382. *The Structure of Potassium Dinitrososulphite.*

By E. G. Cox, G. A. Jeffrey, and H. P. Stadler.

The crystal structure of potassium dinitrososulphite has been determined by *X*-ray analysis in order to discover the configuration of the anion. Without any structural assumptions this configuration has been shown to be $O_3S\cdot N(O){:}NO$; the sulphur atom is surrounded tetrahedrally by three oxygen atoms at 1·43 A. distance and one nitrogen at 1·63 A.; the two nitrogens and the three atoms attached to them are all coplanar, and the N–N distance of 1·30 A. corresponds to a double bond. The two N–O distances are 1·35 A. The anions are situated on mirror planes of the space-group *Pnma*, with the K atoms in general positions approximately half-way between these planes. The conflicting chemical evidence reported in the literature is discussed in relation to these results.

The interesting observation has been made that partial replacement of potassium by sodium causes a reorientation of the anions so that the space-group becomes *Pcmn*.

Although potassium dinitrososulphite was first prepared nearly 150 years ago and has been the subject of many investigations since, its chemical properties appear to show such contradictions that none of the configurational formulæ proposed has been able to command general acceptance. As already briefly reported (Cox, Jeffrey, and Stadler, *Nature*, 1948, **162**, 770), we have now been able to determine its structure by *X*-ray methods, without using chemical evidence which might be open to more than one interpretation. The result enables us to account for many of the properties of the dinitrososulphite ion, but also shows the need for further study of some of its reactions.

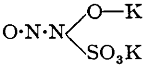
In 1801 Davy (*Bibl. Brit.*, Série Sci. Arts, 1802, **20**, 358) passed nitric oxide into an alkaline solution of potassium sulphite to produce a white crystalline precipitate which evolved nitrous oxide on heating. He called the compound " nitroxide of potash," but did not purify and analyse it. Pelouze (*Ann. Chim. Phys.*, 1835, **60**, 151; *Annalen*, 1835, **15**, 240) synthesized the compound from two volumes of nitric oxide and one volume of sulphur dioxide with excess of alkali, and established the composition as $K_2SO_5N_2$ by direct analysis; he also showed that the excess of alkali stabilized the salt but was not essential for the preparation. Some fifty years later the interest in the constitution of chamber crystals and related compounds stimulated a series of further investigations. Divers and Haga (*J.*, 1885, **47**, 203) found that reduction of the salt with sodium amalgam gave sulphite and hyponitrite, and, regarding this reaction as analogous to the formation of sulphite and sulphide from thiosulphate, they formulated it as

$$(SO_3K){\cdot}(N_2O_2){\cdot}K + 2Na = Na(N_2O_2)K + (SO_3K)Na$$

They called the salt a (hypo-)nitrososulphate, but did not at this stage assign a structure to the N_2O_2 group or discuss its linkage to the sulphur atom.

The formula (I), which, as will be seen, is essentially correct, was proposed a few years later by Raschig (*Annalen*, 1887, **241**, 232) for a different substance which he had prepared and which he thought was an isomer of Divers and Haga's salt. Raschig adopted the structure (I) because his substance gave hydrated potassium hydroxylaminedisulphonate (II) and nitrous oxide when he attempted to recrystallise it from dilute potassium hydroxide, but when Divers and Haga (*J.*, 1895, **67**, 452) showed that the supposed isomer was really a mixed salt of potassium nitrite and hydrated basic hydroxylaminedisulphonate (III) he ("Schwefel- und Stickstoffstudien," 1924, p. 108) withdrew the formula (I) and supported that of Hantzsch (*Ber.*, 1894, **27**, 3264) (IV) for the nitrososulphite.

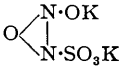
(I.)



(II.) $HO{\cdot}N(SO_3K)_2,2H_2O$

(III.) $(KSO_3)_2N{\cdot}OH,(KSO_3)_2N{\cdot}OK,H_2O$

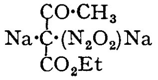
(IV.)



(V.) $NH_2{\cdot}SO_3Na$

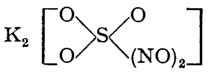
(VI.) $H_2N{\cdot}NH{\cdot}SO_3Na$

(VIII.) $KO{\cdot}N{:}N{\cdot}O{\cdot}SO_3K$



$$\mathrm{Na{\cdot}\underset{CO_2Et}{\overset{CO{\cdot}CH_3}{C}}{\cdot}(N_2O_2)Na}$$

(VII.)



(IX.)

Like Raschig's original formula, Hantzsch's *iso*nitroamine configuration includes an N–S link for which evidence was forthcoming from the reduction to amino- and hydrazino-sulphonates (V) and (VI) (Divers and Haga, *J.*, 1896, **69**, 1610; Raschig, *op. cit.*), but the principal argument in its favour was an analogy with Traube's (*Ber.*, 1894, **27**, 1507) ethyl acetoacetic *iso*nitroamine (VII). Divers and Haga, on the other hand, emphasized the formation of sulphate, both in the reduction with sodium amalgam and quantitatively by decomposition in the presence of acids. They were particularly impressed by the rapidity of the precipitation of barium sulphate on acidification of a solution of the dinitrososulphite and barium chloride; they argued that the sulphate group must be preformed in the original compound, and gave the formula (VIII).

