

prepare material for publication: *BONDLA* (Dreissig, Doherty, Stewart & Hall, 1992), *ATABLE* (Englehardt & Hall, 1992) and *CIFIO* (Hall, 1992b).

We thank Professor Dr Carl Krüger for the possibility to collect the data in his laboratory.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: KA1225). Services for accessing these data are described at the back of the journal.

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Tetramethylammonium Hydrogen Bis[bis(dimethyldithiocarbamyl)acetate]†

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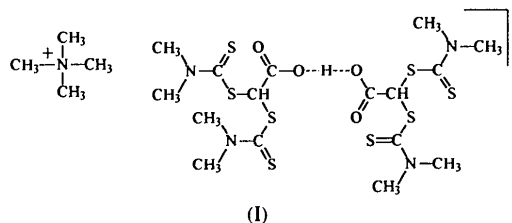
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Abstract

The two carboxylate anions in the title compound, $C_4H_{12}N^+ \cdot C_{16}H_{27}N_4O_4S_8^-$, are linked through an H atom which lies on a center of inversion [$O \cdots O$ 2.484 (3) Å].

Comment

In an earlier study, the C—O and C=O bonds [1.232 (2)–1.241 (3) Å] of the $-CO_2$ group in both independent ion pairs of dicyclohexylammonium bis(*N,N*-dimethyldithiocarbamyl)acetate were found to be indistinguishable from one another (Ng, 1996). The anions are linked through the ammonium N atom across a center of inversion into a dimeric ion pair having an O—C—O \cdots N \cdots O—C—O \cdots N ring. Such hydrogen bonding through N atoms is not possible with the title compound, (I), which crystallizes with a neutral acid molecule.



† Alternative name: tetramethylammonium hydrogen bis[bis(*N,N*-dimethyldithiocarbamylthio)acetate].

The carboxylate anion and the neutral acid molecule are linked through the acidic H atom [O...O 2.486 (3) Å]. The hydrogen-bond distance is similar to that [O...O 2.448 (3) Å] found in bis(dicyclohexylammonium) trithiocarbodiglycolate trithiocarbodiglycolic acid (Ng, 1995); this compound also has its anionic entity hydrogen bonded to an acid molecule.

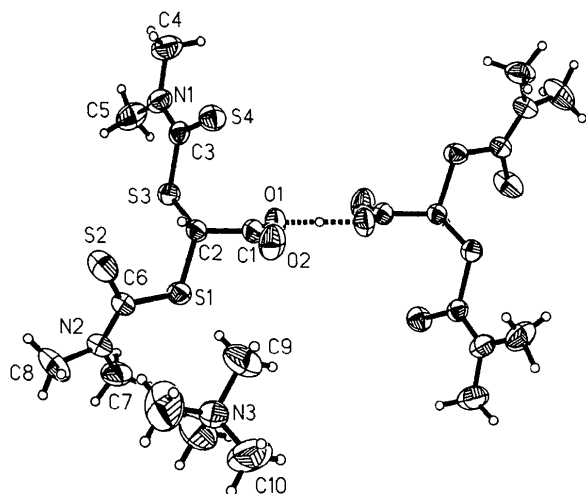


Fig. 1. ORTEP (Johnson, 1976) plot at the 50% probability level. H atoms are drawn as spheres of arbitrary radii.

Experimental

Equimolar quantities of bis(*N,N*-dimethyldithiocarbamyl)-acetic acid (Pluijgers & van der Kerk, 1961) and tetramethylammonium hydroxide were dissolved in a small volume of hot ethanol. The title compound separated on slow evaporation of the solvent.

Crystal data

C₄H₁₂N⁺.C₁₆H₂₇N₄O₄S₈⁻

M_r = 670.04

Monoclinic

*C*2/*c*

a = 29.268 (3) Å

b = 8.9925 (6) Å

c = 13.569 (2) Å

β = 115.063 (6)°

V = 3234.9 (6) Å³

Z = 4

D_x = 1.376 Mg m⁻³

D_m not measured

Data collection

Enraf-Nonius CAD-4 diffractometer

ω scans

Absorption correction:

ψ scans (North, Phillips & Mathews, 1968)

