Crystal and Molecular Structure of Thiocarbonohydrazide Sulphate

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Crystals of the title compound are orthorhombic, space group *Pbca*, with $Z = 8$ in a unit cell of dimensions: $a = 10{\cdot}80(1)$, $b = 15{\cdot}44(2)$, $c = 8{\cdot}26(1)$ Å. The structure has been solved from diffractometer data by three-dimensional Patterson and Fourier methods, and refined by full matrix least-squares methods to R 0·047 for 1250 observed reflections. The structure consists of diprotonated cations, in a *cis,cis*-conformation, with tetrahedral sulphate anions. The distances and angles are comparable with those presented by thiocarbonohydrazide (I) in different conformations and crystals. Rotation angles of the two $-\overset{+}{N}H_3$ around N–N are somewhat different from one another. The whole cation possesses practically a binary axis of symmetry, through C–S. The –NH– and $-\overset{+}{N}H_3$ groups form several N–H · · · O hydrogen bonds with surrounding anions. The i.r. spectrum of the compound is compared with that of the simple molecule.

DURING research on the molecule of thiocarbonohydrazide and its behaviour in different crystal structures [1-4] we have now determined the crystal structure of thiocarbonohydrazide sulphate, $[SC(NH{\cdot}NH_2)_2]H_2SO_4$. In the neutral and monoprotonated species (I) is in the *cis,trans*-conformation, *i.e.* with groups $\cdot NH{\cdot}NH_2$ differently rotated with respect to S–C bond and in diprotonated species in the *cis,cis*-conformation, *i.e.* with both groups bent toward S–C. The present compound can be written either as composed of ions $SC(NH{\cdot}\overset{+}{N}H_3)_2$ and SO_4^{2-} or of ions $SC(NH{\cdot}NH_2)(NH{\cdot}\overset{+}{N}H_3)$ and HSO_4^-, depending upon the assignment of the proton. This is important even in connection with the studies in solution because from the protonation constants of the acids $SC(NH{\cdot}\overset{+}{N}H_3)_2$ and HSO_4^- the former appears in solution to be stronger than the latter and in solution the second formulation would seem to be more appropriate. The determination of the crystal structure can give an answer to this question by presenting evidence for presence in the solid of either the *cis,trans*- or *cis,cis*-form of the cation.

EXPERIMENTAL

Preparation.—Colourless crystals were obtained by evaporating an aqueous solution of thiocarbonohydrazide, after addition of dilute sulphuric acid to pH *ca.* 2·5.

Crystal Data.—$C_2H_8N_4O_4S_2$, $M = 204{\cdot}22$. Orthorhombic, $a = 10{\cdot}80(1)$, $b = 15{\cdot}44(2)$, $c = 8{\cdot}26(1)$ Å, $U = 13{,}774$ Å^3, $D_c = 1{\cdot}969$, $Z = 8$, $D_m = 1{\cdot}971$, $F(000) = 848$. Cu-K_α radiation, $\lambda = 1{\cdot}54178$ Å, $\mu(\text{Cu-}K_\alpha) = 66{\cdot}80$ cm^{-1}. Space group *Pbca* (D_{2h}^{15} No. 61) from systematic absences.

Unit cell parameters were determined from rotation and Weissenberg photographs and refined on an automated single crystal diffractometer.

Intensity Data.—Intensity data were collected on a single-crystal automated Siemens diffractometer, on line to a Siemens 304 P computer, by use of nickel-filtered Cu-K_α radiation and the ω—2θ scan technique. A crystal of dimensions *ca.* $0{\cdot}15 \times 0{\cdot}15 \times 0{\cdot}28$ mm was aligned with its [100] axis along the ϕ axis of the diffractometer and all the reflections with $2\theta \leqslant 140°$ were collected. 1309 Independent reflections were measured of which 1250 were used in the crystal analysis, reflections having intensities less than twice their standard deviations $\{\sigma^2(I) = [\text{total counts} + (0{\cdot}005\,I)^2]\}$ being considered unobserved. Corrections for Lorentz and polarization factors were made in the usual way. No correction was made for absorption effects. The absolute scale factor and mean isotropic temperature factor were obtained by Wilson's method.[5]

