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The Crystal Structure of $N_2O_5.3SO_3$

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The crystals of $N_2O_5.3SO_3$ are monoclinic, with $a = 19{\cdot}54$, $b = 7{\cdot}30$, $c = 7{\cdot}56$ Å, $\beta = 102°$. Systematic absences lead to space groups $C2/c$ or Cc. Although intensity statistics would indicate a center of symmetry, no normal structure in the space group $C2/c$ could be found. On the other hand, it was possible to derive a set of atomic coordinates with symmetry Cc with strong pseudo-symmetry which introduces a false center in one of the projections. The structure consists of NO_2 and S_3O_{10} groups, in agreement with the interpretation of Raman spectra.

1. Introduction

The investigation on compounds $N_2O_5.nSO_3$ was started in order to obtain a better insight into the structures of various nitrating agents. The work in this laboratory has been carried out simultaneously with Ingold's investigations and confirms the latter's results. The preparation of one compound, viz. $N_2O_5.4SO_3$, was described as early as 1908 by Pictet & Karl (1908), but it was impossible to confirm their results. This is in agreement with the results of Ingold and his coworkers (Gillespie, Hughes & Ingold, 1950), who were able to prepare only the compounds with $n = 2$ and $n = 3$. By mixing solutions of N_2O_5 and SO_3 in $POCl_3$, we obtained a relatively pure compound which had the composition $N_2O_5.3SO_3$, containing a few per cent of N_2O_3.

Raman spectra indicate that NO_2^+ ions occur in the compound. The spectra contain a strong line at 1400 cm.$^{-1}$, which is also found in $NO_2.ClO_4$ (Gillespie *et al.*, 1950) and in solid N_2O_5 (Chédin, 1937) and which must be attributed to NO_2^+. The structure of these compounds is known to be $NO_2^+.ClO_4^-$ (Cox, Jeffrey & Truter, 1948) and $NO_2^+.NO_3^-$ (Grison, Eriks & de Vries, 1950) respectively.

These data suggest that the structure of $N_2O_5.3SO_3$ will be $(NO_2^+)_2.S_3O_{10}^{--}$. A complete description of the preparation of the compound, together with the Raman spectroscopic data, has been published elsewhere (Gerding & Eriks, 1952; Eriks, 1952).

2. Crystal data

The compound $N_2O_5.3SO_3$ is a hard white solid with a melting point of about 128° C. Crystals, which can be obtained from the melt, are thin colorless plates, conventionally chosen as parallel to (100). They are very hygroscopic so that a capillary technique must be used for getting X-ray diagrams, and besides they show a strong inclination for twinning on the (100) plane. Suitable single crystals could be selected under the polarizing microscope. The crystals are optically biaxial, positive, with n_γ practically perpendicular to the (100) plane.

Rotation and Weissenberg exposures were obtained with Cu K radiation around the b and c axes. From these diagrams the following cell dimensions were calculated:

$$a = 19{\cdot}54,\ b = 7{\cdot}30,\ c = 7{\cdot}56\ \text{Å},\ \beta = 102°\ .$$

The unit cell contains four molecules $N_2O_5.3SO_3$. Calculated density 2·189 g.cm.$^{-3}$; experimental density 2·17 g.cm.$^{-3}$.

Intensities were estimated visually, using the multiple-film technique. They were corrected for Lorentz and polarization factors. Absorption could not be neglected; it was accounted for by a simplified graphical method based on Albrecht's method (Eriks, 1952).

From the absences, hkl with $h+k = 2n+1$ and $h0l$ with $l = 2n+1$, two space groups are possible,

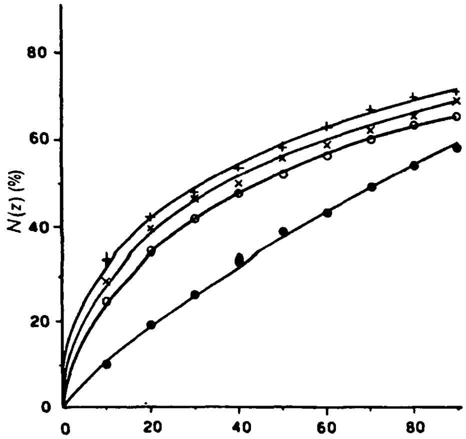

Fig. 1. Results of intensity statistics. ●: empirical curve for non-centrosymmetric structure; ○: empirical curve for centrosymmetric structure; ×: curve, calculated for $h0l$ reflections; +: curve, calculated for $hk0$ reflections.

