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The Crystal and Molecular Structure of Hydrazinium Hydrazinedithiocarboxylate

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The crystal structure of hydrazinium hydrazinedithiocarboxylate, $(\text{N}_2\text{H}_5)(\text{H}_2\text{N}'\text{-NH-CSS})$, has been solved by a new method of sign determination and refined three-dimensionally by differential syntheses. The hydrazinedithiocarboxylate anions form layers parallel to (010) and the hydrazinium cations form hydrogen bonds between one another, normal to (010). The $\text{N}'\text{-N-CSS}$ group, which can be considered as a dithiocarbamate anion, is planar; the main interatomic distances in the anion are: C-S 1.723 and 1.695 Å, C-N 1.330 Å and $\text{N}'\text{-N}$ 1.414 Å. The distance between nitrogen atoms in the hydrazinium cations is 1.436 Å. The whole structure is held together by a network of hydrogen bonds.

Introduction

The study of the crystal structure of hydrazinium hydrazinedithiocarboxylate, $(\text{N}_2\text{H}_5)(\text{H}_2\text{N}'\text{-NH-CSS})$, has been undertaken as an extension of the studies on crystal and molecular structures of salts of hydrazine-carboxylic acid. Hydrazinedithiocarboxylic acid can be considered also as a derivative of dithiocarbamic acid and interesting comparisons can be made with the structures of dithiocarbamates.

Experimental

The compound was prepared by reaction of hydrazine hydrate and carbon sulphide (Curtius & Heidenreich, 1894). The material was recrystallized from water. The crystals obtained were colorless, well formed, fairly unstable prisms. Their composition was confirmed by chemical analysis.

Crystal data

Compound: hydrazinium hydrazinedithiocarboxylate
 $(\text{N}_2\text{H}_5)(\text{H}_2\text{N}'\text{-NH-CSS})$
F.W. 140.24.

Crystal habit: prisms, elongated along [010].

Crystal class: monoclinic, prismatic.

Unit cell: from rotation and Weissenberg photographs around [100] and [010] (Cu $K\alpha$, $\lambda = 1.5418$ Å)
 $a = 7.108(6)$, $b = 6.828(3)$, $c = 11.993(7)$ Å
 $\beta = 90.65(15)^\circ$
 $V = 582.0$ Å³ $Z = 4$
 $D_m = 1.599$ (by flotation), $D_x = 1.600$ g.cm⁻³
 $\mu(\text{Cu } K\alpha) = 70.67$ cm⁻¹.

Space group: $P2_1/c$ (C_{2h}^5 , no. 14), from systematic absences.

Intensity measurements

Integrated reflexions $h0l$, ... $h5l$ and $0kl$, ... $4kl$, obtained by a Weissenberg camera, were measured by a microdensitometer. Absorption corrections were applied as for cylindrical specimens ($\mu\bar{R} = 0.85$).

The structure factor and refinement calculations were performed on the computer Olivetti Elea 6001/S of the Centro Elettronico of the University of Parma. The calculations related to the application of the direct method for sign determination were carried out at the computing centre of the Polytechnic of Milan, on a IBM-7040 computer.

Determination of the structure

The structure has been solved by applying the method of sign determination developed by Allegra (1965) to $h0l$ and $0kl$ projections. Since a fairly detailed description of the method will be given in a subsequent paper dealing with the X-ray structure of bis(tricobalt enneacarbonyl) acetone (Allegra & Valle, 1969) here we will limit ourselves to a concise report on the essential results.

The reflexions of the two projections were treated independently. After the structure factor normalization obtained from a Wilson (1942) plot, the reflexions with $|A| > 0.5 (=2A)$ were selected and the quantities $\alpha_{H, H+L} = th(|A_{H+L} A_{H+L}| \cdot \Sigma f_j^2 \cdot (\Sigma f_j^2)^{-3/2})$ and $\alpha_{K, K+L}$ respectively (H, K and L stand for reciprocal vectors) were calculated. Then 24 reflexions having $|A| > 1.0 (=1A)$ were chosen as base reflexions for each projection, and the most probable combinations of signs were calculated. For each projection only the three combinations with the highest probabilities were then taken into account. The corresponding signs of the non-base reflexions were derived from analysis of the α terms, connecting every non-base reflexion with two base reflexions.