Structure Determination and Refinement.—The structure was solved from the three-dimensional Patterson function by the heavy-atom method. A Fourier synthesis enabled location of all non-hydrogen atoms. Refinement was by full matrix least-squares methods, first with isotropic then with anisotropic thermal parameters. Unit weights were assumed for every reflection. Hydrogen atoms were located directly from a difference-Fourier synthesis calculated after some cycles of least squares. More least-squares cycles were computed, the hydrogen atoms being included with isotropic thermal parameters. The weighting scheme: $1/w = (A + BF_o)^2$ with $A = 2{\cdot}80$ and $B = 0{\cdot}0356$ was applied at this stage. At the end of the refinement R was 0·047

TABLE 1

Fractional atomic co-ordinates $\times 10^4$ with estimated standard deviations in parentheses

	x	*y*	*z*
S(1)	1501(1)	3937(1)	1411(1)
S(2)	3882(1)	1386(1)	2932(1)
O(1)	4273(2)	2254(1)	3460(3)
O(2)	2529(2)	1407(1)	2593(3)
O(3)	4174(2)	0743(2)	4162(3)
O(4)	4528(2)	1160(1)	1416(2)
N(1)	1837(2)	3331(2)	4379(3)
N(2)	0901(2)	2718(2)	4052(3)
N(3)	3295(2)	4258(2)	3526(3)
N(4)	3766(2)	4855(2)	2387(3)
C	2241(3)	3831(2)	3166(4)
H(1)	2292(42)	3316(27)	5442(53)
H(2)	0560(37)	2897(25)	3030(47)
H(3)	1141(38)	2223(25)	3894(47)
H(4)	0133(41)	2750(26)	5014(64)
H(5)	3746(49)	4168(32)	4458(69)
H(6)	3289(41)	5379(30)	2478(57)
H(7)	4524(40)	4956(28)	2540(52)
H(8)	3725(40)	4609(27)	1327(48)

The final atomic co-ordinates and the thermal parameters are given in Tables 1 and 2. Observed and calculated

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[1] A. Braibanti, A. Tiripicchio, and M. Tiripicchio Camellini, *Acta Cryst.*, 1969, *B*, **25**, 2286.

[2] F. Bigoli, A. Braibanti, A. M. Manotti Lanfredi, A. Tiripicchio, and M. Tiripicchio Camellini, *Inorg. Chim. Acta*, 1971, **5**, 392.

[3] A. Braibanti, M. A. Pellinghelli, A. Tiripicchio, and M. Tiripicchio Camellini, *Inorg. Chim. Acta*, 1971, **5**, 523.

[4] A. Braibanti, A. Tiripicchio, and M. Tiripicchio Camellini, preceding paper.

[5] A. J. C. Wilson, *Nature*, London, 1942, **150**, 152.

structure factors are listed in Supplementary Publication No. SUP 20460 (11 pp., 1 microfiche).†

Atomic scattering factors for carbon, nitrogen, and sulphur were taken from ref. 6, and for hydrogen from ref. 7.

All calculations were performed on the CDC 6600 computer of the Centro di Calcolo Elettronico Interuniversitario dell'Italia Nord–Orientale (Bologna), with the programs written by Immirzi.[8]

DISCUSSION

The crystal structure consists of cations, in the *cis,cis*-conformation, with sulphate anions, SO_4^{2-}. Both the conformation of the cation, typical of the diprotonated form, and the analysis of the difference-Fourier map confirm this interpretation and exclude the presence of monoprotonated cations $SC(NH{\cdot}NH_2)(NH{\cdot}\overset{+}{N}H_3)$ and of hydrogen sulphate anions, HSO_4^-.