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$C2/c$ and Cc, differing in the presence or absence of a center of symmetry. In order to decide between the space groups, intensity statistics (Howells, Phillips & Rogers, 1950) were computed for $hk0$, $h0l$ and hll reflections, of which 80, 80 and 140 respectively occurred on the Weissenberg films (Fig. 1). The curve for the reflections hll coincides with that for $hk0$. Though the number of reflections is rather small for the results to be significant, the statistics point in all cases to the presence of a symmetry center, and therefore to the space group $C2/c$. The evidence is not conclusive however, since the number of the—predominantly scattering—sulfur atoms may be really too small to apply statistical methods.

3. Attempt at structure determination in the space group $C2/c$

As this space group was suggested by the statistics and is easiest to handle, we took it as the basis for our trial analysis. The space group $C2/c$ contains fourfold and eightfold positions. Of the total of 8 nitrogen, 12 sulfur and 56 oxygen atoms, 4 of the sulfur atoms must be in fourfold position; as a S_3O_{10} group consisting of three linked tetrahedra cannot have a center of symmetry, but can contain a twofold axis, the only possible position for these fourfold sulfur atoms is (4*e*) of the *International Tables.*

The optical evidence, as well as a projection of the vector map along the *c* axis, suggests that chain-like S_3O_{10} groups are stretched along the normal to the (100) plane. By fitting a model of this group to the ($hk0$) vector map a trial structure was derived and refined, first by Fourier syntheses, later by (F_o-F_c) series. A position for the NO_2 group was found during the refining process. The final Fourier projection along the *c* axis is shown in Fig. 2, containing only the asymmetric unit, i.e. one half of the S_3O_{10} ion and one NO_2 group.

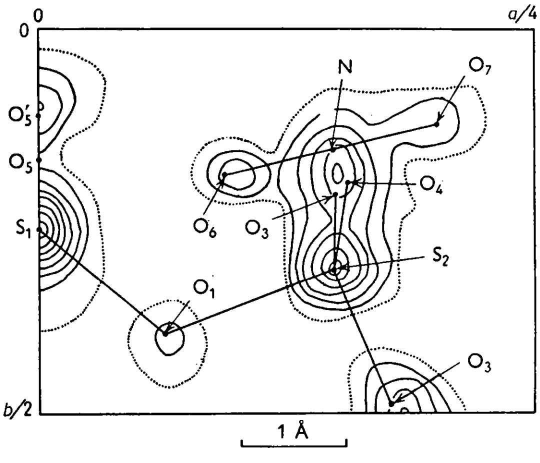


Fig. 2. Projection of electron density along [001]. Contour lines at equal intervals, on arbitrary scale. S_1: central atom of the S_3O_{10}-chain; S_2: non-central atom of this chain; O_1: oxygen atom connecting S_1 and S_2; O_2, O_3, O_4: end oxygens, bound to S_2; O_5: oxygen bound to S_1 only; O_6, O_7: oxygen atoms of the NO_2 group.

z Parameters

According to the projection along [010] of the vector map (Fig. 3) there are two possibilities for the position of S_2 in this projection, as either *OA* or *OB* may represent the S_1–S_2 vector, both having the proper *x* coordinate and a length such as might be expected for the S–S distance. For both configurations, a set of atomic parameters could be found after a refinement procedure analogous to that used for the [001] projection. These two structures, which are practically the mirror image of each other, are shown in Fig. 4, indicated by full and broken lines respectively. The agreement between F_o and F_c of the $h0l$ reflections was fairly satisfactory for both sets of atomic coordinates (R about 0·20). In order to decide between the two structures, F values for the reflections hll were cal-