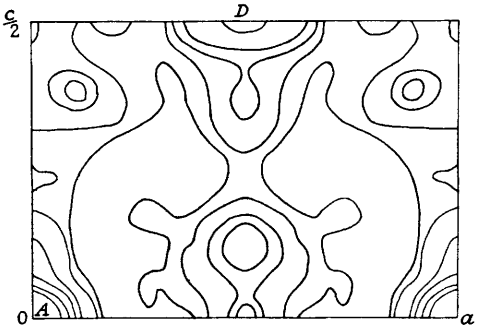
Finally, in 1933, Weitz and Achterberg (*Ber.*, **66**, 1718) showed that $K_2SO_5N_2$ reacted with freshly precipitated ferrous sulphide to form Roussin's black salt, $K[Fe_4(NO)_7S_3]$, and concluded that the nitrososulphite contained a pair of NO groups co-ordinated to the sulphur atom as in (IX). They apparently arrived at no result, however, which in any way enabled them to elaborate upon this formula, which is, in effect, merely a restatement of Divers and Haga's first suggestion of 1885.

There appeared therefore to be little possibility of assigning an entirely satisfactory formula to potassium dinitrososulphite on chemical evidence alone, and the problem seemed appropriate for investigation by *X*-ray structure analysis. The probability of a successful solution of the problem in this way, without recourse to conflicting chemical evidence, was greatly increased when later it was discovered that the ammonium and thallium salts were isomorphous with the potassium salt, and would therefore enable the structure analysis to be made without any preliminary assumptions about the configuration of the molecules.

Preliminary X-*Ray Investigation.*—Potassium dinitrososulphite crystallises in orthorhombic needles with a unit cell of dimensions $a = 7{\cdot}076 \pm 0{\cdot}003$ *kX*, $b = 8{\cdot}13 \pm 0{\cdot}05$ *kX*, $c = 9{\cdot}930 \pm 0{\cdot}007$ *kX*, containing four molecules of $K_2SO_5N_2$. With the first crystals, on which the bulk of the intensity measurements were made, the observed extinctions were $\{0kl\}$ absent for $k + l$ odd, and $\{hk0\}$ absent for h odd, so that the space-group is either *Pna* or *Pnma*. From some crystals, however, there was a moderately strong (110) reflexion which is not in agreement with either of these space-groups. A complete explanation of this was discovered later (see below), but because of the uncertainty it introduced and in view of the nature of the problem, it was decided to proceed as far as possible with the structure analysis without definite commitment as to the space-group.

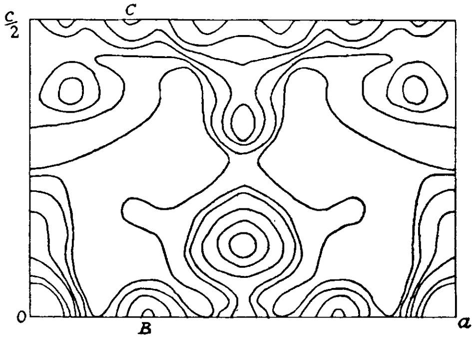
A decision between the possible orthorhombic space-groups is not required for the calculation of the Patterson F^2 syntheses, and so when the necessary intensities had been measured the projections in the three principal zones were computed. Their contour maps showed that the vector peaks were mainly distributed in the layers $y = 0, \pm \frac{1}{4}$, and $\frac{1}{2}$, and suggested that the relatively heavy K and S atoms lie in planes $\frac{1}{4}b$ apart. The F^2 sectional syntheses at $y = 0$, $\frac{1}{4}$, and $\frac{1}{2}$ were therefore evaluated, but owing to the similarity in scattering power of potassium and sulphur, and the uncertainty about the space-group, it was not possible at this stage to identify the various K–S, K–K, and S–S peaks. A similarity between the sections at $y = 0$ and $y = \frac{1}{2}$ (Figs. 1 and 2) confirmed the tendency to a halving of the b-axis, which had previously been inferred from the alternation of weak and strong layer lines in the [b] rotation photograph. When the isomorphous thallium salt was examined, this [b] halving was much more pronounced, providing strong evidence that it was the cationic lattice which was wholly or nearly halved.

FIG. 1.



Patterson section at $y = 0$.

FIG. 2.



Patterson section at $y = \frac{1}{2}$.

On an F^2 ($h0l$) projection of the thallium salt, the Tl–Tl vectors were easily identified, and gave the (x, z)-co-ordinates of four of the cations, the other four being related by a shift of $\frac{1}{2}y$ on the evidence of the pseudo-halving. The translations of the heavy atoms correspond to $(\frac{1}{2} + x, \frac{1}{2} - z)$, $(\frac{1}{2} - x, \frac{1}{2} + z)$, *i.e.*, to the projection group *Pca* (Patterson, *Z. Krist.*, 1935, **90**, 543), which is in accordance with the space-groups *Pna* or *Pnma*.

Fourier Syntheses.—Using the phase relationships of this plane-group, the signs of the structure factors of the planes in the $\{h0l\}$ zone were calculated with the assumption that they were determined solely by the thallium contributions. A Fourier F($h0l$) projection was then obtained which showed several appreciable peaks in addition to those of the thallium atoms. One of these peaks was identified as originating from a sulphur atom, so it was then possible to make a partial interpretation of the F^2 synthesis of the potassium salt at $y = \frac{1}{4}$, *i.e.*, the level at which all the K–S vector peaks were expected to appear.