Fig. 1 shows six Fourier plots, obtained from the non-normalized structure factors; the symbols A, B and C correspond to the three most probable sign combinations for each projection, in decreasing order. The test for correctness of the above plots was based on the existence, on each projection, of two heavy peaks (S atoms), having approximately equal weights and also approximately coherent coordinates along c : as is apparent from inspection of the Figure, the B plot on (xz) projection and the C plot on (yz) projection meet the above requirement, provided that the origin on each projection is conveniently chosen. An accurate inspection of the two Fourier plots revealed both the anion and the cation: as a matter of fact, all the 24 $h0l$ and 24 $0kl$ base reflexions and 90% of the reflexions used proved to have correct signs. The structure was refined by differential syntheses from three-dimensional data (final $R=12\%$, from 1089 observed reflexions only). The anisotropic thermal parameters were refined following the method of Nardelli

& Fava (1960). The final results of the structure determination are reported in Tables 1-4.

Table 1. Fractional atomic coordinates
(with *e.s.d.*'s $\times 10^4$)

	<i>x</i>	<i>y</i>	<i>z</i>
S(1)	0.0182 (3)	0.2437 (4)	0.1621 (1)
C(2)	0.1053 (8)	0.2603 (9)	0.0315 (5)
N(3)	-0.0097 (8)	0.2471 (10)	-0.0565 (4)
N(4)	-0.2071 (10)	0.2215 (11)	-0.0553 (6)
S(5)	0.3416 (2)	0.2841 (3)	0.0042 (1)
N(6)	0.5695 (9)	0.0196 (9)	0.2334 (4)
N(7)	0.3878 (8)	-0.0480 (10)	0.2678 (5)

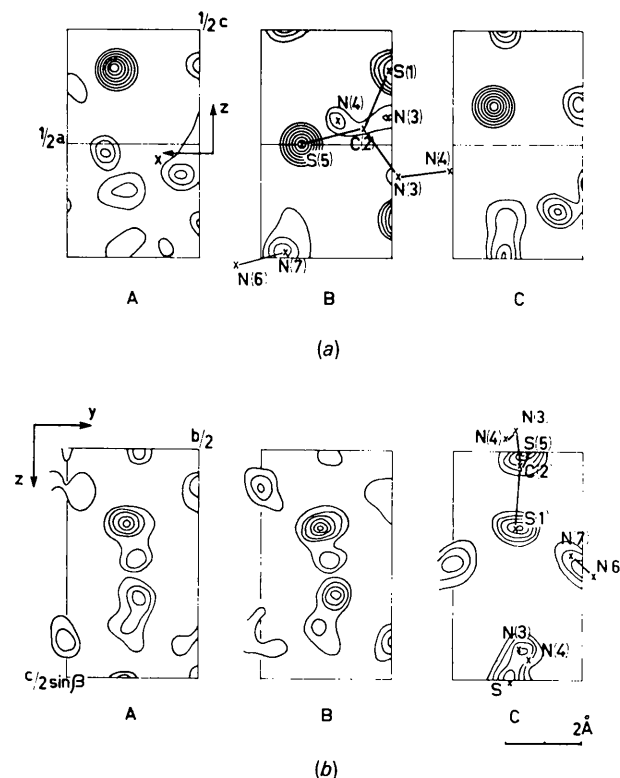


Fig. 1. Electron density maps (contours at arbitrary intervals) corresponding to the *a priori* most probable sign combinations (A, B, C in decreasing order of probability): (a) (x, z) projection; B map has been chosen. (b) (y, z) projection; C map has been chosen.

Table 2. Anisotropic thermal parameters (\AA^2)

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
S(1)	2.581	4.121	1.859	0.291	0.085	0.150
C(2)	1.846	1.767	1.755	0.307	0.057	-0.102
N(3)	1.942	3.181	1.601	0.182	0.372	0.089
N(4)	2.080	3.051	2.294	-0.018	0.121	0.269
S(5)	1.747	2.890	2.239	-0.294	0.048	0.083
N(6)	2.244	2.789	2.258	0.310	0.078	0.052
N(7)	1.796	3.260	2.851	-0.184	-0.235	0.134
Shifts of the last cycle						
$ \Delta B_{ij} _{av}$	0.037	0.051	0.030	0.010	0.006	0.015
$ \Delta B_{ij} _{max}$	0.129	0.093	0.074	0.029	0.012	0.031

in hydrazinecarboxylato chelates. The ensemble, however, of the results obtained shows how the hydrazine-dithiocarboxylato anion is more similar to the dithiocarbamates than to its oxygenated analogue hydrazinecarboxylato anion.