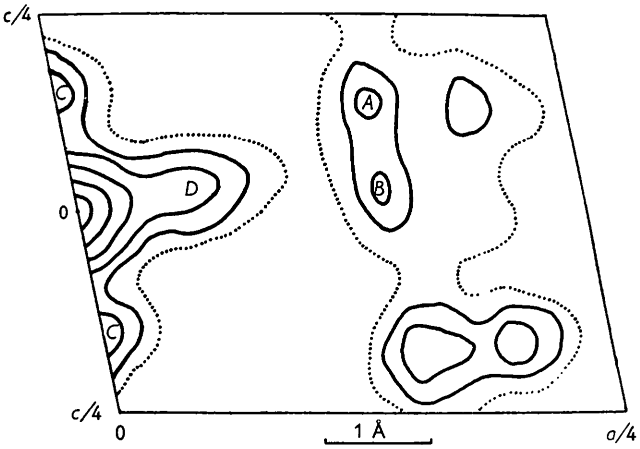


Fig. 3. Patterson projection on (010).

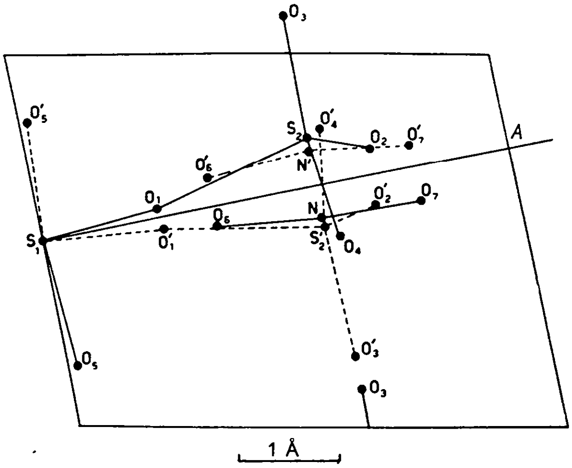
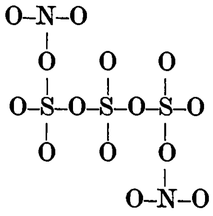


Fig. 4. Atomic positions of the two calculated configurations in space group $C2/c$, projected along the *b* axis. The primed atoms refer to the configuration indicated by broken lines.

culated. Surprisingly, neither of the two possibilities showed the slightest agreement for these reflections. Moreover, both structures appeared suspect on chemical grounds: extremely short distances (about 2 Å) were found in both cases between O_3 and the three atoms of the NO_2 group. Since the position of the nitrogen atom is not very certain, the structures would then rather be described as the condensation product of two NO_2 groups with an S_3O_{10} group, thus:



This description is, however, definitely at odds with the Raman evidence for isolated NO_2 groups, as stated in § 1.

In order to get further information, a Fourier summation was carried out with structure factors hll. For the space group $C2/c$, the following two relations hold for summations carried out with the structure factors $F(hpl)$ of the p'th layer line around the b axis:

$$\sum_{h}\sum_{l}^{l=\text{even}} F(hpl)\cos 2\pi(hx/a+lz/c) = C(p)\sum_{j=1}^{N}\varrho_j(x-x_j, z-z_j)\cos 2\pi p y_j/b\,, \quad (1)$$

$$\sum_{h}\sum_{l}^{l=\text{odd}} F(hpl)\sin 2\pi(hx/a+lz/c) = C(p)\sum_{j=1}^{N}\varrho_j(x-x_j, z-z_j)\sin 2\pi p y_j/b\,. \quad (2)$$

$\varrho_j(x-x_j, z-z_j)$ is the projection of the electron distribution function around the atom j; the summation on the right-hand side is over the atoms in the asymmetric unit. $C(p)$ is a constant for the reciprocal-lattice plane p = constant; its value depends on the analytical form chosen for ϱ_j. Clews & Cochran (1949) derived analogous formulae for the case of atoms not overlapping in the projection; the relations (1) and (2) were, however, derived without this assumption (Eriks, 1952).