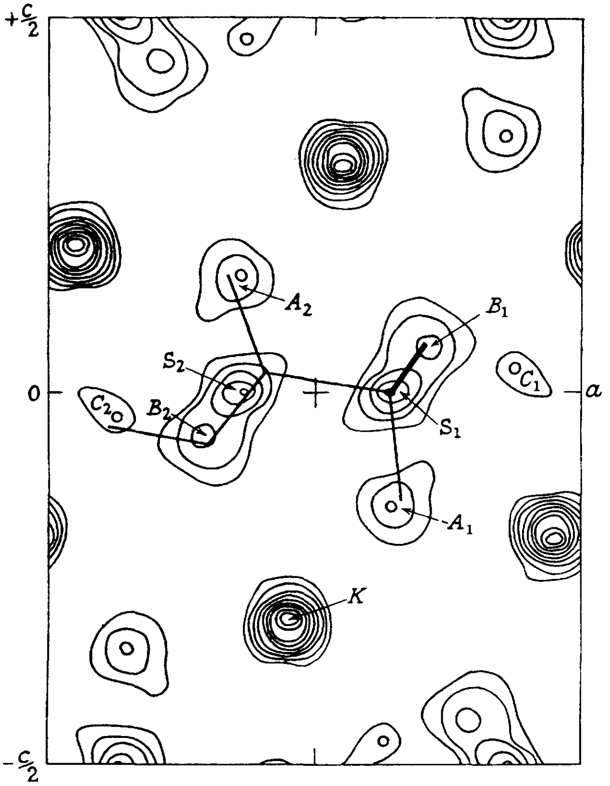
Any further attempts to interpret the thallium projection with the object of locating the lighter atoms was considered injudicious in view of the effect of absorption errors on the intensity measurements. But with the knowledge of both the potassium and sulphur (x, z)-parameters, many of the signs of the $\{h0l\}$ structure factors of the potassium salt could be ascertained. From these a Fourier F projection was calculated which confirmed the K and S positions and showed additional peaks due to oxygen or nitrogen atoms of the anion. When these were also allowed for, an F($h0l$) projection of fairly good resolution was obtained which is shown in Fig. 3*a*. In it the K and S positions (marked as such) are easily identified, and although there is a good deal of overlapping of the anions, the sulphur peak at S_1 appeared to be surrounded tetrahedrally by four light atoms, I placed at A_1, II and III at B_1, and IV overlapping another sulphur at S_2. The distance between the peaks was of the correct order of magnitude for S–O or S–N bonds, and agreed well with the assumption of a tetrahedral arrangement of atoms round the sulphur. From the height of the peaks it seemed likely that another atom could be accommodated at A_1, and of the remaining two light atoms one could be placed at *C*. There was no possibility at that stage of distinguishing between nitrogen and oxygen positions, so it was not known which of the seven light atoms in $K_2SO_5N_2$ had been located in the (x, z)-projection. In the absence of information about the y-co-ordinates it was not possible to postulate a likely configuration of the anion, whereby the position of the last atom could be determined. It had become necessary then to consider the y-parameters in the structure, and at the same time discuss further evidence relating to the space-group. Making an arbitrary choice of origin, the y-levels of the cations were taken as 0 and $\frac{1}{2}$. The sulphur atoms were then expected to lie at $y = \frac{1}{4}$ and $\frac{3}{4}$, in accordance with the Patterson projections and the identification of K–S peaks in the section at $y = \frac{1}{4}$. This was fully confirmed by the following interpretation of the F^2 sectional syntheses.

From the $F(h0l)$ projection, the sulphur co-ordinates in one-sixtieths of the cell edges are $(21, y_1, 0)$, $(39, y_2, 0)$, $(9, y_3, 30)$, $(51, y_4, 30)$. Taking $y_1 = 15$, these give rise to S–S vectors as shown in Table I.

TABLE I.

	21, 15, 0	39, y_2, 0	9, y_3, 30	51, y_4, 30
21, 15, 0	0, 0, 0 *A*	18, y_2-15, 0 *B*	12, y_3-15, 30 *C*	30, y_4, 30 *D*

FIG. 3*a*.



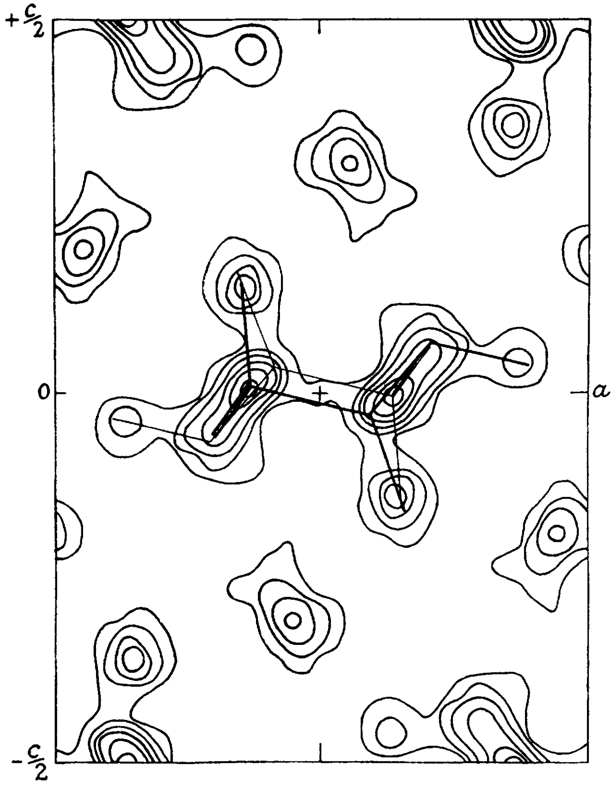
Potassium salt : projection on (010).