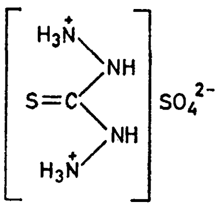

TABLE 2

Thermal parameters (Å) with their estimated standard deviations *

	10^3B_{11}	10^3B_{22}	10^3B_{33}	10^3B_{12}	10^3B_{13}	10^3B_{23}
S(1)	1581(30)	1733(29)	948(27)	−394(23)	−314(21)	171(21)
S(2)	898(25)	1187(27)	826(25)	70(19)	−42(18)	9(19)
O(1)	1851(90)	1726(85)	1744(86)	−151(68)	−224(75)	−532(69)
O(2)	779(70)	2144(82)	1618(77)	28(62)	−166(66)	31(70)
O(3)	2152(92)	2317(96)	1699(88)	651(80)	229(78)	894(76)
O(4)	1510(86)	2370(88)	920(77)	138(71)	372(63)	−395(66)
N(1)	1658(102)	1769(94)	1170(88)	−779(81)	−105(76)	68(78)
N(2)	1582(98)	1328(92)	1332(93)	−339(77)	13(84)	−19(76)
N(3)	1387(98)	1611(98)	1749(103)	−616(80)	−388(79)	355(81)
N(4)	1500(93)	1553(108)	1727(97)	−374(77)	−9(82)	84(84)
C	1049(104)	1266(96)	1501(102)	192(85)	97(91)	−184(84)
	10^2B					
H(1)	323(92)					
H(2)	220(78)					
H(3)	225(81)					
H(4)	340(94)					
H(5)	463(117)					
H(6)	360(97)					
H(7)	287(81)					
H(8)	256(85)					

* Anisotropic thermal parameters are in the form: $\exp[-0{\cdot}25(h^2a^{*2}B_{11} + \ldots 2klb^*c^*B_{23})]$.

The distances and angles in the diprotonated cation (Figure 1a, Table 3) agree well with values found for the same cation in the crystal structure of thiocarbonohydrazide dihydrochloride dihydrate.[3] The diprotonated cation presents an approximate binary axis of symmetry along the C–S bond. A comparison of distances and angles of molecule (I) in different conformations and different crystals (Table 4) shows how the main variations observed concern the C–S bond and the angles N–C–N, S–C–N(1), and C–N–N. The variations of the angles N–C–N and S–C–N(1) are probably also related to steric factors due to the transition from the *cis,trans*- to the *cis,cis*-conformation; the contraction of the C–S bond, apparent in protonated forms, can be explained by field effects of the positive charge on the electron distribution of the conjugated system $S{-}C{<}^{N}_{N}$. The same attractive field effect explains the decreasing of the angles C–N–N in protonated groups. The possibility of considering N(2)–H(2) · · · S(1) and N(4)–H(8) · · · S(1) as intramolecular hydrogen bonds has been taken into account; such S · · · N hydrogen bonds however have been excluded, notwithstanding the short distances H(2) · · · S(1) [2·32(4)] and H(8) · · · S(1) [2·62(4) Å], because of the small angles H(2) · · · S(1)–C [68·9(10)° and H(8) · · · S(1)–C [67·7(9)°] and the short distances C · · · H(2) [2·32(4)] and C · · · H(8) [2·51(4) Å]. On the whole it seems more likely that the field interaction of H(2) and H(8) is with the electron cloud midway

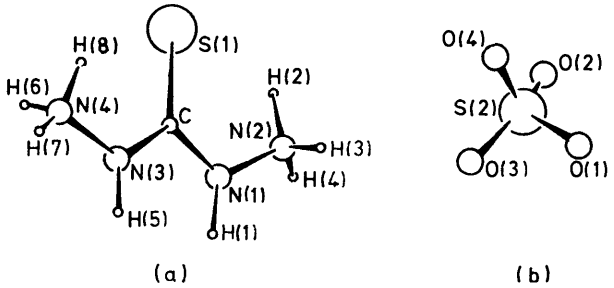

FIGURE 1 (a) The diprotonated *cis,cis*-cation, and (b) the sulphate anion, showing the numbering system used in the analysis

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† For details see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20.

[6] D. T. Cromer and J. B. Mann, *Acta Cryst.*, 1968, *A*, **24**, 321.

[7] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

[8] A. Immirzi, *Ricerca Sci.*, 1967, **37**, 743.

between carbon and sulphur rather than with single carbon or sulphur atoms.

TABLE 3

Diprotonated thiocarbonohydrazide cation, $SC(NH-\overset{+}{N}H_3)_2$. Main interatomic bond distances and angles estimated standard deviations in parentheses[a]

(a) Distances (Å)

C–S(1)	1·663(4)	N(2)–H(3)	0·82(4)
C–N(1)	1·338(4)	N(2)–H(4)	1·15(5)
C–N(3)	1·349(4)	N(3)–H(5)	0·92(6)
N(1)–N(2)	1·411(4)	N(4)–H(6)	0·96(5)
N(3)–N(4)	1·412(4)	N(4)–H(7)	0·84(4)
N(1)–H(1)	1·01(4)	N(4)–H(8)	0·96(4)
N(2)–H(2)	0·96(4)		

(b) Angles (deg.)

