Acta Cryst. (1957). **10**, 383

Unit cell and space group of thallous nitrate, $TlNO_3$.

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(*Received* 6 *March* 1957)

In view of the discrepancies in the published data on the structure of orthorhombic thallous nitrate, some results we have recently obtained with single crystals of this material may be of interest.

The unit cell dimensions were found to be

$$a = 6{\cdot}22,\quad b = 12{\cdot}32,\quad c = 7{\cdot}90\ \text{Å}$$

and the space group $Pbnm$ (No. 62) or $Pbn2_1$ (No. 23) from systematic absences.

The space group differs from that reported by Rivoir & Abbad (1943), but is in agreement with that determined by Ferrari & Cavalca (1950).

We find the true c parameter of the unit cell to be twice that found by the former workers, and though this was tentatively proposed by Ferrari & Cavalca, they suggested that it might be due to twinning.

Our single crystals were very carefully selected, including an examination under the polarizing microscope, so as to eliminate this possibility. They included specimens as received from Messrs British Drug Houses (not less than 98% purity), and also after recrystallization from aqueous solution, and needle-shaped crystals were found in each case. One was finally selected from each batch and in the crystal as received, the c axis was found to lie along the length of the needle, while in the recrystallized specimen the b axis lay in this direction. The unit-cell c dimension of the crystal from each growth habit, however, was found to be the same.

Oscillation photographs were taken about the three axes, using Cu $K\alpha$ radiation, and complete indexing of all observed reflexions was possible only by assigning a value to the c parameter of 7·90 Å.

In the oscillation photographs about the [001] axis, the alternate layer-line reflexions with l odd were very weak, which suggests that the true unit cell may be regarded, to a first approximation, as being equivalent to the stacking, in the direction of the c axis, of two smaller cells possessing c parameters of half the true value.

Structural changes are reported to take place in thallous nitrate at elevated temperatures (Finbak & Hassel, 1937); it is proposed to investigate these in a further study.

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FINBAK, C. & HASSEL, O. (1937). *Z. phys. Chem.* **35**, 25.

RIVOIR, L. & ABBAD, M. (1943). *An. Soc. esp. Fis. Quim.* **39**, 306.

Acta Cryst. (1957). **10**, 383

Bifurcated hydrogen bonds and the structure of cycloserine hydrochloride.

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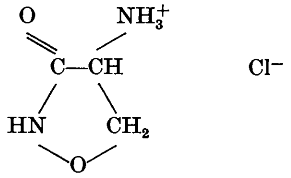
(*Received* 22 *January* 1957)

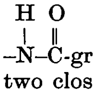
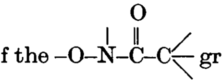
The crystal structure of the hydrochloride of 'cycloserine' (4-amino-3-isoxazolidone):



has been recently determined by Turley & Pepinsky (1956). Their discussion of the structure consists largely of the tabulation of the standard errors in the atomic positional parameter and the resulting probable errors in the interatomic distances and interbond angles, and concludes with several brief statements concerning the hydrogen bonding and the planarity of the heterocyclic ring.

In any X-ray study in which the data are not sufficiently accurate to locate the hydrogen atoms directly, the positions of these atoms can often be deduced by other considerations, among which are the requirements of molecular structure, or the formulation of a hydrogen-bonding arrangement in accord with the established geometrical properties of these bonds. The many examples where this procedure has been followed are certainly too well known to cite or enumerate here.

In the case of cycloserine hydrochloride there are four hydrogen atoms available for hydrogen bonding (three on the $-NH_3^+$ group, one on the ring imino nitrogen atom), and three atoms to serve as hydrogen-bond acceptors (chloride ion, carbonyl oxygen, and ring oxygen). The cation, however, has seven neighbors close enough to be examined in detail for possible hydrogen-bond formation.