(*Note : The contours in Figs.* 3—5 *are on an arbitrary scale, and the contour interval on* S *and* K *peaks double that elsewhere.*)

The peaks *B* and *C* were found on the F^2 section at $y = \frac{1}{2}$ (Fig. 2), and *D* appeared at $y = 0$ (Fig. 1), whence it follows that $y_2 = y_3 = \frac{3}{4}$, and $y_1 = y_4 = \frac{1}{4}$. This gives four positions to the sulphur atoms which are of the form $(x, \frac{1}{4}, z)$, $(\bar{x}, \frac{3}{4}, \bar{z})$, $(\frac{1}{2} - x, \frac{3}{4}, \frac{1}{2} + z)$ and $(\frac{1}{2} - x, \frac{1}{4}, \frac{1}{2} - z)$, and correspond to the four-fold positions of the space-group *Pnma*. It appears, therefore, that both the potassium and the sulphur atoms have parameters which conform to *Pnma*, and, for the sole purpose of calculating the phases of $\{hk0\}$ and $\{0kl\}$, the structure was assumed to have the symmetry of this space-group. This meant that the anion was assumed to have a mirror plane of symmetry; it also meant that the (110) reflexion was being ignored at this stage in the analysis. The Fourier projections from the structure factors in the $\{hk0\}$ and $\{0kl\}$ zones confirmed the tetrahedral arrangement of light atoms around the sulphur but, apart from showing a concentration of unresolved peaks at $y = \pm\frac{1}{4}$, did not materially add to the information about the structure. In particular, they gave no clue as to the whereabouts of the missing atom, and it became apparent that the solution of the configurational problem had to be sought by interpreting the (*h*0*l*) projection.

Although the ammonium salt had been reported by Pelouze as $(NH_4)_2SO_5N_2,H_2O$ it was found on *X*-ray examination to be isomorphous with the potassium and the thallium salt, so this salt too must be anhydrous. This isomorphism provided a new approach to the problem of determining the (*h*0*l*) phases. Comparing the relative intensities of corresponding reflexions of the ammonium and potassium salts, if $|F_{\text{K salt}}| > |F_{\text{NH}_4\text{ salt}}|$ then $F_{\text{K salt}}$ must have the same sign as the cation contribution, and if $|F_{\text{K salt}}| < |F_{\text{NH}_4\text{ salt}}|$, then $F_{\text{NH}_4\text{ salt}}$ must have the opposite sign to the cation contribution. Since the cation contribution could be calculated, the sign of the other member of the inequality could usually be inferred by equating $|F_{\text{K salt}}| - |F_{\text{NH}_4\text{ salt}}|$ to the difference between the two cation components.

FIG. 3*b*.

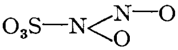


Ammonium salt : projection on (010).

In this way it was possible to obtain an F(*h*0*l*) projection for the ammonium salt which was independent of the previously derived anion positions, and was more reliable because absorption errors are very much smaller for the ammonium than for the potassium salt. Thus it was hoped that the peak corresponding to the seventh light atom, thought to be obscured in the potassium salt projection, would be located; but the ammonium salt projection was found to confirm in every detail that of the potassium salt, and thus definitely showed that the seventh atom must be in a position overlapping other atoms in a region of high electron density on the projection.

A useful guide to the solution of the problem was found in the optical and morphological properties of the crystals, which are highly birefrigent with the highest refractive index along [100] and the lowest along [010]. This indicates [100] as the direction of the highest bond density and probably therefore that of elongation of the anion, a choice which is supported by a marked cleavage on (001). The low refractive index along [010] and the fact that this is the needle direction of the crystals pointed to a structure in layers parallel to (010).

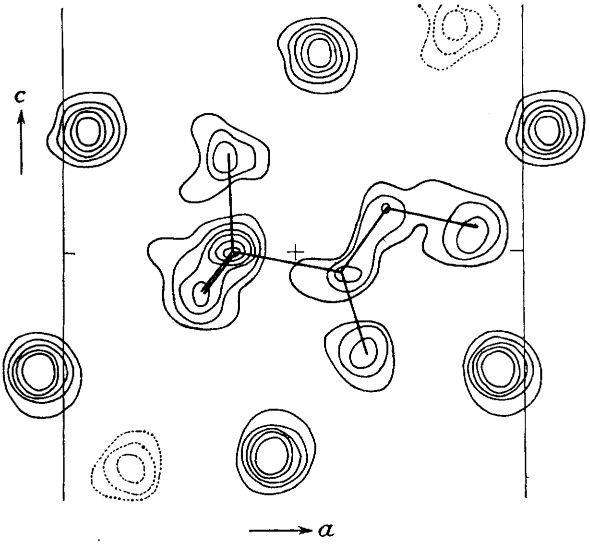
A configuration which corresponds to these general observations and fits the projections was obtained by connecting an atom V at C_2 (Fig. 3*a*) to the sulphur at S_1 through a chain of two atoms VII and IV; the previously missing atom VII overlaps II and III of the other anion at B_2 and IV is superimposed on the sulphur at S_2, giving an ion in which all the atoms except II and III (projected at B_1) lie in a mirror plane parallel to (010). As a result the two anions overlap in the (*h*0*l*) projection as shown in Fig. 3*b*. The only possible chemical identification of the light atoms in this arrangement is



$\mathrm{O_3S{-}N}\begin{smallmatrix}\nearrow \mathrm{N{-}O}\\ \searrow \mathrm{O}\end{smallmatrix}$ (see also Fig. 7).