N(1)–C–S(1)	123·6(2)	H(3)–N(2)–H(4)	112·3(34)
N(1)–C–N(3)	113·1(3)	C–N(3)–N(4)	118·4(2)
S(1)–C–N(3)	123·3(2)	C–N(3)–H(5)	123·8(32)
C–N(1)–N(2)	118·5(2)	H(5)–N(3)–N(4)	117·7(32)
H(1)–N(1)–C	120·5(25)	N(3)–N(4)–H(6)	107·7(28)
H(1)–N(1)–N(2)	120·1(25)	N(3)–N(4)–H(7)	111·8(29)
N(1)–N(2)–H(2)	104·5(23)	N(3)–N(4)–H(8)	109·5(25)
N(1)–N(2)–H(3)	115·5(29)	H(6)–N(4)–H(7)	110·7(40)
N(1)–N(2)–H(4)	110·8(22)	H(6)–N(4)–H(8)	112·4(38)
H(2)–N(2)–H(3)	104·5(36)	H(7)–N(4)–H(8)	104·8(39)
H(2)–N(2)–H(4)	108·5(34)		

[a] Estimated standard deviations in this and the following Tables are given in units of the last digit.

The analysis of the planarity of the molecule confirms that the thioureide group is practically planar. The best plane through N(1),C,S,N(3) has the equation $0{\cdot}5283X - 0{\cdot}7638Y - 0{\cdot}3709Z + 4{\cdot}2178 = 0$ [where X, Y, and Z are co-ordinates in Å, $X \equiv x$, $Y \equiv y$, and $Z \perp (X,Y)$]. Deviations from the plane with their estimated standard deviations are: S(1) —0·0008(13), C 0·0086(32), N(1) —0·0039(28), and N(3) —0·0039(28) Å. The terminal groups $-\overset{+}{N}H_3$ are again the relatively loose part of the molecule. Atoms N(2) and N(4) are in fact displaced 0·2851(28) and —0·0902(28) Å from the plane through N(1),C,S,N(3). The same situation with the two terminal groups displaced toward opposite sides of the plane has been found in the diprotonated cation of the dihydrochloride.[3] The rotation angles around the line N–N, of the N–H bonds with respect to the plane defined by C–N–N show (Figure 2) that there is a *ca.* 43° rotation from the exact gauche position for N(2) and a *ca.* 18° rotation for N(4). These rotations are connected with the short distances H(2) · · · S(1) and H(8) · · · S(1), already mentioned.

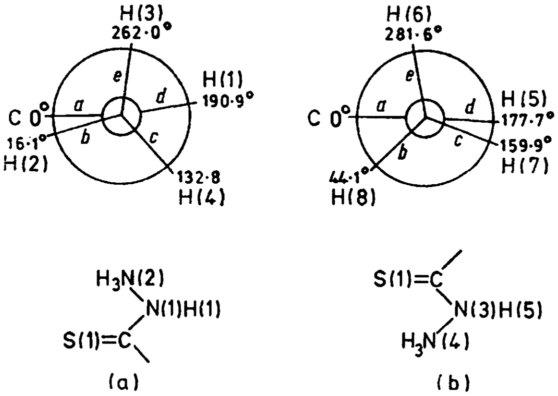

FIGURE 2 Rotation angles around the line N–N

TABLE 4

Distances and angles of the thiocarbonohydrazide (tcaz) molecule (I) in different crystals

(a) Distances (Å)