Examining first the situation with regard to the  $-\overset{\overset{\mathrm{H}}{|}}{\mathrm{N}}-\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}-$group, we note that the carbonyl oxygen atom has two close neighbors: an imino nitrogen at 2·89 Å, and a heterocyclic oxygen at 2·92 Å. The suggestion of Turley & Pepinsky that as a result of these two approaches 'it seems at least possible that a bifurcated hydrogen bond exists here', is clearly impossible unless this group has (unexpectedly) assumed the enol configuration, a situation which was not mentioned by those authors, and moreover, is not supported by the observed bond distances. Since the imino nitrogen atom is a hydrogen-bond donor, its presumed acceptor, the carbonyl oxygen atom, is expected to lie on or near the N–H axis. Calculations show that this oxygen atom lies within 0·05 Å of the plane of the  $-\mathrm{O{-}\underset{|}{N}{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}C\!\lessdot}$ group, but that the angles C–N ··· O (of 165°) and O–N ··· O (of 78°) represent a great deviation from the linearity expected for the atoms N–H ··· O in a good hydrogen bond. (It is not possible to predict accurately just what the angles C–N–H and O–N–H would be in a heterocyclic system of this sort, but presumably they would both be within about 10° of 120°.) We accordingly conclude that the imino nitrogen is involved in a rather weak hydrogen bond, and that the O ··· O distance of 2·92 Å is *not* indicative of a bifurcated hydrogen bond, but an entirely normal van der Waals contact. The rarity of bifurcated hydrogen bonds has been emphasized previously (Pauling, 1940; Wells, 1949; Donohue, 1952).

With regard to the $-NH_3^+$ group, which has three close chloride ion neighbors, at 3·15, 3·18 and 3·23 Å, Turley & Pepinsky remark that 'these distances indicate weak hydrogen bonds, and the calculations of the N–Cl–N angles show that the four atoms lie nearly in a plane'. The existence of these short N ··· Cl distances does not, of course, ensure the presence of hydrogen bonds. Moreover, the fact that the arrangement of the hydrogen-bond donors about the chloride-ion acceptor is planar is irrelevant, for the question to be asked is whether or not C–N ··· Cl and Cl ··· N ··· Cl angles are compatible with a tetrahedral nitrogen atom. A convenient method for depicting the situation about an $-NH_3^+$ group is that of the stereographic projection, using the C–N bond as the polar axis. The projection for this group of cycloserine hydrochloride is shown in Fig. 1, where, happily, it is seen that a satisfactory hydrogen-bond situation obtains. It seems probable, from the lengths of the N ··· Cl distances here as compared with other hydrochlorides, that these three N–H ··· Cl hydrogen bonds are of such strength as to dominate the structure of this substance and largely determine the molecular arrangement.

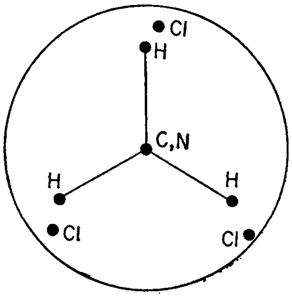


Fig. 1. Stereographic projection of the environment of the NH_3^+ group, viewed down the C–N bond. The bond angles involving the hydrogen atoms have been assumed to be tetrahedral.

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Wells, A. F. (1949). *Acta Cryst.* **2**, 128.

Notes and News

Announcements and other items of crystallographic interest will be published under this heading at the discretion of the Editorial Board. Copy should be sent direct to the British Co-editor (R. C. Evans, Crystallographic Laboratory, Cavendish Laboratory, Cambridge, England).

Acta Crystallographica

The Editors regret that the publication of this and the next few issues of *Acta Crystallographica* may be somewhat delayed owing to pressure of work in connexion with the preparation and printing of the abstracts of the communications to be read at the Fourth General Assembly of the Union.

The Use of the IBM 650 for Crystal Structure Analysis Computations

A conference was held at the University of Pittsburgh on 6 February 1957 for the purpose of exchanging information on IBM 650 programs which were already available or in the process of development for crystal structure analysis computations. There were seven principal speakers and fifty persons attended the conference. In the morning session the speakers gave a general account of their programs, with emphasis on the range of application and performance. The following is a summary of this information.

Prof. Preston M. Harris (Ohio State University) described an *hkl*, non-centric structure-factor program for up to 32 unique atoms of four different kinds in the asymmetric unit. The scattering factors were interpolated to an accuracy of 0·6% and individual isotropic temperature factors for each of the four atom kinds could be included. The program was not applicable to the triclinic case, since it required at least one orthogonal axis. It had been tested on trinitrotoluene, *Pca*, 32 unique atoms, for which it computed at the rate of 9·0 sec./structure factor. The program had 500 instructions and had not been optimized.

Miss Dorothy Booth (Bell Telephone Laboratories) described programs for (i) θ functions, (ii) *hkl* structure factors, (iii) two-dimensional Fourier syntheses.

Program (i) included d-spacings (except triclinic), $\sin\theta/\lambda$, $\sin\theta$, and atomic scattering factor or Lorentz factors or both. The time for these computations is of the order of 10 min. for $\beta \neq 90°$, $d_{\text{min.}} = 1{\cdot}0$ Å.

Program (ii) computes the A and B parts of the general form of the structure factor separately and can accommodate up to 200 atoms. A supplementary program gives