T_{min} = 0.706, *T_{max}* = 0.916

Mo Kα radiation

λ = 0.71073 Å

Cell parameters from 25 reflections

θ = 12.0–13.0°

μ = 0.586 mm⁻¹

T = 298 (2) K

Block

0.50 × 0.50 × 0.15 mm

Colorless

2314 reflections with

I > 2σ(*I*)

R_{int} = 0.013

θ_{max} = 24.97°

h = -31 → 34

k = 0 → 10

l = -16 → 9

3578 measured reflections
2842 independent reflections

Refinement

Refinement on *F*²

R[*F*² > 2σ(*F*²)] = 0.039

wR(*F*²) = 0.104

S = 1.037

2842 reflections

233 parameters

All H atoms were located and refined; an EADP instruction was used for each set of methyl H atoms (Sheldrick, 1993)

3 standard reflections
frequency: 60 min
intensity decay: none

w = 1/[σ²(*F_o*²) + (0.0647*P*)² + 0.9189*P*]

where *P* = (*F_o*² + 2*F_c*²)/3

(Δ/σ)_{max} = 0.001

Δρ_{max} = 0.347 e Å⁻³

Δρ_{min} = -0.223 e Å⁻³

Extinction correction: none

Scattering factors from

International Tables for Crystallography (Vol. C)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

$$U_{eq} = (1/3)\sum_i \sum_j U^{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U_{eq}</i>
S1	0.41978 (2)	0.20502 (7)	0.67335 (5)	0.0426 (2)
S2	0.33846 (3)	0.43656 (9)	0.56577 (6)	0.0662 (3)
S3	0.35494 (2)	0.01125 (7)	0.50556 (5)	0.0412 (2)
S4	0.34583 (3)	0.09739 (8)	0.28391 (5)	0.0501 (2)
O1	0.46225 (6)	0.0125 (2)	0.5191 (2)	0.0515 (5)
O2	0.46325 (8)	0.2561 (2)	0.4896 (2)	0.0666 (6)
N1	0.29239 (8)	-0.1122 (2)	0.3261 (2)	0.0498 (5)
N2	0.38140 (8)	0.3716 (2)	0.7755 (2)	0.0454 (5)
N3	1/2	0.6731 (4)	3/4	0.0516 (8)
C1	0.44494 (9)	0.1445 (3)	0.5092 (2)	0.0426 (6)
C2	0.39781 (9)	0.1658 (3)	0.5298 (2)	0.0363 (5)
C3	0.32778 (8)	-0.0060 (3)	0.3621 (2)	0.0381 (5)
C4	0.2678 (1)	-0.1466 (4)	0.2090 (3)	0.0682 (9)
C5	0.2765 (1)	-0.1949 (4)	0.3982 (3)	0.0675 (9)
C6	0.3773 (1)	0.3452 (3)	0.6757 (2)	0.0374 (5)
C7	0.4138 (1)	0.2851 (4)	0.8713 (2)	0.0623 (8)
C8	0.3538 (2)	0.4923 (5)	0.7966 (4)	0.082 (1)
C9	0.4961 (2)	0.5718 (5)	0.6576 (3)	0.088 (1)
C10	0.5455 (2)	0.7673 (7)	0.7833 (5)	0.115 (2)

Table 2. Geometric parameters (Å, °)

S1—C2	1.809 (2)	N1—C5	1.455 (4)
S1—C6	1.780 (2)	N2—C6	1.328 (3)
S2—C6	1.660 (2)	N2—C7	1.466 (4)
S3—C2	1.807 (2)	N2—C8	1.453 (4)
S3—C3	1.770 (3)	N3—C9	1.515 (4)
S4—C3	1.657 (3)	N3—C9 ⁱ	1.515 (4)
O1—C1	1.276 (3)	N3—C10	1.479 (5)
O2—C1	1.218 (3)	N3—C10 ⁱ	1.479 (5)
N1—C3	1.339 (3)	C1—C2	1.531 (3)
N1—C4	1.473 (4)		
C2—S1—C6	103.0 (1)	C10—N3—C10 ⁱ	110.1 (6)
C2—S3—C3	102.8 (1)	O1—C1—O2	126.7 (2)
C3—N1—C4	119.5 (3)	O1—C1—C2	116.5 (2)
C3—N1—C5	122.5 (2)	O2—C1—C2	116.8 (2)
C4—N1—C5	118.0 (3)	C1—C2—S1	106.5 (2)
C6—N2—C7	123.6 (2)	C1—C2—S3	118.7 (2)
C6—N2—C8	121.2 (2)	S1—C2—S3	104.4 (1)
C7—N2—C8	115.2 (3)	N1—C3—S4	125.0 (2)
C9—N3—C9 ⁱ	106.0 (4)	N1—C3—S3	112.4 (2)
C9—N3—C10	109.8 (3)	S3—C3—S4	122.6 (1)
C9—N3—C10 ⁱ	110.5 (3)	N2—C6—S1	112.5 (2)
C9 ⁱ —N3—C10	110.5 (3)	N2—C6—S2	124.0 (2)
C9 ⁱ —N3—C10 ⁱ	109.8 (3)	S1—C6—S2	123.5 (1)