A detailed model was then constructed using the bond lengths found in the potassium sulphamate structure (Brown and Cox, *J.*, 1940, 1) for the bonds round the sulphur atom, *viz.*, $\mathrm{S{-}O} = 1{\cdot}44$, $\mathrm{S{-}N} = 1{\cdot}57$ A., which seemed compatible with the projection. The remaining interatomic distances were chosen by comparing the projection with models based on values given by Pauling (" Nature of the Chemical Bond "). The best agreement was obtained with $\mathrm{N}\overline{-}\mathrm{N} = 1{\cdot}28$ A., $\mathrm{N_{IV}{-}O_{VI}} = 1{\cdot}36$ A., and $\mathrm{N_{VII}}\overline{-}\mathrm{O_V} = 1{\cdot}15$ A., which were then used as basis for (*h*0*l*) structure factor calculations. A comparison of the calculated and measured values gave an average difference (" agreement index ") $\Delta = \Sigma(\,|F_{\text{obs.}}| \sim |F_{\text{calc.}}|\,)/\Sigma\,|F_{\text{obs.}}| = 0{\cdot}28$, and indicated that the model was sufficiently close to the real structure to justify proceeding with a three-dimensional Fourier refinement of the parameters.

FIG. 4.



Section projection from y = 0 *to* y = ½, *showing an anion with its complete cation environment.*

Since all the evidence so far pointed to the existence of a mirror plane of symmetry in the ion, this assumption was made in calculating the phase angles of the general (*hkl*) structure factors. A section projection of a single anion was thus obtained from a synthesis evaluated between the limits $y = 0$ and $\frac{1}{2}$ (Fig. 4).

$$\int_{y=0}^{\frac{1}{2}} \rho(xyz)\,.\,dy = 4/A\,.\,[\underset{h+l\ \text{even}}{\Sigma\Sigma} F(h0l)\,.\cos 2\pi hx/a\,.\cos 2\pi lz/c\ -$$

$$\underset{h+l\ \text{odd}}{\Sigma\Sigma} F(h0l)\,.\sin 2\pi hx/a\,.\sin 2\pi lz/c]\ -$$

$$8/A\,.\,[\underset{h+l\ \text{even},\ k\ \text{even}}{\Sigma\Sigma\Sigma} \frac{1}{\pi k}\,[F(hkl)\,.\sin 2\pi hx/a\,.\cos 2\pi lz/c\ +$$

$$\underset{h+l\ \text{odd},\ k\ \text{odd}}{\Sigma\Sigma\Sigma} \frac{1}{\pi k} F(hkl)\,.\cos 2\pi hx/a\,.\sin 2\pi lz/c]$$

The changes in the atomic co-ordinates which resulted from this section projection were very small, and so it was followed by the calculation of the sectional syntheses at $y = \frac{1}{4}$, 0, and $\frac{1}{12}$, which are shown superimposed in Fig. 5. The y-parameters of O_{II} and K were obtained by line syntheses.

The co-ordinates from these syntheses are shown in Table II, and the bond lengths and angles in Table III. Fig. 6*a* gives a general view of the whole structure.

TABLE II.

Table of co-ordinates.

Atoms in positions (*c*) and (*d*) of space-group *Pnma* ("Int. Tables for the Determination of Crystal Structures," p. 138.)

$$(c)\ (x, \tfrac{1}{4}, z),\ (\bar{x}, \tfrac{3}{4}, z),\ (\tfrac{1}{2} - x, \tfrac{3}{4}, \tfrac{1}{2} + z),\ (\tfrac{1}{2} + x, \tfrac{1}{4}, \tfrac{1}{2} - z)$$

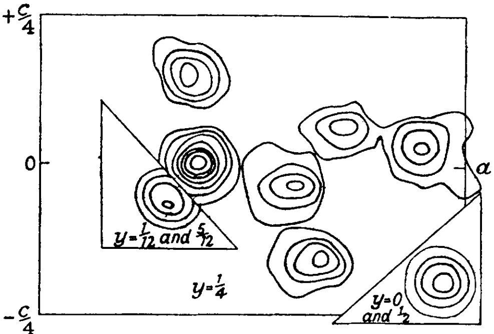
$$(d)\ \pm \mid (x, y, z),\ (\tfrac{1}{2} + x, \tfrac{1}{2} - y, \tfrac{1}{2} - z),\ (x, \tfrac{1}{2} - y, z),\ (\tfrac{1}{2} + x, y, \tfrac{1}{2} - z) \mid$$

8 K in positions	(*d*)	at	(0·055, 0·995, 0·190), etc.
8 O_{II} and O_{III} at	(*d*)	,,	(0·290, 0·110, 0·935), etc.
4 S in positions	(*c*)	,,	(0·365, 0·250, 0·005), etc.
4 O_{I} ,,	(*c*)	,,	(0·350, 0·250, 0·150), etc.
4 N_{IV} ,,	(*c*)	,,	(0·590, 0·250, 0·965), etc.
4 O_{VI} ,,	(*c*)	,,	(0·650, 0·250, 0·835), etc.
4 O_{V} ,,	(*c*)	,,	(0·895, 0·250, 0·030), etc.
4 N_{VII} ,,	(*c*)	,,	(0·715, 0·250, 0·065), etc.

