Acta Cryst. (1975). B31, 2355

Hydrazinium(1+) Hydrogen Sulphide

BY F. LAZARINI AND M. VARDJAN-JAREC

Department of Chemistry, Faculty of Natural Sciences and Technology, University of Ljubljana, Murnikova 6, 61000 *Ljubljana, Yugoslavia*

(*Received* 10 *March* 1975; *accepted* 7 *April* 1975)

Abstract. N_2H_5HS, monoclinic, $P2_1/c$, $a=7{\cdot}175$ (9), $b=7{\cdot}824$ (2), $c=12{\cdot}318$ (4) Å, $\beta=99{\cdot}66$ (8)°, $D_m=1{\cdot}26$ g cm^{-3}, $Z=8$, $D_c=1{\cdot}285$ g cm^{-3}. The structure consists of $N_2H_5^+$ and HS^- ions. The $-NH_3$ part of each $N_2H_5^+$ ion is connected by three weak hydrogen bonds with three different HS^- ions; each HS^- ion is linked by hydrogen bonds with three different $N_2H_5^+$ ions.

Introduction. Needle-shaped single crystals of N_2H_5HS were grown at room temperature from a gas phase containing H_2S and N_2H_4 (Vardjan-Jarec, 1975). The crystals were very sensitive to moisture and for that reason they were sealed into Lindemann-glass capillaries. Intensities of 872 non-zero independent reflexions were visually estimated from multiple-film Weissenberg photographs about the *a* axis (0*kl*–3*kl*) using Cu $K\alpha$ radiation and from precession photographs about the *b* axis (*h*0*l*–*h*2*l*) using Mo $K\alpha$ radiation. An absorption correction (*International Tables for X-ray Crystallography*, 1967) for the Weissenberg data was applied [μ(Cu $K\alpha$) = 58·5 cm^{-1}, $\mu R=1{\cdot}0$; μ(Mo $K\alpha$) = 6·3 cm^{-1}]. From precession data only those reflexions with $h\geq 4$ were taken into account.

The structure was solved by direct methods. An *E* map showed unequivocally only the positions of two sulphur atoms of the asymmetrical set, while the four nitrogen atoms were found from a subsequent F_o synthesis. The structure was partially refined by full-matrix least-squares calculations with anisotropic temperature factors. Cruickshank's (1961) weighting scheme was applied. The hydrogen atoms were located from a few successive difference maps. The hydrogen atom parameters were included in the structure-factor calculation but only the positional parameters of the $N_2H_5^+$ hydrogen atoms were refined. The final *R* values are: $R_1=\sum||F_o|-|F_c||/\sum|F_o|=0{\cdot}058$ and $R_2=\{\sum w(F_o-F_c)^2/\sum wF_o^2\}^{1/2}=0{\cdot}082$. The average ratio parameter shift: error was 0·017 in the final cycle. All calculations were performed on the CDC CYBER 72 computer of RRC Ljubljana using the X-RAY 72 system of crystallographic programs (Stewart, Kruger, Ammon, Dickinson & Hall, 1972). The atomic scattering factors for sulphur and nitrogen were those of Cromer & Waber (1965) and for hydrogen those from *International Tables for X-ray Crystallography* (1962).

Table 1. *Final positional parameters with standard deviations in parentheses*

	x	*y*	*z*
S(1)	0·1287 (2)	0·2710 (2)	0·5112 (1)
S(2)	0·3943 (2)	0·5303 (2)	0·2783 (1)
N(1)	0·0588 (8)	0·1257 (6)	0·2598 (3)
N(2)	0·1521 (8)	−0·0355 (6)	0·2854 (4)
N(3)	0·3210 (8)	0·6592 (6)	0·5202 (3)
N(4)	0·3988 (8)	0·8282 (7)	0·5117 (4)
H(1)	0·107 (10)	0·206 (8)	0·320 (5)
H(2)	0·073 (10)	0·184 (8)	0·190 (6)
H(3)	−0·058 (12)	0·123 (11)	0·237 (6)
H(4)	0·168 (10)	−0·057 (8)	0·360 (6)
H(5)	0·262 (12)	−0·025 (11)	0·286 (6)
H(6)	0·123	0·095	0·532
H(7)	0·325 (10)	0·591 (8)	0·546 (6)
H(8)	0·382 (10)	0·595 (8)	0·580 (6)
H(9)	0·188 (12)	0·653 (10)	0·526 (5)
H(10)	0·511 (11)	0·812 (11)	0·503 (6)
H(11)	0·408 (11)	0·871 (9)	0·574 (5)
H(12)	0·397	0·345	0·255

Table 2. *Final thermal parameters with standard deviations in parentheses*

The anisotropic and isotropic temperature factors are in the form $\exp[-2\pi^2(U_{11}h^2a^{*2}+U_{22}k^2b^{*2}+U_{33}l^2c^{*2}+2U_{12}hka^*b^*+2U_{13}hla^*c^*+2U_{23}klb^*c^*)]$ and $\exp[-8\pi^2U(\sin\theta/\lambda)^2]$ respectively. All values have been multiplied by 10^4.