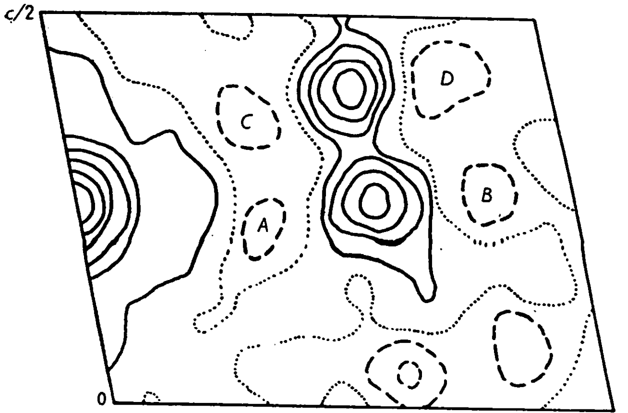


Fig. 5. Result of the Fourier summation, given by equation (2). $F(hll)$ only with odd l's. Dotted line: zero contour line; full lines indicate positive area; broken lines indicate negative area.

The summation (2), carried out with $p = 1$ and with signs corresponding to the position shown in full lines in Fig. 4, gave the particularly interesting result shown in Fig. 5. The negative areas A, B, C and D can be attributed only to O_6 and O_7 of the NO_2 group, y_j for these atoms being 0·819 and 0·878 respectively. Now, these four regions appear exactly in the places where the two oxygen atoms of NO_2 were found in the *two* sets of atomic coordinates of Fig. 4, as calculated from the b-axis projection. Moreover, the peak corresponding to S_2 is too low; the weight, sin 118°, should make this peak nearly as high as that of S_1 at $x = 0, y \approx \frac{1}{4}$, $z = \frac{1}{4}$, whereas the peak at $x \approx \frac{1}{6}$, $z \approx \frac{1}{4}$, composed of an oxygen with weight sin 66° and nitrogen with weight sin $-65°$ should be practically absent in this synthesis.

A similar synthesis based on the signs of the configuration shown in broken lines in Fig. 5 gives essentially the same result, although several terms change signs. In fact, the map Fig. 5 suggests strongly the superposition of two configurations, such as occurs when the electron density of an acentric structure is calculated with a 'false' center of symmetry, introduced by phases derived from the—centrosymmetric—configurations of heavy atoms; or when phases in absolute magnitudes have been estimated by isomorphous substitution and are carried into the synthesis both with + and − sign (Bokhoven, Schoone & Bijvoet, 1951).

4. Structure determination in the space group *Cc*

It seems, therefore, that the space group $C2/c$ is not the correct one, despite the evidence offered by the statistical test. The interpretation of Fig. 5 outlined in the last paragraph of § 3 then suggests that we should combine the left half of one configuration of the S_3O_{10} group with the right half of the other.

It is arbitrary whether we take the right half of the configuration shown in broken lines and the left half of that shown in full lines, or the centrosymmetric configuration. We chose the first alternative (Fig. 6). Moreover, in order to avoid abnormal short distances between O_3 and NO_2, the NO_2 configuration shown in broken lines was superimposed on the half of the S_3O_{10} group shown in full lines, and vice versa.

This supposition worked like magic; not only did the R factor drop to 0·15 in both projections after one refinement cycle but also the recalcitrant hll reflections capitulated: R = 0·22.

As a precision determination was not aimed at, and was, moreover, practically impossible in view of the

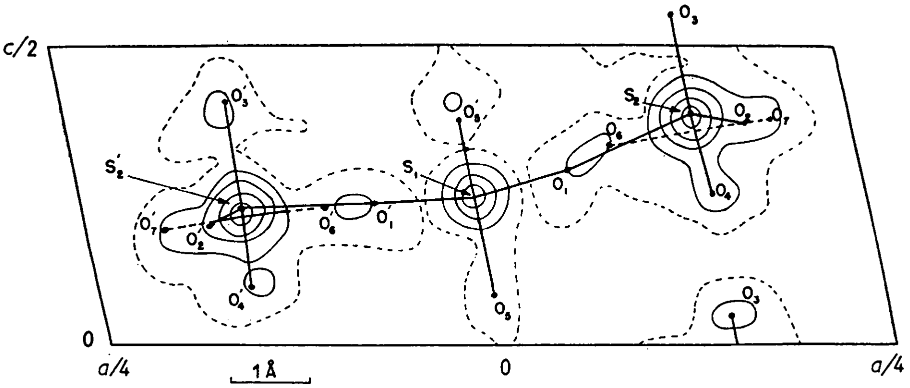


Fig. 6. Electron-density map and atomic position for space group *Cc*, projected along the *b* axis.