From these atomic parameters the structure factors of the principal zones were calculated for both the ammonium and the potassium salt, and compared with those measured experimentally. The agreement indices were calculated separately for different values of k, and showed no systematic tendency to decrease for increasing orders of k, such as would arise from any deviations from the mirror plane of symmetry. There is no doubt, therefore, that the atomic arrangement conforms very closely to the symmetry of *Pnma*, and that, as already inferred from the Patterson syntheses, the structure of $K_2SO_5N_2$ should be assigned to this space-group rather than to *Pna*.

We have not attempted further refinement of the structure analysis of the potassium salt because we do not consider that the accuracy of the structure factors warranted it. It is clear that greater accuracy can be obtained by a detailed study of the isomorphous ammonium salt where the errors due to absorption of X-rays are much smaller, and this work is now in progress.

FIG. 5.

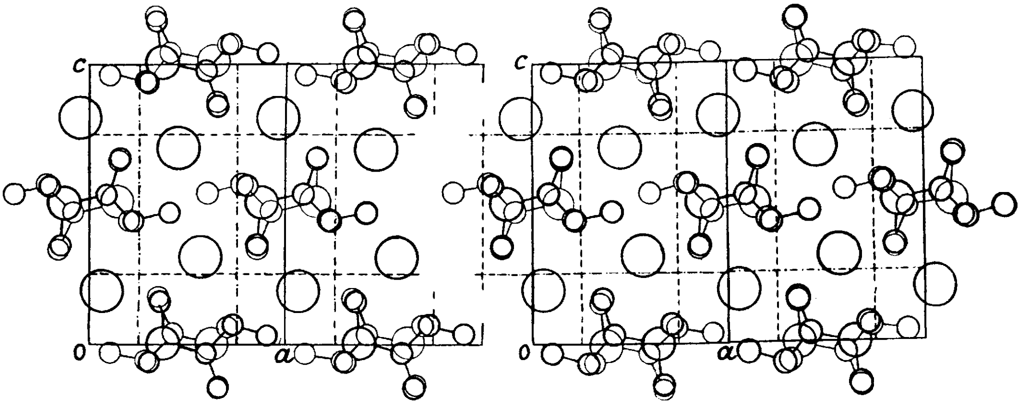


Three-dimensional Fourier sections at $y = 0, \frac{1}{12}$, *and* $\frac{1}{4}$.

It was mentioned above that some crystals showed a moderately strong (110) reflexion which is forbidden by the space-groups *Pna* and *Pnma*. In searching for an explanation of this, the effect of added cations was studied. It was found that the addition of ammonium ions produced crystals which did not show a (110) reflexion, whereas a batch of crystals containing sodium and potassium ions in the ratio of approximately 1 : 3 gave strong (110) reflexions and showed on further examination other reflexions forbidden by *Pnma*; the extinctions observed corresponded closely, in fact, to those required by *Pcmn* (or *Pcn*) although a few faint reflexions occurred which were forbidden by *Pcmn* and permitted by *Pnma*. It thus appears that the pure potassium and ammonium salts have the space-group *Pnma*, and from the transitional character of the mixed KNa crystals it is probable that the pure sodium salt (or possibly a 1 : 1 compound $KNaSO_5N_2$) has the space-group *Pcmn* or *Pcn*. (Attempts to prepare crystals of the pure sodium salt have not so far been successful on account of its high solubility.) The 3 : 1 KNa crystals showed no appreciable lattice contraction, nor were there any weak odd layer-lines to indicate the existence of a superlattice.

The transformation of the whole structure from the symmetry *Pnma* to that of *Pcmn* can be brought about with little change in energy, by merely interchanging the y-levels of every other row of anions as in Fig. 6. As the cation positions are very nearly at $y = 0$ and $\frac{1}{2}$, they conform to both space-groups alike, so that no alteration in the cationic lattice is necessary to bring about the change in symmetry. The replacement of potassium by sodium ions is presumably random.

FIG. 6*a*. FIG. 6*b*.



Structure of $K_2SO_5N_2$: *space-group* Pnma. *Probable structure of* $(K, Na)_2SO_5N_2$: *space-group* Pcmn.

Anions in heavy lines are b/2 *above those in light lines.*

It is noteworthy that apart from the height of the cation peaks the projections along [*y*] will be the same for both arrangements, but the definition of any three-dimensional syntheses would be considerably reduced by the coexistence of the two forms in the specimen examined (*i.e.*, it might easily happen that different domains in the same apparently homogeneous crystal belonged to the different space-groups). The good resolution obtained in the section projection and the sections reproduced in Figs. 4 and 5 make it fairly certain that the crystals on which the structure analysis has been based were of the pure *Pnma* form.

DISCUSSION.

The bond lengths and bond angles of the dinitrososulphite ion as calculated from the atomic co-ordinates are given in Table III (see also Fig. 7). They are estimated as reliable to within ±0·06 A. Some recent bond-length measurements are quoted for comparison, and various calculated values are also given.

TABLE III.

Bond lengths (*in* A.).