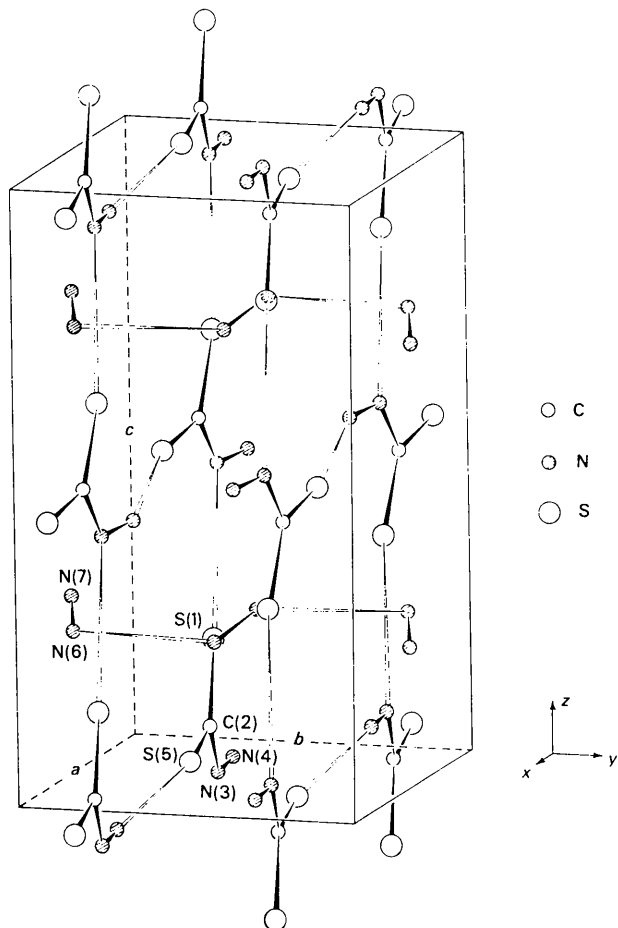


Fig. 2. Projection of the structure of $(\text{N}_2\text{H}_5)(\text{H}_2\text{N}'\text{-NHCSS})$.

The angle $\text{S}(1)\text{-C}(2)\text{-S}(5)$, 123.3° , is larger than the corresponding angle in dithiocarbamates, where, however, there can be some strain due to chelation of the sulfur atoms with the metal cation. The distances $\text{C}(2)\text{-S}(1)$, 1.695 , and $\text{C}(2)\text{-S}(5)$, 1.723 Å, practically conform with the corresponding distances in dithiocarbamates. The difference between $\text{C}(2)\text{-S}(1)$ and $\text{C}(2)\text{-S}(5)$, although statistically significant, is not apparently justified by chemical evidence, $\text{S}(1)$ and $\text{S}(5)$ being equidistant from the cation N_2H_5^+ .

The intermolecular contacts $\text{S}\cdots\text{N} < 3.38$ Å and $\text{N}\cdots\text{N} < 3.08$ Å can be considered as weak hydrogen bonds (Wallwork, 1962) though the angles between these presumed hydrogen bonds are sometimes different from the expected tetrahedral value. These deviations are explained if the hydrogen atoms can lie out of the $\text{S}\cdots\text{N}$ or $\text{N}\cdots\text{N}$ line. At any rate these

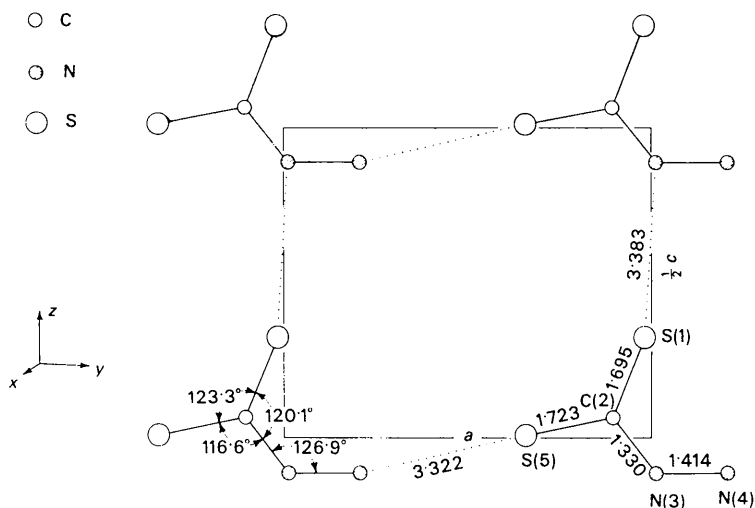


Fig. 3. Layer of hydrazinedithiocarboxylato anions parallel to (010).