uncertainties in the absorption correction, we stopped the refinement at this point. The final coordinates are shown in Table 1.

Table 1. *Final coordinates*

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
S_1	0	0·264	0·250				
S_2	0·1472	0·314	0·390	S'_2	0·8528	0·314	0·233
O_1	0·0625	0·398	0·292	O'_1	0·9375	0·398	0·236
O_2	0·1764	0·489	0·376	O'_2	0·8236	0·489	0·202
O_3	0·1488	0·217	0·550	O'_3	0·8512	0·217	0·408
O_4	0·1542	0·200	0·256	O'_4	0·8458	0·200	0·100
O_5	0·0	0·175	0·086	O'_5	0·0	0·122	0·380
O_6	0·0930	0·814	0·333	O'_6	0·9070	0·814	0·233
O_7	0·2000	0·876	0·378	O'_7	0·8000	0·876	0·197
N	0·1472	0·844	0·356	N	0·8528	0·844	0·217

The Fourier projection along the *b* axis and the atomic positions are shown in Fig. 6. The calculated and experimental structure factors have been given by Eriks (1952). The calculated structure factors contain a temperature factor $\exp(-3{\cdot}0 \sin^2 \theta/\lambda^2)$.

5. Interatomic distances and angles

Distances were calculated from the atomic parameters, for both left and right half of the molecule. Results are shown in Table 2.

6. Discussion of the structure

The crystal structure determination gives a confirmation of the original idea: that $N_2O_5.3SO_3$ has to be considered as a mainly ionic compound containing NO_2^+ and $S_3O_{10}^{--}$ ions. The structure of this $S_3O_{10}^{--}$ ion has not been investigated before, but it is supposed to exist in $K_2S_3O_{10}$ (Baumgarten & Thilo, 1938).

Although the space group does not reveal it, the ion S_3O_{10} has a marked pseudo symmetry plane. It may be remarked that in the related structure $HNO_3.3SO_3 = S_3O_{10}H.NO_2$ the anion S_3O_{10} does have such a symmetry plane according to space group requirements (Steeman, unpublished). In the present structure, this symmetry plane extends also over the position of the two NO_2 ions and in fact over whole layers parallel to the (100) plane and of thickness $\frac{1}{2}d_{(100)}$, but is lost in the stacking of these layers. If it is extended into the stacking of three subsequent layers, a twin on (100) is formed; the frequency of these twins was mentioned in § 2. The structure is further in agreement with the optical behavior:

Table 2. *Interatomic distances and angles*

Distances within S_3O_{10} group

	Left	Right		Left	Right
S_1–S_2	2·88 Å	2·87 Å	O_1–O'_1	2·40 Å	—
S_1–O_1	1·55	1·54	O_1–O_2	2·29	2·28
S_2–O_1	1·76	1·78	O_1–O_3	2·68	2·65
S_2–O_2	1·40	1·41	O_1–O_4	2·36	2·36
S_2–O_3	1·50	1·40	O_1–O_5	2·45	2·40
S_2–O_4	1·30	1·34	O_1–O'_5	2·50	2·52
S_1–S_5	1·44	1·40	O_3–O'_5	3·04	3·00
O_2–O_3	2·50	2·50	O_4–O_5	3·06	3·02
O_2–O_4	2·32	2·30	O_5–O'_5	2·25	—
O_3–O_4	2·30	2·25			