Bond.	Obs. values, $K_2SO_5N_2$.	Pauling : * Single bond.	Pauling : * Double bond.	S. and S. : † Single bond.	Gordy : † Double bond.	Other observed values.‡
SO	1·43	1·70	1·49	1·69	1·48	1·44[a], 1·45[b], 1·43[c], 1·44[d]
SN	1·63	1·74	1·54	1·74	1·53	1·57[a]
NN	1·30	1·48	1·28	1·48	1·24	1·26[e]
NO	1·35	1·36	1·18	1·43	1·16	1·25[e]

Bond angles :

N–S–O 106°, 105° S–N–O 121° O–N–N 118°
O–S–O 108°, 116° S–N–N 121° N–N–O 119°

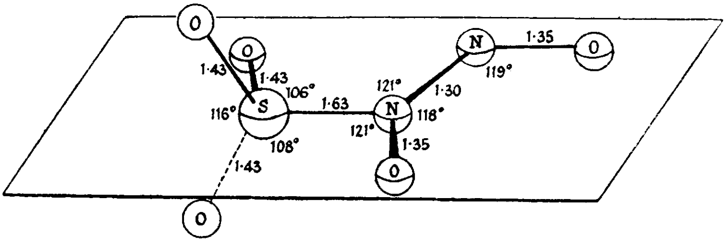
* Values for single and double bonds according to Pauling (" Nature of the Chemical Bond," 1945) assuming additivity of covalent radii.

† Values according to Schomaker and Stevenson (*J. Amer. Chem. Soc.*, 1941, **63**, 37) for single bonds, and according to Gordy (*J. Chem. Physics*, 1947, **15**, 81) for double bonds, calculated from more recent bond lengths, and allowing for an electronegativity correction β in the form $r_{AB} = r_A + r_B - \beta | x_A - x_B |$, where x_A and x_B are electro-negativities and $\beta = 0{\cdot}09$ for single and 0·06 for double bonds.

‡ (*a*) $K{\cdot}SO_3{\cdot}NH_2$ (Brown and Cox, *J.*, 1940, 1); (*b*) $SOCl_2$ (Palmer, *J. Amer. Chem. Soc.*, 1938, **60**, 2360); (*c*) SO_2Cl_2 (Palmer, *loc. cit.*); (*d*) β-isoprene sulphone (Cox and Jeffrey, *Trans. Faraday Soc.*, 1942, **38**, 241); (*e*) $(CH_3)_2N{\cdot}NO_2$ (Costain and Cox, *Nature*, 1947, **160**, 826).

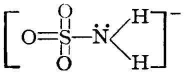
The S–O bond length 1·43 A. agrees with those observed in the more reliable investigations of structures containing tetrahedral S–O bonds, and although this is 0·06 A. shorter than the sum of Pauling's covalent double-bond radii, it seems hardly conceivable that more than four electrons should be involved in each S–O link. It appears then that the value of 1·44 A. should be taken as the upper limit for the length of a pure double bond. From this the double-bond covalent radius of sulphur, r_d^S, can be recalculated by using Gordy's empirical formula, giving $r_d^S = 0{\cdot}90$; if we add 0·10 A., which is the constant difference between single- and double-bond radii in Pauling's table of covalent radii of atoms in the second period, the single-bond radius of sulphur becomes 1·00 A. [cf. 1·02 A. in Me_2S_2 and H_2S_2 (Stevenson and Beach, *J. Amer. Chem. Soc.*, 1938, **60**, 2872) and $(C_2H_4I)_2S_3$ (Dawson and Robertson, *J.*, 1948, 1256)] and the calculated sulphur-to-nitrogen distances become S–N = 1·69 A. and S=N = 1·49 A. These values should be sufficiently reliable to form a basis for discussion of the S–N bond orders in the sulphamate and the nitrososulphite ions.

FIG. 7.

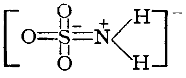


Anion bond-lengths and bond-angles.

The observed length of 1·57 A. for S–N in the $[SO_3{\cdot}NH_2]^-$ ion corresponds to a bond order of about 1·5; thus, having regard to the accuracy achieved in the structure analysis of potassium sulphamate, it is certain that the link cannot adequately be described as either a pure single or a pure double bond. As pointed out by Evans and Gergely (*Nature*, 1948, **162**, 771) in their treatment of the structure of the dinitrososulphite ion itself, the five valency electrons of the nitrogen atom can be regarded as being distributed to form three singly occupied [sp^2] orbitals and a doubly occupied p orbital, so that coplanar single bonds with trigonal symmetry about the nitrogen can be postulated for the S–N and the two N–H bonds; the additional bond strength of the S–N link would then be due to some sharing of the nitrogen p^2 electrons with sulphur. In terms of bond diagrams, the structure can be described as (X) and (XI), both contributing to about the same extent. Unfortunately, there are no intermolecular distances corresponding to NH · · · · · O bridges in potassium sulphamate, which might reveal the directions of the N–H bonds and provide more direct evidence of the nitrogen hybridisation.



(X.)



(XI.)

In the dinitrososulphite ion, the S–N bond, with a value of 1·63 A., is 0·06 A. longer than in the sulphamate. This may well be significant, indicating that the replacement of the hydrogens by other atoms has diminished the electron density in the S–N link, which now approximates more closely to the pure single S–N bond. Evans and Gergely have accordingly assumed a bond order of unity and, using a molecular orbital method, have given a very satisfactory description of the electronic structure of the N_2O_2 group. As indicated in Table IV, their calculations account very well for the marked double-bond character between the nitrogen atoms, but may possibly over-emphasize the departure of the N–O links from pure single-bond character.

TABLE IV.

Observed and calculated bond lengths.

Bond.	Obs., A.	Calc., A.	Bond order (calc.).
N–N	1·30	1·30	1·72
$N–O_V$	1·36	1·31	1·45
$N–O_{VI}$	1·36	1·31	1·45

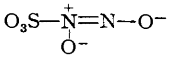
With the proviso that there may be appreciable departures from integral bond orders (which can more appropriately be discussed when the detailed analysis of the ammonium salt has been completed) the best conventional representation of the.the ion is (XII).