Table 4. Atomic peak heights ($e.\text{Å}^{-3}$), curvatures ($e.\text{Å}^{-5}$) and e.s.d.'s

		ρ	$-A_{hh}$	$-A_{kk}$	$-A_{ll}$	A_{hk}	A_{hl}	A_{kl}
S(1)	obs.	33.5	357	286	382	11	6	-8
	calc.	34.5	358	294	379	10	6	-8
C(2)	obs.	11.1	109	120	119	-1	0	4
	calc.	11.1	110	117	119	-1	0	5
N(3)	obs.	11.7	121	99	141	2	7	-2
	calc.	12.0	125	100	140	2	7	-2
N(4)	obs.	10.0	97	91	91	1	3	-3
	calc.	10.3	98	92	93	1	3	-4
S(5)	obs.	36.7	420	348	399	-19	8	-9
	calc.	37.6	419	350	400	-17	8	-10
N(6)	obs.	11.8	108	112	117	7	4	-3
	calc.	12.0	109	111	117	8	5	-3
N(7)	obs.	11.3	109	103	109	3	-3	-2
	calc.	11.5	108	102	111	3	-3	-2
e.s.d.'s		0.2	3	3	3	2	2	2

Table 5. *Main interatomic distances and angles*

Asymmetric unit transformations:							
'	$-x$	$-y$	$-z$	vi	$-x$	$-\frac{1}{2}+y$	$\frac{1}{2}-z$
''	x	$\frac{1}{2}-y$	$\frac{1}{2}+z$	vii	$-x$	$1-y$	$-z$
'''	$1+x$	y	z	viii	$1-x$	$-y$	$-z$
iv	$1-x$	$\frac{1}{2}+y$	$\frac{1}{2}-z$	ix	$1+x$	$-\frac{1}{2}-y$	$\frac{1}{2}+z$
v	$1-x$	$-\frac{1}{2}+y$	$\frac{1}{2}-z$				
Hydrazinedithiocarboxylato anion							
S(1)-C(2)	1.695 (6) Å	N(4)-N(3)-C(2)	126.9 (6)°				
S(5)-C(2)	1.723 (6)	N(3)-C(2)-S(1)	120.1 (5)				
N(3)-C(2)	1.330 (8)	S(1)-C(2)-S(5)	123.3 (4)				
N(3)-N(4)	1.414 (9)	S(5)-C(2)-N(3)	116.6 (5)				
S(1)-S(5)	3.008 (3)						
S(1)-N(4)	3.048 (8)						
Hydrazinium cation							
N(6)-N(7)	1.436 (9) Å						
Hydrogen bonds							
N(7) ... N(6 ^v)	2.968 (9) Å	N(6 ^v)-N(7)-N(4')	69.8 (2)				
N(7) ... N(4')	3.078 (10)	S(1 ^{vi})-N(7)-S(5'')	85.6 (1)				
N(7) ... S(1 ^{vi})	3.334 (7)	S(1 ^{vi})-N(7)-N(4')	72.0 (2)				
N(7) ... S(5'')	3.378 (7)	S(5'')-N(7)-N(4')	148.9 (2)				
N(4''') ... S(5)	3.322 (8)	N(6 ^v)-N(7)-S(5'')	123.1 (2)				
N(3'') ... S(1)	3.383 (6)	N(6 ^v)-N(7)-S(1 ^{vi})	70.5 (2)				
		N(6)-N(7)-S(1 ^{vi})	173.3 (4)				
		N(6)-N(7)-N(6 ^v)	103.1 (4)				
		N(6)-N(7)-N(4')	104.7 (4)				
		N(6)-N(7)-S(5'')	99.6 (4)				
		N(7)-N(6 ^v)-N(7 ^v)	114.4 (4)				
		N(3''')-N(4'')-S(5)	161.2 (5)				
		N(4'')-N(3'')-S(1)	94.7 (4)				
		C(2'')-N(3'')-S(1)	138.4 (4)				
Short intermolecular distances							
S(1) ... N(3')	3.583 (7) Å	C(2) ... N(3')	3.544 (9) Å				
S(1) ... N(7)	3.521 (7)	C(2) ... N(3 ^{vii})	3.445 (9)				
S(5) ... N(4 ^{vii})	3.563 (8)	C(2) ... N(4')	3.380 (9)				
S(5) ... N(6 ^{viii})	3.586 (6)	N(4) ... N(6 ^{ix})	3.461 (10)				
S(5) ... N(6 ^{iv})	3.584 (6)	N(6) ... N(6 ^{iv})	3.578 (9)				
S(5) ... N(7 ^{iv})	3.517 (6)	N(6) ... N(6 ^v)	3.577 (9)				

