1—N3—H3B	120.2
O4—Ca1—O1	85.59 (17)	H3A—N3—H3B	120.0
O5—Ca1—O1	96.42 (19)	N3—C1—N1	117.5 (5)
O5^{i}—Ca1—O1	83.58 (19)	N3—C1—S2	123.7 (4)
O4^{i}—Ca1—O1^{i}	85.59 (17)	N1—C1—S2	118.8 (5)
O4—Ca1—O1^{i}	94.41 (17)	N2—C2—C3	119.1 (6)
O5—Ca1—O1^{i}	83.58 (19)	N2—C2—H2	120.5
O5^{i}—Ca1—O1^{i}	96.42 (19)	C3—C2—H2	120.5
O1—Ca1—O1^{i}	180.0	C8—C3—C4	117.7 (5)
O4^{i}—Ca1—H5C	83.1	C8—C3—C2	119.9 (5)
O4—Ca1—H5C	96.9	C4—C3—C2	122.3 (5)
O5—Ca1—H5C	16.4	C5—C4—C3	120.7 (5)
O5^{i}—Ca1—H5C	163.6	C5—C4—S1	117.3 (4)
O1—Ca1—H5C	111.4	C3—C4—S1	121.9 (4)
O1^{i}—Ca1—H5C	68.6	C4—C5—C6	120.9 (6)
O3—S1—O2	113.0 (3)	C4—C5—H5	119.5
O3—S1—O1	112.4 (3)	C6—C5—H5	119.5
O2—S1—O1	112.7 (3)	C5—C6—C7	119.1 (6)

O3—S1—C4	106.2 (3)	C5—C6—H6	120.4
O2—S1—C4	106.4 (3)	C7—C6—H6	120.4
O1—S1—C4	105.5 (2)	C8—C7—C6	119.9 (6)
S1—O1—Ca1	133.1 (2)	C8—C7—H7	120.1
Ca1—O4—H4C	134.2	C6—C7—H7	120.1
Ca1—O4—H4D	117.6	C7—C8—C3	121.6 (6)
H4C—O4—H4D	108.2	C7—C8—H8	119.2
Ca1—O5—H5C	113.7	C3—C8—H8	119.2
Ca1—O5—H5D	137.2		

O3—S1—O1—Ca1	−98.8 (4)	C8—C3—C4—S1	177.3 (4)
O2—S1—O1—Ca1	30.3 (5)	C2—C3—C4—S1	−3.8 (7)
C4—S1—O1—Ca1	145.9 (3)	O3—S1—C4—C5	115.4 (5)
O4^{i}—Ca1—O1—S1	−131.7 (4)	O2—S1—C4—C5	−5.2 (5)
O4—Ca1—O1—S1	48.3 (4)	O1—S1—C4—C5	−125.1 (5)
O5—Ca1—O1—S1	137.3 (4)	O3—S1—C4—C3	−61.0 (5)
O5^{i}—Ca1—O1—S1	−42.7 (4)	O2—S1—C4—C3	178.4 (4)
O1^{i}—Ca1—O1—S1	61 (12)	O1—S1—C4—C3	58.5 (5)
C1—N1—N2—C2	−175.4 (5)	C3—C4—C5—C6	−1.1 (9)
N2—N1—C1—N3	−6.2 (8)	S1—C4—C5—C6	−177.5 (4)
N2—N1—C1—S2	176.3 (4)	C4—C5—C6—C7	0.9 (9)
N1—N2—C2—C3	179.4 (5)	C5—C6—C7—C8	−0.8 (9)
N2—C2—C3—C8	4.4 (8)	C6—C7—C8—C3	0.9 (9)
N2—C2—C3—C4	−174.4 (5)	C4—C3—C8—C7	−1.0 (8)
C8—C3—C4—C5	1.1 (8)	C2—C3—C8—C7	−179.9 (5)
C2—C3—C4—C5	180.0 (5)		

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

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N3—H3*A*···N2	0.86	2.28	2.636 (7)	105
O5—H5*C*···O2^{i}	0.85	2.07	2.840 (9)	150
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