	C–S	C–N(1)	C–N(3)	N(1)–N(2)	N(3)–N(4)
(II)[a]	1·663(4)	(*c*) 1·338(4)[b]	(*c*) 1·349(4)	(*c*) *1·411*(4)[c]	(*c*) *1·412*(4)
$(tcaz)H_2Cl_2,2H_2O$[d]	1·645(3)	(*c*) 1·363(5)	(*c*) 1·363(5)	(*c*) *1·418*(6)	(*c*) *1·418*(6)
$(tcaz)_2HCl$[e] {tcazH+	1·694(2)	(*t*) 1·327(3)	(*c*) 1·349(3)	(*t*) 1·415(3)	(*c*) *1·416*(3)
$(tcaz)_2HCl$[e] {tcaz	1·705(2)	(*t*) 1·336(3)	(*c*) 1·333(3)	(*t*) 1·417(2)	(*c*) 1·417(3)
(I)[f]	1·724(10)	(*t*) 1·335(9)	(*c*) 1·315(11)	(*t*) 1·407(14)	(*c*) 1·404(9)
$(tcaz)_2CdCl_2$[g]	1·74(2)	(*t*) 1·28(3)	(*c*) 1·35(2)	(*t*) 1·41(3)	(*c*) 1·39(4)

(b) Angles (deg.)

	S–C–N(1)	S–C–N(3)	N(1)–C–N(3)	C–N(1)–N(2)	C–N(3)–N(4)
(II)[a]	(*c*) *123·6*(2)	(*c*) *123·3*(2)	113·1(3)	(*c*) *118·5*(2)	(*c*) *118·4*(2)
$(tcaz)H_2Cl_2,2H_2O$[d]	(*c*) *124·4*(*1*)	(*c*) *124·4*(1)	111·1(2)	(*c*) *117·8*(2)	(*c*) *117·8*(2)
$(tcaz)_2HCl$[e] {tcazH+	(*t*) 120·7(1)	(*c*) *123·4*(2)	115·8(2)	(*t*) 120·3(1)	(*c*) *118·9*(2)
$(tcaz)_2HCl$[e] {tcaz	(*t*) 120·1(1)	(*c*) 122·4(2)	117·5(2)	(*t*) 120·6(2)	(*c*) 121·9(2)
(I)[f]	(*t*) 118·3(6)	(*c*) 124·2(5)	117·5(7)	(*t*) 118·8(7)	(*c*) 122·4(7)
$(tcaz)_2CdCl_2$[g]	(*t*) 119·2(13)	(*c*) 121·5(17)	119·2(17)	(*t*) 120·4(18)	(*c*) 124·3(17)

[a] Present work. [b] (*c*) = groups in *cis* position with respect to S:C:; (*t*) = groups in *trans* position with respect to S:C:. [c] Figures in italics are for protonated groups $\cdot NH\cdot\overset{+}{N}H_3$. [d] Ref. 3. [e] Ref. 4. [f] Ref. 1. [g] Ref. 2.

The diprotonated cation is bound *via* hydrogen bonds to SO_4^{2-} anions and to other cations (Figure 3). The whole environment (Table 5) is completed by short intermolecular contacts. One of the sulphur–nitrogen intermolecular contacts, N(3) · · · S(1^{VIII}) [3·498(4) Å], can in no way be considered, on the grounds of angles and H · · · S distances, as a possible hydrogen bond.[9] On the other hand, the distances N(2) · · · S(1^{VII}) [3·278(4)] and N(4) · · · S(1^{VIII}) [3·423(4) Å] cannot absolutely preclude the existence of any weak, bent hydrogen bonding. Each NH group forms one hydrogen bond N–H · · · O with the anions. The $\overset{+}{N}H_3$ group corresponding to N(2) forms three N–H · · · O hydrogen bonds. One of these

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[9] J. Donohue, *J. Mol. Biol.*, 1969, **45**, 231.

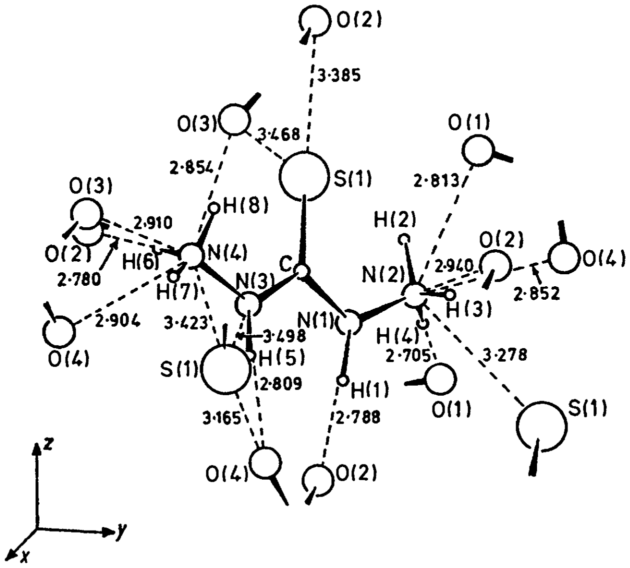

FIGURE 3 Clinographic projection of the structure

TABLE 5

Environment of diprotonated thiocarbonohydrazide cation

(*a*) Hydrogen bonds

(i) Distances (Å)