Table 6. *Deviations from the plane of the hydrazinedithiocarboxylato group*

Equation of the plane: $-0.79365x + 6.78480y + 0.15536z = 4.74180$					
Atom	S(5)	C(2)	N(3)	N(4)	S(1)
Δ	0.01145	-0.01886	-0.00689	0.00995	0.00436 Å
	$\Sigma (\Delta/\sigma)^2 = 4.0 \quad \chi^2_{95\%} = 5.99$				

The five atoms lie on the same plane with $P > 95\%$.
(P = probability; x, y, z are fractional coordinates; Δ is the distance from the plane).

contacts are shorter than any other in the structure and must imply intermolecular interactions stronger than those at the other contacts.

The intermolecular hydrogen bonds within the layer formed by the anions at $x\frac{1}{2}z$ are $S(5) \cdots N(4) = 3.322$ and $S(1) \cdots N(3) = 3.383$ Å (Fig. 3). These parallel layers are held together in the structure by interlayer hydrogen bonds $N(7) \cdots S(1) = 3.334$ and $N(7) \cdots S(5) = 3.378$ Å and by hydrogen bonds $N(4) \cdots N(7) = 3.078$ Å. Further hydrogen bonds $N(6) \cdots N(7) = 2.968$ Å are formed between hydrazinium cations (Fig. 4). Owing

to the high number of hydrogen bonds formed by N(7) it seems very likely that this atom is the positive end of the cation $H_2N-NH_3^+$. The distance $N(6)-N(7)$, 1.436 Å, is in agreement with those generally found in the hydrazinium cation: 1.45 (Sukurai & Tomiie, 1952*a, b*), 1.432 (Bryden, 1958), 1.432 Å (Braibanti, Manotti Lanfredi & Tiripicchio, 1967).

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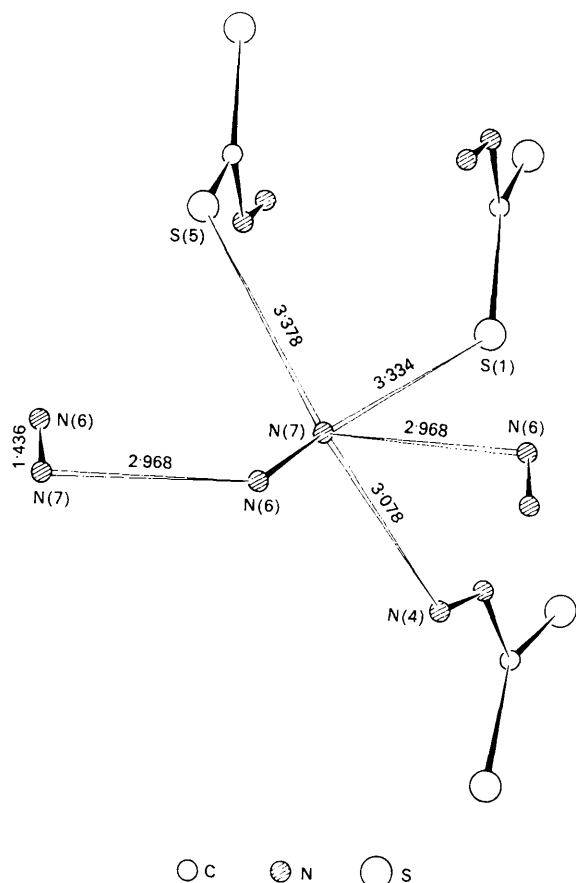


Fig. 4. Environment of the hydrazinium cation, here represented by atoms N(6'') and N(7'').

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