

On the Crystal Structure of $\text{ZnSO}_3 \cdot 2\frac{1}{2}\text{H}_2\text{O}$

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The crystal structure of zinc sulfite hydrate has been investigated. From $hk0-hk2$ X-ray single-crystal data obtained with Ni-filtered $\text{CuK}\alpha$ radiation a preliminary structure has been derived.

The sample of $\text{ZnSO}_3 \cdot 2\frac{1}{2}\text{H}_2\text{O}$ used in this work was prepared according to Pannetier *et al.*¹

The triclinic unit cell, which contains four formula units, has the dimensions (calculated from a powder pattern obtained with a Hagg-Guinier camera)

$$a = 7.675(3) \text{ \AA} \quad b = 7.567(3) \text{ \AA} \quad c = 9.115(3) \text{ \AA} \\ \alpha = 90.26(3)^\circ \quad \beta = 88.37(5)^\circ \quad \gamma = 93.89(3)^\circ$$

The distribution of the 598 normalized structure factors (including 164 unobserved) indicated that the crystal was centrosymmetric. Accordingly, the crystal was assigned to the $P\bar{1}$ space group. The crystal structure was solved by the

symbolic addition procedure described by Karle and Karle,² using the program GAASA.³⁻⁴ The phases of the largest 110 normalized structure factors were determined. A Fourier map with E_H as coefficients revealed the structure. Full-matrix least-squares refinements of the nonhydrogen atoms with isotropic temperature factors resulted in a discrepancy factor $R = 0.093$.

The structure may be described in terms of pyramidal sulfite ions ($\text{S}-\text{O}$ mean distance 1.54 Å), ZnO_4 tetrahedra ($\text{Zn}-\text{O}$ mean distance 1.99 Å) and ZnO_6 octahedra ($\text{Zn}-\text{O}$ mean distance 2.10 Å). The tetrahedral coordination around half of the zinc atoms is provided by four oxygen atoms of four SO_3^{2-} groups. The octahedral coordination around the rest of the zinc atoms is provided by two oxygen atoms of two SO_3^{2-} groups and four oxygen atoms of water molecules. A schematic drawing showing the linking of the polyhedra is given in Fig. 1. In addition to the linking of the polyhedra, the structure is held together by a network of hydrogen bonds involving every oxygen atom in the sulfite groups.

The structure is to be refined further using complete X-ray data and a full report of the

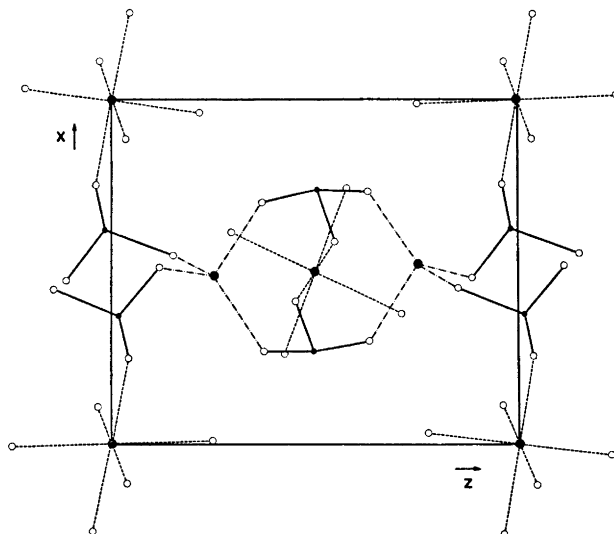


Fig. 1. A projection of the structure of $\text{ZnSO}_3 \cdot 2\frac{1}{2}\text{H}_2\text{O}$ on the xz plane. Large filled circles denote zinc atoms, small filled circles denote sulfur atoms and open rings denote oxygen atoms.

structure determination will be given elsewhere.

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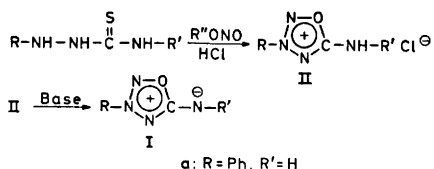
The Reversible Ring Opening of *N*-[3-Phenyl-5-(1,2,3,4-oxatriazolio)]amide to 2-Phenyl-2-nitroso-1-cyanohydrazidate Ion

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In a recent paper¹ we showed that treatment of 1-substituted or 1,4-disubstituted thiosemicarbazides with nitrous acid leads to mesoionic 3-substituted *N*-[5-(1,2,3,4-oxatriazolio)]amides.*

* For the sake of consistency, all mesoionic compounds in this paper and in Ref. 1 are referred to only by the oxatriazolio names and formulas. This is done without prejudice toward the contribution of other mesomeric structures and should therefore not be taken as a statement of the electron distribution in the compounds in question. The names and formulas are in agreement with an example authorized by The International Union of Pure and Applied Chemistry, Nomenclature of Organic Chemistry, Section C (1965) p. 69, Butterworths.



The same reaction was earlier carried out by Busch and coworkers,^{2,3} (in their numerous examples the 1-substituent of the thiosemicarbazide always was an aryl group (R = Ar)). These authors were unable to formulate the products satisfactorily.

Among Busch's compounds one is especially interesting, namely that derived from 1-phenylthiosemicarbazide, which according to our formulation is *N*-[3-phenyl-5-(1,2,3,4-oxatriazolio)]amide (Ia). The relatively unstable free base could be obtained by neutralization of the corresponding hydrochloride IIa with weak bases (e.g. NH₃ or NaHCO₃). Busch *et al.*³ found that the free base was amphoteric in that with ethanolic potassium hydroxide it gave a colorless, crystalline potassium salt, stable to boiling ethanol. With benzoyl chloride the salt and the base (Ia) gave the same monobenzoyl derivative. Recently Masuda *et al.*⁴ synthesized IIa from phenylhydrazine by successive treatment with cyanogen bromide, nitrogen oxides, and hydrogen chloride. They also prepared and studied the free base (Ia) and the benzoyl derivative, but were unaware of the identity of their compounds with those of Busch and coworkers. Masuda *et al.* did not examine the reaction of the base (Ia) with strong bases and therefore did not detect its acidic character.

In our investigation in this series, we have synthesized the benzoyl compound of Busch and coworkers by nitrosation of 4-benzoyl-1-phenylthiosemicarbazide and can thus confirm the structure, *N*-[3-phenyl-5-(1,2,3,4-oxatriazolio)]benzamidate III, assigned by Masuda *et al.*⁴