$N(1) \cdots O(2^{VII})$	2·788(5)	$H(5) \cdots O(4^{VII})$	1·89(6)
$H(1) \cdots O(2^{VII})$	1·85(4)	$N(4) \cdots O(2^{VI})$	2·780(4)
$N(2) \cdots O(1^{X})$	2·813(4)	$H(6) \cdots O(2^{VI})$	1·82(5)
$H(2) \cdots O(1^{X})$	2·11(4)	$N(4) \cdots O(3^{IX})$	2·854(5)
$N(2) \cdots O(1^{I})$	2·705(4)	$H(8) \cdots O(3^{IX})$	1·93(4)
$H(4) \cdots O(1^{I})$	1·57(5)	$N(4) \cdots O(3^{XI})$	2·910(4)
$N(2) \cdots O(2)$	2·940(4)	$H(7) \cdots O(3^{XI})$	2·33(4)
$H(3) \cdots O(2)$	2·23(4)	$N(4) \cdots O(4^{XI})$	2·904(4)
$N(3) \cdots O(4^{VII})$	2·809(4)	$H(7) \cdots O(4^{XI})$	2·29(4)

(ii) Angles (deg.)

$H(1)-N(1) \cdots O(2^{VII})$	16·6(25)
$N(1)-H(1) \cdots O(2^{VII})$	154·5(38)
$H(2)-N(2) \cdots O(1^{X})$	35·5(23)
$N(2)-H(2) \cdots O(1^{X})$	129·1(31)
$H(4)-N(2) \cdots O(1^{I})$	5·9(24)
$N(2)-H(4) \cdots O(1^{I})$	169·8(41)
$H(3)-N(2) \cdots O(2)$	26·0(28)
$N(2)-H(3) \cdots O(2)$	144·8(37)
$H(5)-N(3) \cdots O(4^{VII})$	5·6(32)
$N(3)-H(5) \cdots O(4^{VII})$	171·7(47)
$H(6)-N(4) \cdots O(2^{VI})$	2·4(27)
$N(4)-H(6) \cdots O(2^{VI})$	176·3(41)
$H(8)-N(4) \cdots O(3^{IX})$	12·3(26)
$N(4)-H(8) \cdots O(3^{IX})$	161·6(38)
$H(7)-N(4) \cdots O(3^{XI})$	40·2(29)
$N(4)-H(7) \cdots O(3^{XI})$	126·3(37)
$H(7)-N(4) \cdots O(4^{XI})$	37·3(29)
$N(4)-H(7) \cdots O(4^{XI})$	129·8(37)

(*b*) Short intermolecular distances (Å)

$N(2) \cdots O(4^{X})$	2·852(4)	$O(3) \cdots S(1^{VII})$	3·468(4)
$N(3) \cdots S(1^{VIII})$	3·498(4)	$O(4) \cdots S(1^{II})$	3·165(3)
$N(2) \cdots S(1^{VII})$	3·278(4)	$O(2) \cdots S(1^{VII})$	3·385(4)
$N(4) \cdots S(1^{VIII})$	3·423(4)		

Roman numerals as superscripts refer to the following transformations with respect to the reference molecule at *x*, *y*, *z*:

I $-\frac{1}{2} + x, \frac{1}{2} - y, 1 - z$
II $\frac{1}{2} + x, \frac{1}{2} - y, -z$
III $-x, \frac{1}{2} + y, \frac{1}{2} - z$
IV $\frac{1}{2} - x, -y, \frac{1}{2} + z$
V $-x, -y, -z$
VI $\frac{1}{2} - x, \frac{1}{2} + y, z$
VII $x, \frac{1}{2} - y, \frac{1}{2} + z$
VIII $\frac{1}{2} + x, y, \frac{1}{2} - z$
IX $x, \frac{1}{2} - y, -\frac{1}{2} + z$
X $-\frac{1}{2} + x, y, \frac{1}{2} - z$
XI $1 - x, \frac{1}{2} + y, \frac{1}{2} - z$

deviates only slightly from linearity [N(2)–H(4) ··· O(1^{I}) 169·8°], but the other two are rather bent [N(2)–H(2) ··· O(1^{X}) 129·1 and N(2)–H(3) ··· O(2) 144·8°]. The $\overset{+}{N}H_3$ group corresponding to N(4) forms four hydrogen bonds, two single and one bifurcated bond. The single bonds present small deviations from linearity as shown by the angles N(4)–H(6) ··· O(2^{VI}) 176·3 and N(4)–H(8) ··· O(3^{IX}) 161·6°; the bifurcated bond deviates strongly from linearity, as shown by the angles N(4)–H(7) ··· O(3^{XI}) 126·3 and N(4)–H(7) ··· O(4^{XI}) 129·8°. The short contact N(2) ··· O(4^{X}) 2·852 Å falls within the range expected for hydrogen bonds, but the hydrogen atoms deviate too much from the linearity for such a bond to exist.

The sulphate anion (Figure 1b, Table 6) has a nearly tetrahedral arrangement as shown by the angles O–S–O.

TABLE 6

Sulphate anion. Main interatomic bond distances and angles

(*a*) Distances (Å)

S(2)–O(1)	1·471(3)	S(2)–O(3)	1·455(3)
S(2)–O(2)	1·488(3)	S(2)–O(4)	1·475(2)

(*b*) Angles (deg.)

O(1)–S(2)–O(2)	108·5(1)	O(2)–S(2)–O(3)	111·0(1)
O(1)–S(2)–O(3)	110·6(2)	O(2)–S(2)–O(4)	108·0(1)
O(1)–S(2)–O(4)	109·3(1)	O(3)–S(2)–O(4)	109·2(1)

There are some differences in the sulphur–oxygen distances, but those are probably related to the number and strength of the hydrogen bonds around the oxygen atoms (Figure 4).

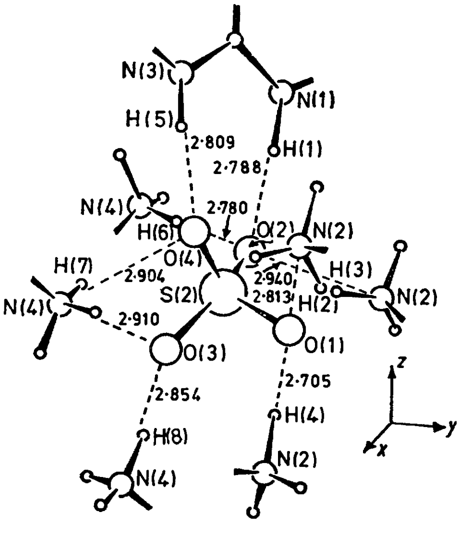

FIGURE 4 Environment of the sulphate anion

The analysis of the i.r. spectrum of (II) in KBr discs shows it to contain the same features as already found in the spectra of (I) [10] and its compounds. The maxima of the simple substance at 3200—3300 cm^{-1} due to NH and NH_2 stretching vibrations are mingled in a broad

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[10] G. R. Burns, *Inorg. Chem.*, 1968, **7**, 277.

band ranging from 2400—3300 cm^{-1}. The group of peaks due to bending vibrations of NH and NH_2 (1500—1650 cm^{-1}) appear at 1609, 1585, 1549, and 1503 cm^{-1} instead of those of the simple molecule at 1635, 1619, 1539, and 1489 cm^{-1}. The band of the simple molecule at 1285 cm^{-1}, attributable to ν(CS) + ν(CN) is split into four bands; following the trend of the distances, that at 1331 or that at 1370 cm^{-1} could be attributed to the stretching vibration ν(CS) and those at 1205 and 1241 attributed to the stretching vibration ν(CN).

We thank the Consiglio Nazionale delle Ricerche, Rome, for financial aid and Professors L. Cavalia and M. Nardelli (Centro di Studio per la Strutturistica Diffrattometrica) for facilities.

[2/699 *Received, 22nd March,* 1972]