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
S(1)	353 (8)	480 (7)	406 (6)	9 (8)	104 (5)	−43 (5)
S(2)	373 (8)	504 (7)	373 (6)	40 (8)	80 (5)	10 (5)
N(1)	432 (33)	502 (23)	393 (20)	64 (30)	68 (21)	−6 (17)
N(2)	424 (29)	486 (23)	514 (23)	54 (34)	74 (23)	34 (18)
N(3)	424 (30)	499 (22)	406 (20)	1 (31)	156 (21)	30 (18)
N(4)	466 (33)	494 (23)	501 (23)	−3 (32)	163 (23)	−30(18)

	U
H(1)–H(5) and H(7)–H(11)	393
H(6) and H(12)	494

The positional and thermal parameters are listed in Tables 1 and 2. Fig. 1 shows the structure in its *b* axial projection. The important interatomic distances and angles are given in Table 3.*

Table 3. *Interatomic distances* (Å) *and angles* (°) *with standard deviations in parentheses*

D–H···*A*	*D*–H	H···*A*	*D*···*A*
N(1)–H(1)···S(1)	0·99 (6)	2·38 (7)	3·257 (4)
N(1)–H(2)···S(1^{i})	1·00 (7)	2·33 (7)	3·286 (4)
N(1)–H(3)···S(2^{ii})	0·84 (8)	2·49 (8)	3·291 (7)
N(3)–H(7)···S(2)	0·96 (7)	2·38 (7)	3·270 (5)
N(3)–H(8)···S(2^{iii})	0·93 (6)	2·38 (6)	3·291 (5)
N(3)–H(9)···S(1^{iv})	0·97 (9)	3·32 (8)	3·231 (7)

N(1)–N(2)	1·438 (7)	N(3)–N(4)	1·446 (7)
N(2)–H(4)	0·93 (7)	N(4)–H(10)	0·84 (8)
N(2)–H(5)	0·79 (8)	N(4)–H(11)	0·83 (7)
S(1)–H(6)	1·40 (7)	S(2)–H(12)	1·48 (7)

N(2)–N(1)–S(1)	96·1 (3)	N(4)—N(3)–S(2)	95·3 (3)
N(2)–N(1)–S(1^{i})	106·3 (3)	N(4)—N(3)–S(2^{iii})	105·6 (3)
N(2)–N(1)–S(2^{ii})	104·2 (3)	N(4)—N(3)–S(1^{iv})	103·1 (3)
S(1)–N(1)–S(1^{i})	141·0 (2)	S(2)—N(3)–S(2^{iii})	111·9 (2)
S(1)–N(1)–S(2^{ii})	101·9 (2)	S(2)—N(3)–S(1^{iv})	104·6 (1)
S(1^{i})–N(1)–S(2^{ii})	103·0 (1)	S(2^{iii})–N(3)–S(1^{iv})	130·4 (2)

Symmetry code

i	$x, \frac{1}{2}-y, -\frac{1}{2}+z$	ii	$-x, -\frac{1}{2}+y, \frac{1}{2}-z$
iii	$1-x, 1-y, 1-z$	iv	$-x, 1-y, 1-z$

Discussion. The structure consists of $N_2H_5^+$ and HS^- ions interlinked by hydrogen bonds. The hydrogen atoms of the $-NH_3$ group of the cation form three weak hydrogen bonds to three different anions (N–H···S distances between 3·231 and 3·291 Å, N–H···S angles vary from 146 to 165°). The hydrogen atoms of the $-NH_2$ group of the cation are not engaged in hydrogen bonds. Each HS^- ion is connected by hydrogen bonds to three different cations. There is a significant difference between the structures of N_2H_5HS, N_2H_5F and N_2H_5Cl in the hydrogen-bonding schemes. In the case of N_2H_5F (Golič & Lazarini, 1974) all hydrogen atoms of the $N_2H_5^+$ cations form hydrogen bonds either to the anions (N–H···F) or between the cations (N–H···N). In the case of N_2H_5Cl (Sakurai & Tomiie, 1952) only hydrogen bonds between the cations (N–H···N) were found. The N–N distances of the two very similar $N_2H_5^+$ cations of the asymmetrical set (1·438 and 1·446 Å) are in reasonable agreement with those found in related compounds.

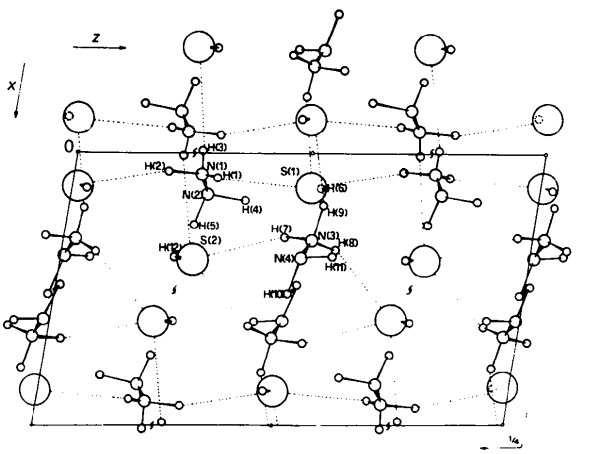

Fig. 1. Projection of the structure along **b**.

The authors thank Professor J. Slivnik for suggesting this work and Professor L. Golič for valuable discussions.

References

Cromer, D. T. & Waber, J. T. (1965). *Acta Cryst.* **18**, 104–109.

Cruickshank, D. W. J. (1961). *Computing Methods and the Phase Problem in X-ray Crystal Analysis.* Oxford: Pergamon Press.

Golič, L. & Lazarini, F. (1974). *Mh. Chem.* **105**, 735–741.

International Tables for X-ray Crystallography (1967). Vol. II, pp. 295–298. Birmingham: Kynoch Press.

International Tables for X-ray Crystallography (1962). Vol. III, pp. 202–203. Birmingham: Kynoch Press.

Sakurai, K. & Tomiie, Y. (1952). *Acta Cryst.* **5**, 293–294.

Stewart, J. M., Kruger, G. J., Ammon, H. L., Dickinson, C. & Hall, S. R. (1972). The X-RAY System. Tech. Rep. TR-192, Univ. of Maryland, College Park, Maryland.

Vardjan-Jarec, M. (1975). Thesis, Univ. v Ljubljani.

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31063 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.