N–O distances in the NO_2-group on both sides

N–O_6 = 1·06 Å N–O_7 = 1·05 Å

Shortest distances between NO_2 and the oxygen atoms of S_3O_{10}

	Left	Right		Left	Right
O_3–O_6	2·48 Å	2·59 Å	O_4–N	2·72 Å	2·72 Å
O_3–O_7	2·67	2·56	O_2–O_6	2·85	2·85
O_3–N	2·38	2·36	O_2–O_7	2·85	2·85
O_4–O_6	3·17	3·16	O_2–N	2·65	2·65
O_4–O_7	2·69	2·63			

Shortest distances between oxygen atoms of neighboring groups

O_7–O_7	3·21 Å	O_5–O_5	2·70 Å
O_3–O_4	3·39	O_2–O_3	3·22
O_5–O_6	2·80		

Calculated bond angles in the S_3O_{10} group

O_1–S_1–O_1	100°	O_1–S_2–O_3	114°
O_5–S_1–O_5	107	O_1–S_2–O_4	99
O_1–S_1–O_5	113	O_2–S_2–O_4	116
S_1–O_1–S_2	122	O_3–S_2–O_4	116
O_1–S_2–O_2	93	O_2–S_2–O_3	132

positive double refraction with maximum elongation along the normal to (100).

The distances, especially between O_3 and the NO_2 oxygens, are appreciably shorter than twice the van der Waals radius of oxygen, which might be explained by assuming a weak bonding between this O_3 atom and the NO_2^+ ion. In this case the NO_2^+ would probably not be linear, the N atom being shifted somewhat towards O_3. It is to be regretted that the exact position of this N atom could not be determined in either projection as it coincides with O_4 in the one and with S_2 in the other. The Raman spectra seem to indicate, however, that such a slight deviation from linearity of the NO_2^+ ion actually occurs (Gerding & Eriks, 1952).

The N–O distance found in NO_2^+ is shorter than that of 1·16 Å, found in N_2O_5 for the same ion. This, again, may result from the inaccuracy in the position of nitrogen.

There exists a striking difference between the two single S–O distances (1·55 Å and 1·77 Å). The comparatively long S_2–O_1 distance may well give an explanation for the observation by Baumgarten and Thilo (1938) that the $S_3O_{10}^{--}$ ion in $K_2S_3O_{10}$ loses one molecule of SO_3 at about 150° C., to yield $S_2O_7^{--}$.

7. Pseudo-homometric structures

A few remarks may finally be made about the difficulties encountered in the structure determination, especially with respect to the space group. It is clear that a number of coincidences have combined to confuse the issue of the space-group determination. First, in the [001] projection of the structure in *Cc* there appeared to be no reason to introduce different *y* coordinates for both halves of the molecules, except for O_5 and O_5' (cf. Table 1); so there is a pseudo center of symmetry in this projection owing to the accidental values of the *y* coordinates. Secondly, from inspection of Fig. 4 it is more or less clear why *two* configurations in the space group *C*2/*c* give a fairly good fit in the projection along the *b* axis: the position of S_2 in the one configuration is occupied by N and O_4 in the other and these two atoms together are practically equivalent to S in scattering power. In fact, on inspection of Fig. 4 it is seen that the *b* projections of S–O distances in both sets are closely similar if $N+O_4$ are considered to be equivalent to S. Both vector sets show some divergence from that of the 'true' structure (Fig. 6), corresponding to a drop in *R* from about 0·20 to 0·15. It may, however, be remarked that in the space group *C*2/*c* a distinctly better fit could be arrived at by taking an *averaged* structure of the two sets of Fig. 4, combined with the *y* parameters of Fig. 3. This averaged structure is pseudo-homometric with the structure in the space group *Cc*, and accordingly gives a satisfactory agreement with observed intensities, in particular with those of reflections *hll*. In fact, the difference in *R* between this averaged structure in *C*2/*c* and the normal one in *Cc* is so small that the former was discarded rather on general grounds and because it leads to some improbably small interionic O–O distances.

This being a case of pseudo-homometry between a set with symmetry *Cc* and one with symmetry *C*2/*c*, it is clear that the Wilson test was bound to fail.

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