Symmetry code: (i) 1 - *x*, *y*, ½ - *z*.

Data collection: *CAD-4 VAX/PC Software* (Enraf–Nonius, 1988). Cell refinement: *CAD-4 VAX/PC Software*. Data reduction: *NRCVAX* (Gabe, Le Page, Charland, Lee & White, 1989). Program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *SHELXL93*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: KH1134). Services for accessing these data are described at the back of the journal.

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N,N'-Diphenylguanidinium Hydrogenselenite Monohydrate

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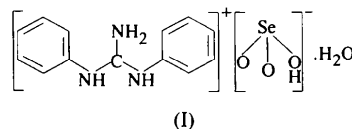
Abstract

In the crystal structure of the title compound, $C_{13}H_{14}N_3^+ \cdot HSeO_3^- \cdot H_2O$, the phenyl rings lie *syn* to the

unsubstituted N atom of the cation and the geometry of the guanidinium group is close to that expected for a central C_{sp^2} atom. The crystal packing is stabilized by an extensive network of hydrogen bonds. The anion is an acceptor of the N—H guanidinium groups and the water molecule forms a four-membered hydrogen-bonded ring with the anion.

Comment

The title compound belongs to a series of new selenite compounds of organic moieties synthesized as part of a project to study new materials with potentially interesting optical and dielectric properties (de Matos Gomes *et al.*, 1995; Paixão *et al.*, 1997). Selenite compounds are particularly interesting due to the fact that they often exhibit ferro- or antiferroelectric properties and structural phase transitions at low temperature associated with the onset of the polar phases, as found in the alkali trihydrogenselenites (Shulalov, Ivanov, Gordeeva & Kirpichnikova, 1970). Phase transitions have been observed in the novel compound benzytrimethylammonium trihydrogen selenite (de Matos Gomes *et al.*, 1995), but DSC measurements failed to show any peculiar feature for the present compound while cooling from room temperature down to 233 K.



The $HSeO_3^-$ ion is pyramidal with two shorter Se—O bonds [1.649 (2) and 1.665 (2) Å] and one longer Se—OH bond [1.768 (2) Å]. The average value of an Se—O bond is 1.65 Å and that of an Se—OH bond is about 1.75 Å (Chomnilpan, Liminga, Sonneveld & Visser, 1981). The O—Se—O angles, 99–105°, are in the same range as those observed in other hydrogenselenite and trihydrogen selenite compounds (Chomnilpan, Tellgren & Liminga, 1978). The geometry of the inorganic moiety, namely the presence of the two short Se—O bond distances, clearly implies that the diphenylguanidinium molecule is protonated.

Regarding the geometry of the *N,N'*-diphenylguanidinium cation ($dpgH^+$) it is pertinent to make a comparison with a similar compound, *N,N'*-diphenylguanidinium *m*-chlorobenzeneseleninate (Antolini *et al.*, 1991). Also relevant for discussion are the structures of *N*-adamant-1-yl-*N'*-(2-iodophenyl)guanidinium chloride (Weakley, Scherz & Keana, 1990), of the unprotonated molecules of *N,N'*-diphenylguanidine (*dpg*) (Zakharov, Andrianov & Struchkov, 1980) and of *N,N'*-bis(2-methylphenyl)guanidine (Brown & Gash, 1984).

The bond lengths C1—N1 [1.342 (4) Å] and C1—N3 [1.335 (4) Å] of the guanidinium group are close to the standard value of a delocalized C=N bond [1.339 (5) Å]