The co-ordination of the ionic lattice is 12 : 6, and the anions and cations lie in alternate layers with a separation of $y = \frac{1}{4}$. Each anion has 12 cation neighbours arranged in two irregular hexagons, one in the layer above, and the other in the layer below, whereas each cation is co-ordinated to six dinitrososulphite ions, three in each layer above and below. As shown in Table V, the K–O distances lie within the usual range observed in compounds of this type. The K–N distances are considerably greater, and it is interesting to note that the larger separation corresponds to the greater positive charge as calculated by Evans and Gergely.

TABLE V.

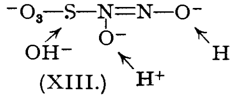
	$K_2SO_5N_2$.	$K{\cdot}SO_3{\cdot}NH_2$ (Brown and Cox, *loc. cit.*).
KO_I	2·95, 3·00	2·75
KO_{II}	2·85, 3·10	2·96
KO_V	2·80, 3·20	—
KO_{VI}	2·95, 2·95	—
KN_{IV}	3·60, 3·60, 3·95	3·10
KN_{VII}	3·40, 3·40, 3·60	—
KS	3·50, 3·90, 4·00	—

The long controversy over the structure of the dinitrososulphites was largely due to the difficulty of reconciling a structure involving an S–N link with the ease of the qualitative decomposition to sulphate and nitrous oxide. Unfortunately, no kinetic measurements of the decomposition of salts in weakly acid solution have been made, but on the basis of the configuration and charge distribution described in this paper, hydrolysis of the S–N link to sulphate and hyponitrous acid can be postulated as in (XIII). As is well known, hyponitrous acid decomposes to nitrous oxide in acid solution.



$$O_3S{-}\overset{+}{\underset{\underset{\displaystyle O^-}{|}}{N}}{=}N{-}O^-$$

(XII.)



(XIII.)

The potassium salt decomposes rapidly when heated to about 110° (Divers and Haga, *J.*, 1895, **67**, 452) and various amounts of potassium sulphite have been reported in the sulphate product; we have also found that a crystal of the dinitrososulphite may decompose over a period of several months at room temperature, leaving a transparent aggregate of potassium sulphate crystals in which the [*c*] axes tend to be oriented parallel to the [*b*] axis of the original crystal. It is reasonable to suppose that these dry reactions are also due to hydrolysis by traces of water adsorbed on the crystals, a view which is supported by reports that the compound is considerably more stable in a dry, non-acid atmosphere.

EXPERIMENTAL.

For the preparation of potassium dinitrososulphite the method of Weitz and Achterberg (*loc. cit.*) was found to give good yields, but it was necessary to recrystallise from 15% potassium hydroxide at 50° to obtain crystals suitable for *X*-ray analysis; *i.e.*, of 0·1—0·2 mm. diameter and as evenly developed as possible. However, by using a more dilute solution in the preparation, and by leaving it undisturbed during absorption of the nitric oxide, sufficiently large crystals can be obtained directly. The same method of preparation was used for the ammonium salt, whereas crystals of the thallium salt were grown by letting solutions of thallium perchlorate and sodium dinitrososulphite diffuse together into a saturated solution of ether in water. The analyses were : Found, in potassium salt : K, 35·64; S, 14·61 (Calc. for $K_2SO_5N_2$: K, 35·81; S, 14·69%). Found, in thallium salt : Tl, 74·52 (Calc. for $Tl_2SO_5N_2$: Tl, 74·48%).

Photographs were taken with Cu-K_α radiation. The cell dimensions, determined from high-order reflexions by the Straumanis method (Buerger, " *X*-Ray Crystallography," 1942, p. 394), are given on p. 1784. The density of the crystals determined by flotation is 2·56 ± 0·02 g./c.c. (Calc. for 4 molecules per unit cell, 2·54 ± 0·02).

The approximate minimum and maximum refractive indices are $\alpha = 1{\cdot}48$ along [*b*], $\gamma = 1{\cdot}66$ along [*a*].

The intensities of the reflexions were recorded photographically on complete sets of 15° oscillations about [010] and [100], and equi-inclination Weissenberg photographs for all layer-lines with equi-inclination angle $\nu < 20°$. A multiple film technique was used and about 5000 intensity measurements were made visually. These were correlated, corrected for absorption, and multiplied by the appropriate geometrical and polarisation factors, and the relative structure amplitudes of 469 planes were finally derived. For zero layer-line photographs the ordinary absorption correction for cylindrical specimens (Int. Tables, p. 584) was used; in the case of equi-inclination Weissenberg photographs this correction is still valid if the specimen radius r is replaced by $r \sec \nu$. For non-equatorial layer-lines on oscillation photographs of small diameter crystals it was found that a satisfactory correction factor was obtained by taking the mean of factors for specimens of radius r and $r \operatorname{cosec} \phi$ respectively (ϕ = half angle of layer-line cone). The deviations from cylindrical shape, however, and the uncertainty of the crystal dimensions, make it impossible to calculate the absorption errors accurately, and on this account alone the corrected intensities may be in error by as much as 25% in the worst cases.

We wish to record our indebtedness to the Government Grants Committee of the Royal Society and the Department of Scientific and Industrial Research for financial support, and to Birkbeck College and the University of Leeds for scholarships awarded to one of us (H. P. S.).

We wish to thank Mr. F. J. Garrick and Mr. A. White for assistance with some chemical work, especially the preparation and analysis of the thallium salt.

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[*Received, January 27th,* 1949.]