

Fig. 2. The idealized structure of tetragonal $(W_{0.38}V_{0.65})_2O_5$.

$V_{0.65})_2O_5$ with $Z=16$. The space group symmetry $I4/mmm$ was confirmed by inspection of Weissenberg photographs and the structure was solved by means of Patterson syntheses. The subsequent least squares refinement based on diffractometer data resulted in a final R -value of 0.056.

The idealized structure is shown in Fig. 2. It is composed of MO_6 octahedra at two levels; $M=(W,V)$ with different W/V ratios at the three non-equivalent metal positions. 4×4 octahedra at the same level share corners and form, together with identical polyhedra above and below, a block of ReO_3 -type infinite along c . Such blocks are mutually connected by component octahedra having edges in common. Two equivalent sets of mutually perpendicular shear planes are thus formed and the structure can formally be derived from the ReO_3 -type structure by displacement of $(4 \times 4 \times \infty)$ -blocks the vectors $(\frac{1}{2}a + \frac{1}{2}c)$ and $(\frac{1}{2}b + \frac{1}{2}c)$ relative to each other along the two sets of shear planes, respectively; a , b , and c being the edges of the ReO_3 -type subcell. If a shear mechanism operates in a basic ReO_3 -type structure in two stages, first along one set of shear planes and thereafter along the other, the present structure type is formed.

A large number of "block structures" have been described by Roth and Wadsley.⁵ These and other multiple-shear structures have been systematized by Andersson.^{4,6} Although the present structure is obviously of this type, it does not fit into the classification, but forms the first known member of a new group of structures with a very simple shear mechanism. Further

members of this group can be obtained by variation of the block-size according to the principles of homologous series.³ It may be noticed that there is a relationship between this structure and that of $N-Nb_2O_5$ which is also composed of 4×4 blocks⁷ but with a different shear mechanism.

Full details of the investigations reported above will shortly be published elsewhere.

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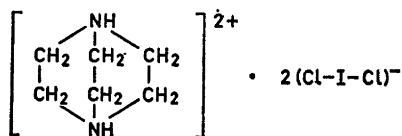
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On the Structure of the Dichloriodide Ion

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The crystal structure of triethylenediammonium bis-dichloriodide,



has been investigated by two-dimensional X-ray methods. The structure of the amine was known previously¹ and our chief interest was the structure of the anion, the symmetry of which generally seems to depend on the size of the cation.

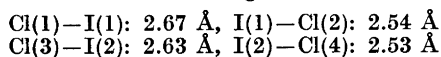
The crystals are orthorhombic with unit cell parameters $a = 9.92 \text{ \AA}$, $b = 19.86 \text{ \AA}$, and $c = 7.58 \text{ \AA}$ and containing four formula units. The two space groups $Pnn2$ and $Pnmm$ are both compatible with the systematic absent reflections, but the latter eventually turned out to be the more probable.

The structure was solved from the projections along the a and c axes using Patterson methods; least-squares refinements gave final conventional R -values of 14 % and 10 % for the $(hk0)$ and $(0kl)$ data, respectively.

Large standard deviations in the positional parameters of the lighter atoms do not permit a discussion of the structure of the cationic part of the salt, but there were no significant deviations from the structure of the amine, however.

There are two non-equivalent dichloroiodide ions; both are linear within the accuracy of the measurement and both are non-symmetrical.

The relevant bond lengths are



with standard deviations of 0.03 \AA . The Cl(1) and Cl(3) atoms are situated closer to nitrogen atoms than the other halogen atoms, and are thus probably carrying the negative charge. This agrees well with the results obtained in the structure determination of piperazinium bis-dichloroiodide² where a corresponding geometric arrangement was found, the two Cl-I bond lengths being 2.69 \AA and 2.47 \AA , respectively.

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Preparation of 2-Nitrothiophene of High Isomeric Purity

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In connection with current work on nitration of -I-M substituted thiophenes¹ it was necessary to obtain an isomerically pure sample of 2-nitrothiophene. The direct nitration of thiophene invariably seems to result in an isomeric mixture consisting of about 85 % 2-nitrothiophene and 15 % of the 3-isomer.² Since this mixture is difficult to separate in its components, the isomers have instead been obtained through the selective dechlorosulfonation of the synthetic mixture of 5-nitro- and 4-nitro-2-thiophene-sulphonylchloride.³ The yield, however, of 2-nitrothiophene is only about 4 %, contaminated with about 5 % 3-nitrothiophene, but under favorable conditions the method may yield practically pure 2-nitrothiophene.² On the other hand 3-nitrothiophene is always obtained in reasonable yields in 99 % isomeric purity^{1,2} with the same method.

Since 4-nitro-2-thiophenesulphonylchloride is dechlorosulfonated at about 130°C and the 5-nitro-isomer at about 160°C ³ and since the reaction is probably reversible, it is to be expected that the chlorosulfonation of a mixture of 2- and 3-nitrothiophene, if interrupted at an early stage, would give a mixture of 4-nitro-2-thiophene-sulphonylchloride and 2-nitrothiophene. Also investigations of mono-substituted -I-M thiophenes indicate that the 5-position in 3-nitrothiophene is nitrated faster than the same position in 2-nitrothiophene.¹

Thus the isomeric mixture of nitrothiophene obtained from nitration of thiophene (Experimental) was chlorosulfonated with chlorosulphonic acid at 40°C , and the course of reaction was followed with NMR. Since the 2-proton quartet of 3-nitrothiophene is shifted downfield with about 24 cps from the lowest field quartet (3-proton) of 2-nitrothiophene a convenient measure of change in isomeric composition is at hand. Thus, as the reaction proceeded the 2-proton quartet gradually disappeared and was replaced with an AB quartet with $J_{AB} = 1.8$ cps, which