The Geometry of the Charge Transfer Complex $(CH_3)_3N,SO_2$ in the Solid State

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Summary The crystal structure of the charge transfer complex $(CH_3)_3N,SO_2$ is reported.

ALTHOUGH there have been numerous investigations of the crystal structure of charge transfer (CT) complexes,[1] there is apparently no information available about the structure of solid CT complexes of SO_2. Recently, spectral and thermodynamic data have been reported for the complex between trimethylamine (TMA) and SO_2.[2,3] The donor–acceptor bond in TMA,SO_2 is among the strongest yet encountered in CT chemistry and the complex is one of the few for which accurate gas phase, as well as solution, data are available.

We report here preliminary results of a study of the crystal structure of TMA,SO_2, determined at 25° by single-crystal *X*-ray diffraction. The complex, prepared by vapour phase reaction of the components, crystallizes in the space group $P2_1/c$ with $Z = 4$ and cell dimensions of $a = 5{\cdot}906$, $b = 10{\cdot}912$, $c = 10{\cdot}577$ Å and $\beta = 108{\cdot}33°$. Integrated three-dimensional intensity data were collected on a G.E. XRD-5 diffractometer using Cu-K_α radiation. The intensities were measured with the crystals sealed in a glass capillary under nitrogen atmosphere. Of the 1209 reflections with 2θ less than 140°, 900 had intensities distinguishable from the background radiation. The structure was found from a sharpened Patterson synthesis. Relatively large isotropic temperature factors were obtained in the least-squares refinement indicating that a lower experimental temperature would be desirable. All hydrogen atoms were located from a difference Fourier. The present

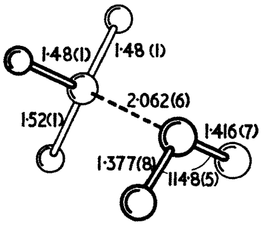

FIGURE 1. *Bond distances. Standard deviations for the last digit are given in parentheses.*

R value is 14%. The data will be retaken at lower temperature for further refinement.

Interesting features of the structure are the charge transfer (N · · · S) bond length (2·06 Å, Figure 1), the angle (68°) between the plane of the SO_2 molecule and the (N · · · S) bond and the approximate C_s symmetry of the complex (Figure 2). The standard deviations are underestimated due to the high temperature movement of the atoms. The present results, therefore, do not warrant a discussion of a possible change in SO_2 geometry.

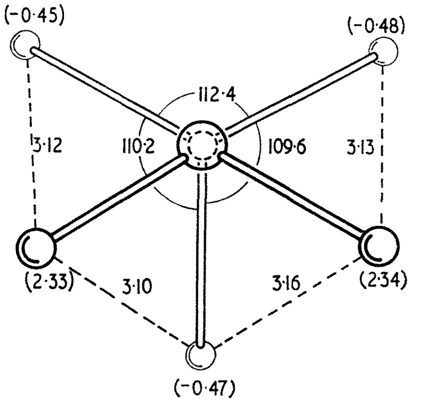

FIGURE 2. *A projection of the structure down the* S · · · N *charge-transfer bond. The numbers in parentheses are the distances above and below the plane in A°, perpendicular to the* S · · · N *bond. The heights of* N *and* S *are* 0 *and* 2·062 Å *respectively.*

The structure is in agreement with the assumption of Grundnes and Christian[3] and also Moede and Curran[4] of a nonzero angle between the threefold axis of trimethylamine and the plane of the SO_2 molecule. In the lowest unoccupied molecular orbital in SO_2 a $3p$–$3d$ hybridized atomic orbital of sulphur is used. The coefficients for this atomic orbital have been calculated.[5] If the lone pair p-orbital of trimethylamine is pointed at the sulphur atom, as it is observed in the present structure determination (Figure 2), one can calculate that this atomic orbital has a maximum overlap when the angle between S · · · N and the SO_2 plane is 55° (observed 68°). The only intermolecular interactions, besides the charge-transfer bond, in the crystal structure are of the van der Waals' type.

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