

Reversible Isomerization of Cyclo-octasulphur Monoxide; Preparation and X-Ray Crystal Structure of $S_8O \cdot SbCl_5$

By RALF STEUDEL, TORSTEN SANDOW, and JURGEN STEIDEL

(*Institut für Anorganische und Analytische Chemie, Technische Universität Berlin, D-1000 Berlin 12, Federal Republic of Germany*)

Summary The reaction of S_8O and $SbCl_5$ in CS_2 gave $S_8O \cdot SbCl_5$ (71% yield) which was shown by X-ray crystallography to contain S_8O in an isomeric conformation compared with pure S_8O which can be recovered from the adduct in its usual conformation by recrystallization from acetone or carbon disulphide

CYCLO-OCTASULPHUR MONOXIDE S_8O is prepared by the oxidation of S_8 with CF_3CO_3H [†] and crystallizes as an unstable orange material containing puckered S_8 rings with exocyclic oxygen atoms in axial positions² In an attempt to prepare more stable derivatives the synthesis of adducts with metal halides as electron acceptors was investigated

Reaction of S_8O with $SbCl_5$ in CS_2 at 20 °C and subsequent cooling to -50 °C for 9 days yielded an orange crystalline product of composition $S_8O \cdot SbCl_5$ (yield 71%)

Crystal data $S_8O \cdot SbCl_5$, orthorhombic, space group $Pcmm$, $a = 1052(5)$, $b = 880(3)$, $c = 1621(6)$ pm, $Z = 4$, $D_c = 2.53$ g cm⁻³ (-100 °C), $M = 571.5$ (Mo- K_α , $\lambda = 71.069$ pm, $\mu = 37.7$ cm⁻¹) Data were collected at -100 °C using a Syntex $P2_1$ diffractometer The intensities of 1621 reflections were measured ($2\theta < 50^\circ$), 1336 which had $I_{obs} > 2\sigma(I_{obs})$ were considered observed and used in the structure analysis The structure was solved by Patterson synthesis and refined to $R = 0.083$ using anisotropic thermal parameters but without absorption correction †

† The atomic co-ordinates for this work are available on request from Prof Dr G Bergerhoff, Institut für Anorganische Chemie, Universität, Gerhard-Domagk-Str 1, D-5300 Bonn 1, West Germany Any request should be accompanied by the full literature citation for this communication

The crystal lattice consists of $S_8O \cdot SbCl_5$ molecules of C_s symmetry with only van der Waals type intermolecular interactions. The S_8O unit differs from molecular S_8O by an equatorially-bonded oxygen atom as well as by significantly different SO and SS bond lengths (see Figure 1).

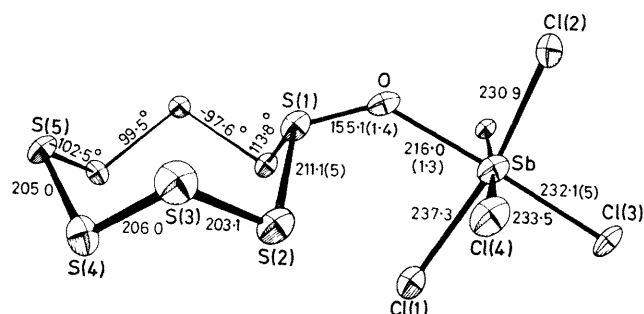


FIGURE 1 Molecular structure, bond lengths (pm) and torsional angles of $S_8O \cdot SbCl_5$.

While the SO bond length has increased from 148.3(9) in S_8O to 155(1) pm, the adjacent bonds S(1)–S(2) have decreased in length from 220.0(4) in S_8O to 211.1(5) pm which is consistent with the explanation of electron delocalization from the oxygen atom into antibonding molecular orbitals at the neighbouring sulphur atoms;³ removal of electrons from the oxygen by co-ordination of $SbCl_5$ diminishes this effect. The bond angle at oxygen is 133.3(7)°.

The co-ordination at the Sb atom is approximately octahedral with a mean Sb–Cl distance of 233 pm and angles Cl–Sb–Cl between 86 and 94°. Three Cl atoms are located on the molecular mirror plane. This is the second structural determination of a sulphoxide– $SbCl_5$ adduct, although only incomplete information about the structure of $Ph_2SO \cdot SbCl_5$ is available.⁴

At 25 °C solid $S_8O \cdot SbCl_5$ decomposes within 5 min to $SOCl_2$, $SbCl_3$, and S_8 . On dissolution of the adduct in

acetone and subsequent cooling and recrystallization from dilute solutions in CS_2 , pure S_8O was obtained whose Raman spectrum was identical to that of an original sample, prepared by oxidation of S_8 and which therefore must consist of molecules with axially-bonded oxygen atoms. Since pyramidal inversion at the trico-ordinated sulphur atom is unlikely at low temperatures^{5,6} a conformational inversion of the eight-membered ring is likely to take place during preparation and dissociation of $S_8O \cdot SbCl_5$ (see Figure 2).

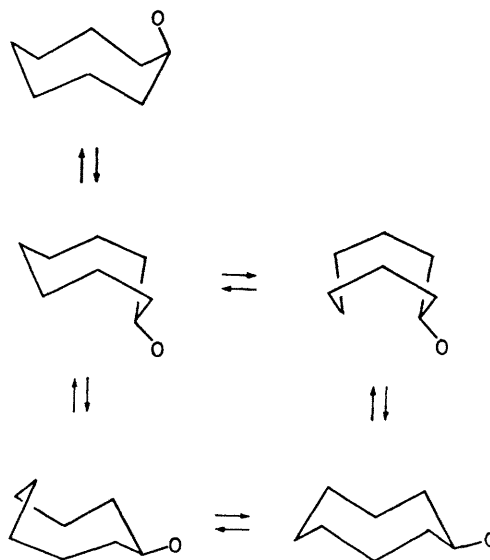


FIGURE 2. Possible pathway for the exchange of the oxygen atom between axial and equatorial positions by S_8 ring inversion.

We thank Priv.-Doz. Dr. J. Pickardt for assistance in solving the X-ray structural analysis.

(Received, 29th October 1979; Com. 1147.)

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